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## Stockholm Convention on Persistent Organic Pollutants

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### Persistent Organic Pollutants Review Committee

#### Fourteenth meeting

Rome, 17–21 September 2018

Agenda item 4 (c)

**Technical work: 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 Convention**

### **Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride**

#### **Note by the Secretariat**

At its fourteenth meeting, by its decision POPRC-14/3, the Persistent Organic Pollutants Review Committee decided to submit to the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants the report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) prepared by the Committee based on information submitted by Parties and observers, and taking into account the reports and recommendations previously produced by the Committee. This report is set out in the annex to the present note. The present note, including its annex, has not been formally edited.

**Annex**

**Report on the assessment of alternatives to  
perfluorooctane sulfonic acid (PFOS), its salts  
and perfluorooctane sulfonyl fluoride (PFOSF)**

**January 2019**

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## Executive summary

1. Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) are listed in Annex B to the Stockholm Convention on Persistent Organic Pollutants. In accordance with Part III of Annex B to the Convention, acceptable purposes and specific exemptions are defined for the production and use of PFOS, its salts and PFOSF. According to paragraph 5 of part III of Annex B to Convention, the Conference of the Parties should evaluate the continued need for PFOS, its salts and PFOSF for the acceptable purposes and specific exemptions based on available scientific, technical, environmental and economic information.
2. The purpose of this report is to provide an assessment of alternatives to PFOS, its salts and PFOSF, based on information submitted by Parties and Observers, and taking into account the reports and recommendations previously produced by the Committee, including the previous assessment (UNEP/POPS/POPRC.10/INF/7/Rev.1) and consolidated guidance on alternatives to PFOS and its related chemicals (UNEP/POPS/POPRC.12/INF/15/Rev.1).
3. The assessment report considers each of the existing acceptable purposes and specific exemptions, specified for PFOS, its salts and PFOSF. This includes an assessment of the commercial availability, suitability (i.e. technical and economic feasibility), level of implementation of alternatives in these uses (Chapter 2) and an assessment of POPs characteristics of chemical alternatives to PFOS, its salts and PFOSF identified (Chapter 3). It should be noted that the assessment of POPs characteristics as part of this report is not intended to imply that the Persistent Organic Review Committee (POPRC) has fully considered whether alternative chemicals have met the Annex D criteria.
4. For most uses covered, technically feasible chemical alternatives to PFOS, its salts and PFOSF are readily available on the commercial market globally. For some uses (e.g., metal plating, fire-fighting foam, insect baits) the chemical formulation of some alternatives is known, but in many cases within these and other uses the composition of alternatives is unclear as these are subject to trade secret restrictions. In some applications, the development of non-chemical alternatives or alternative processes that reduce or avoid the use of PFOS have been rapidly developed and facilitated the reduction and elimination of the use of PFOS. For example, the use of digital photography has been attributed as a key contributing factor in the phase-out of PFOS in photoimaging, and the use of Cr(III) decorative plating could in principle avoid the need for PFOS-based mist suppressants in Cr(VI) metal plating.
5. The technical feasibility and economic viability of PFOS-free alternatives is demonstrated in many of the applications covered in the current report, where sufficient information is available to make an assessment. For some applications (e.g. hard metal plating in a closed loop or insect baits for control of leaf cutting ants), there is conflicting evidence available concerning the operational performance of alternatives for their desired purpose. Evidence exists that a number of performance, practical or environmental limitations may impact the feasibility of some alternatives in these applications, while it is also indicated that use of alternative chemical substances or non-chemical processes may be suitable for some applications within different sectors. The suitability of alternatives in these uses will need to be considered on a case-by case basis.
6. Information received both from industry and Parties, demonstrates that the use of PFOS, its salts and PFOSF in many of the applications covered is rapidly declining, has been or will be phased out (e.g. semi-conductor sector, photoimaging, fire-fighting foams), suggesting the switch to chemical and non-chemical alternatives is very advanced. For other uses, there is a lack of available data on levels of continued PFOS use. For most applications, evidence suggests that PFOS can be replaced for most wide-scale applications, but there may be some speciality applications, where replacement with alternatives is harder to achieve.
7. In the case of insect baits for control of leaf cutting ants, the open application use of sulfluramid is ongoing and is considered by Brazil (2018) to be the only chemical control agent available for all leaf cutting ant species in all desired applications. Information from Brazil indicated the levels of production, use and export of sulfluramid are increasing over time. Focus therefore needs to be placed on further minimising the use of sulfluramid where possible. Non-chemical alternatives are commercially available and used by some farmers in Brazil for certain species, but the wide-scale operational potential of these non-chemical methods have not been fully demonstrated for all desired uses and species at present.
8. Based on the assessment of availability, suitability and implementation of alternatives, the Committee has agreed upon recommendations on the continued need for the existing acceptable purpose or specific exemption for the uses considered. For most uses, the Committee recommends either converting the existing acceptable purpose to a specific exemption (fire-fighting foams, hard metal plating in a closed loop), or for the other applications, removal of the acceptable purpose or specific exemption under the Convention entirely. The acceptable purpose for insect baits for control of leaf cutting ants is maintained with a number of additional recommendations made regarding the research and development of alternatives and monitoring activities.
9. Key data gaps and limitations are identified for each of the uses discussed. Common themes among the information gaps identified include: a lack of recent data on the continued use/need of PFOS in the countries that maintain notifications; lack of data on the potential environmental impacts of alternatives or degradation products; lack of data on the technical feasibility and relative performance of 'novel' substances or processes in practice at field-scale.

10. An initial screening of potential bioaccumulation (B) and persistence (P) characteristics of ‘additional’ alternatives (i.e. those not previously assessed) was conducted for 51 substances and products. 49 substances were subject to prioritization, with two products used in fire-fighting foams not screened due to lack of available information. Four substances were selected as screening category I (potential persistent organic pollutants<sup>1</sup>; three substances as screening category II (candidates for further assessment); six as screening category III (candidates for further assessment with limited data); 31 substances as screening category IV (not likely to fulfil the criteria on persistence and bioaccumulation difficult to classify due to insufficient data). Additionally, one substance and seven commercial products were added to category V, being difficult to classify due to insufficient data.

11. A more in-depth assessment was performed, considering the chemical substances identified in the initial screening (Categories I and II) in terms of their characteristics against the Convention Annex D criteria (including persistence, bioaccumulation, (eco)toxicity and long-range transport). The results identified three chemical substances, i.e. one used in fire-fighting foams, Metafumizone, and two used in aviation hydraulic fluids, tricresyl phosphate and o-tolyl-phosphate, that are assigned as Class 2: Substances considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data.

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<sup>1</sup> Based on the substances being identified as potentially both persistent and bioaccumulative

## Summary of recommendations

Application(s)	Recommendation
Photo-imaging	The acceptable purpose for the use of PFOS, its salts and PFOSE for photo-imaging should no longer be available under the Convention.
Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)	The acceptable purpose for the use of PFOS, its salts and PFOSE for photo-resist and anti-reflective coatings for semi-conductors and as etching agent for compound semi-conductors and ceramic filters should no longer be available under the Convention.
Aviation hydraulic fluids	The acceptable purpose for the use of PFOS, its salts and PFOSE for aviation hydraulic fluids should no longer be available under the Convention.
Metal-plating (Metal plating (hard metal plating) only in closed-loop systems; Metal plating (hard metal plating); Metal plating (decorative plating))	<p>The use of PFOS, its salts and PFOSE for hard metal plating (only in closed-loop systems) should be converted from an acceptable purpose to a specific exemption.</p> <p>The specific exemptions for the use of PFOS its salts and PFOSE for metal plating (hard metal plating) and metal plating (decorative metal plating) should no longer be available under the Convention.</p>
Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in vitro diagnostic medical devices, and CCD colour filters)	Alternatives for the use of PFOS, its salts and PFOSE for certain medical devices are available and therefore recommended that the use of PFOS, its salts and PFOSE for certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in vitro diagnostic medical devices, and CCD colour filters) should no longer be available under the Convention.
Fire-fighting foam	<p>The acceptable purposes for the production and use of PFOS, its salts and PFOSE for fire-fighting foam should be amended to a specific exemption for the use of fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) already in installed systems, including both mobile and fixed systems, and with the same conditions specified in paragraphs 2 (a)-(d) and 3 of the annex to decision POPRC-14/2 on perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds.</p> <p>The Committee recognized that a transition to the use of short-chain per- and polyfluoroalkyl substances (PFASs) for dispersive applications such as fire-fighting foam is not a suitable option from an environmental and human health point of view and that some time may be needed for a transition to alternatives without PFASs.</p>
Insect baits for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp.	<p>The acceptable purpose is to be maintained and the text of the use entry in the Annex be clarified as follows:</p> <p>“insect baits with sulfluramid (CAS Number 4151-50-2) as an active ingredient for control of leaf-cutting ants from <i>Atta</i> spp. and <i>Acromyrmex</i> spp. for agricultural use only.”</p> <p>The Committee encourages additional research and development of alternatives and, where alternatives are available, that they be implemented.</p> <p>The Committee further encourages Parties to consider monitoring activities for sulfluramid, PFOS and other relevant degradation products in the different environmental compartments (soil, ground water, surface water) of the application sites.</p>
Photo masks in the semiconductor and liquid crystal display (LCD) industries	The specific exemption for the use of PFOS, its salts and PFOSE for photo masks in the semiconductor and liquid crystal display (LCD) industries should no longer be available under the Convention
Electric and electronic parts for some colour printers and colour copy machines	The specific exemption for the use of PFOS its salts and PFOSE for electric and electronic parts for some colour printers and colour copy machines should no longer be available under the Convention.

<b>Application(s)</b>	<b>Recommendation</b>
Insecticides for control of red imported fire ants and termites	The specific exemption for the use of PFOS, its salts and PFOSF for insecticides for control of red imported fire ants and termites should no longer be available under the Convention.
Chemically driven oil production	The specific exemption for the use of PFOS, its salts and PFOSF for chemically driven oil production should no longer be available under the Convention.
Expired specific exemptions (Carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, rubber and plastics)	There are no longer any Parties registered for specific exemptions for production or use in these sectors. It is indicated that alternatives to PFOS in most uses are widely available and technically viable and have been implemented globally.

# 1 Introduction

## 1.1 Background and objectives

12. At COP-4 in 2009, the Conference of the Parties, by decision SC-4/17, listed perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) in Annex B to the Stockholm Convention on Persistent Organic Pollutants.

13. In accordance with Part III of Annex B to the Convention, the following acceptable purposes, or use as an intermediate in the production of chemicals with the following acceptable purposes are specified:<sup>2</sup>

- (a) Photo-imaging;
- (b) Photo-resist and anti-reflective coatings for semi-conductors;
- (c) Etching agent for compound semiconductors and ceramic filters;
- (d) Aviation hydraulic fluids;
- (e) Metal plating (hard metal plating), only in closed-loop systems;
- (f) Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in-vitro diagnostic medical devices, and CCD colour filters);
- (g) Fire-fighting foam;
- (h) Insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*

14. In accordance with Part III of Annex B to the Convention, specific exemptions for the following specific uses, or use as an intermediate in the production of chemicals with the following specific uses are specified:<sup>3</sup>

- (a) Photo masks in the semiconductor and liquid crystal display (LCD) industries;
- (b) Metal plating (hard metal plating);
- (c) Metal plating (decorative plating);
- (d) Electric and electronic parts for some colour printers and colour copy machines;
- (e) Insecticides for control of red imported fire ants and termites;
- (f) Chemically driven oil production;
- (g) Carpets;\*
- (h) Leather and apparel;\*
- (i) Textiles and upholstery;\*
- (j) Paper and packaging;\*
- (k) Coatings and coating additives;\*
- (l) Rubber and plastics.\*

15. According to paragraph 5 of part III of Annex B to the Stockholm Convention on Persistent Organic Pollutants, the Conference of the Parties to the Convention should evaluate the continued need for PFOS, its salts and PFOSF for the acceptable purposes and specific exemptions listed above, based on available scientific, technical, environmental and economic information. The ultimate aim being that safer alternatives should replace the need for acceptable purposes and specific exemptions under the Convention. As stated in paragraph 6 of part III of Annex B to the Convention, the evaluation shall take place no later than in 2015 and every four years thereafter, in conjunction with a regular meeting of the Conference of the Parties.

<sup>2</sup> The Register of Acceptable Purposes on PFOS, its salts and PFOSF pursuant to paragraph 1 of part III of annex B of the Stockholm Convention is available here : <http://chm.pops.int/Implementation/Exemptions/AcceptablePurposes/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx>

<sup>3</sup> The Register of Specific Exemptions for PFOS, its salts and PFOSF pursuant to paragraph 1 of part III of annex B of the Stockholm Convention is available here : <http://chm.pops.int/Implementation/Exemptions/AcceptablePurposes/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx>

\* The Conference of the Parties, in its decision SC-7/1, noted that in accordance with paragraph 9 of Article 4 of the Convention, no new registrations may be made with respect to those applications.

16. At its fifth meeting, the Persistent Organic Pollutants Review Committee adopted general guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals, outlining how suitable chemical and non-chemical alternatives can be identified and evaluated (UNEP/POPS/POPRC.5/10/Add.1).

17. This guidance covers the following key aspects, to be considered in an assessment of alternatives (please see UNEP/POPS/POPRC.5/10/Add.1 for full details):

- (a) Identification of potential alternatives;
- (b) Assessment of risks related to alternatives;
- (c) Social and economic assessment of alternatives.

18. An assessment of alternatives to PFOS, its salts and PFOSF was performed in 2014 (UNEP/POPS/POPRC.10/INF/7/Rev.1). In this assessment, alternatives to PFOS, its salts and PFOSF underwent a two-step screening process: i) prioritization to screen for those alternatives that had a potential to be POPs based on, bioaccumulation (B) and persistence (P) (i.e., criteria (b) and (c) of Annex D to the Convention, and ii) a more detailed assessment of the POPs characteristics of alternatives that had been identified as having a potential to be POPs.

19. In this assessment, of 58 alternatives to PFOS screened, 54 substances were subject to prioritization (with a further four transformation products which were not assessed), of which one substance was selected as category I (potential persistent organic pollutants), 13 substances as category II (candidates for further assessment), 34 substances were category III (candidates for further assessment with limited data) and 6 substances were selected as category IV (not likely to fulfil the criteria on persistence and bioaccumulation in Annex D).

20. By decision SC-8/5 at COP.8 (May 2017), the Conference of the Parties decided to undertake an evaluation of PFOS, its salts and PFOSF at the following meeting (COP.9) due to be held in April-May 2019, this is in accordance with the process set out in its decision SC-6/4. As part of this decision, Parties and others were invited to submit information to the Secretariat, by 15 February 2018, for use by the Secretariat in preparing its next report on the evaluation of PFOS, its salts and PFOSF in accordance with paragraph 6 of the annex to decision SC-6/4 and by the Committee in its future updating of the guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals:

- (a) Information on the production and use of sulfluramid;
- (b) Information on local monitoring of releases of perfluorooctane sulfonic acid from the use of sulfluramid;
- (c) Information on research on and the development of safe alternatives to PFOS, its salts and PFOSF as stipulated in paragraph 4 (c) of part III of Annex B to the Convention.

21. Accordingly, the Committee, at its thirteenth meeting (2017), agreed on the terms of reference for the assessment of alternatives to PFOS, its salts and PFOSF.<sup>4</sup>

22. In accordance with the terms of reference, the purpose of this document is to provide an updated assessment, based on information submitted by Parties and Observers in response to the request for information, as outlined in Decision SC-8/5, of the availability, suitability and implementation of alternatives currently available for PFOS and related compounds, with specific reference to the acceptable purposes and specific exemptions outlined above. This will focus primarily on the availability, suitability and implementation of alternatives to PFOS, its salts and PFOSF (Chapter 2) as well as consideration of the of POPs characteristics of chemical alternatives to PFOS, its salts and PFOSF (Chapter 3).

## 1.2 Structure of the report

23. This report is an assessment of alternatives to PFOS, its salts and PFOSF, based on the information submitted to the Secretariat by Parties and Observers (see Table 1), and taking into account the reports and recommendations produced by the Committee (see Section 1.3).

24. In Chapter 2, the current knowledge of the availability, suitability and implementation of chemical alternatives and non-chemical alternatives (including alternative processes) is discussed for each application listed as acceptable purposes or specific exemptions for PFOS, its salts and PFOSF (see section 1.1).

25. In accordance with the terms of reference, the discussion on ‘availability’ of alternatives will consider the available information on the extent to which commercial products are available and accessible on the market and whether there are geographic, legal or other limiting factors affecting the use of alternative. The discussion of ‘suitability’ of alternatives considers the available information on the economic viability and technical feasibility of

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<sup>4</sup> UNEP/POPS/POPRC.13/INF/9.

alternatives, for example whether the alternative has demonstrated equivalent function and provides similar product performance characteristics. The discussion of ‘implementation’ of alternatives considers the available information on the extent to which alternatives are already being used for the different applications. This includes an assessment of the continued use or need for PFOS, its salts and PFOSF, based on the notifications to the Secretariat on ongoing production and/or use, and, where information is available, recent trends in PFOS-use over time.

26. In Chapter 3, an assessment of the health and environmental effects of alternatives, including POPs characteristics (based on Annex D) and other hazards is provided. It should be noted that 40 substances and 11 commercial brands were already considered in document UNEP/POPS/POPRC.10/INF/7/Rev.1, of which 9 chemical alternatives were presented in the factsheets in document UNEP/POPS/POPRC.10/INF/8/Rev.1. It should be noted that the assessment of POPs characteristics as part of this report is not intended to imply that the POPRC has fully considered whether alternative chemicals have met the Annex D criteria.

27. In Chapter 4, a summary table of overall conclusions and recommendations is provided.

### 1.3 Source of information

28. In preparing the draft report, in addition to the information submitted by Parties and others by 15 February 2018 (see Table 1 below), information in the following documents (and references therein) has been consulted:

(a) Decision 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;

(b) UNEP/POPS/POPRC.10/INF/7/Rev.1: Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride;

(c) UNEP/POPS/POPRC.10/INF/8/Rev.1: Factsheets on alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride;

(d) UNEP/POPS/COP.7/INF/11: Report for the evaluation of information on perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride;

(e) Decision POPRC-8/8: Perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals in open applications;

(f) 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;

(g) UNEP/POPS/POPRC.12/INF/15/Rev.1: Consolidated guidance on alternatives to PFOS and its related chemicals;

(h) UNEP/POPS/POPRC.5/10/Add.1: General guidance on considerations related to alternatives and substitutes for listed persistent organic pollutants and candidate chemicals;

(i) 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 (2017);

(j) UNEP/POPS/POPRC.13/7/Add.2: Further assessment of information on PFOA, its salts and PFOA-related compounds.

29. The Secretariat compiled information submitted by Parties and Observers as requested based on the 15 February 2018 deadline. The information received is summarised in Appendix 1 to the present report.<sup>5</sup>

<sup>5</sup> Submissions are available at:

<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOSInfoSubmission/tabid/6176/Default.aspx>.

## 2 Availability, suitability and implementation of alternatives to PFOS, its salts and PFOSF

### 2.1 Introduction

30. In this section, a discussion of available information on the availability, suitability and implementation of chemical and non-chemical alternatives to PFOS, its salts and PFOSF is provided, focussing on the uses for which acceptable purposes or specific exemptions are defined (see Chapter 1). This discussion is based on the information submitted by Parties and Observers, and taking into account the reports and recommendations previously produced by the Committee. For each use, an introductory section is provided to outline what the application entails, the specific functionality that is/was provided by PFOS or related compounds, which must be replicated by the alternatives, the current status of this use in the context of the Convention, and which Parties currently have notifications for the production or use of PFOS and related compounds for these applications.

31. The consideration of the availability, suitability and implementation of alternative, with consideration of the defined terms of reference, focuses on the following:

(a) Availability – whether the alternative is on the market and ready for immediate use; if commercial products and trade names are known; if the chemical formulation of products is known or confidential; if geographic, legal or other limiting factors affecting whether the alternative can be used;

(b) Suitability – whether the alternative is technically feasible, i.e. has demonstrated equivalent function and provides similar product performance characteristics; information on efficacy, including performance, benefits and limitations of the alternative;

(c) Implementation – whether the alternative has been implemented or is at the trial or proposal stage; for example, taking into account the number of Parties with existing notifications for production or use and time trends in production, use and export of PFOS.

32. It should be noted that the level of detail provided in the discussion for each use is confined by the amount of available information on alternatives for those uses. Some uses have a very limited amount of available information, and in many cases, the specific exemptions for most or all Parties has now expired. In these cases, a brief overview of available information is provided.

### 2.2 Photo-imaging

#### 2.2.1 Introduction and background

33. Photo-imaging is listed as an acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of acceptable purposes, as of May 2018, the following Parties are registered for this use: Canada, China, Czech Republic, European Union, Japan, Norway, Switzerland, Turkey and Vietnam. This use is not considered as an open application. In the photographic industry, PFOS, its salts and PFOSF have been used in manufacturing of film, photographic paper and photographic plates.<sup>6</sup> 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. The specific uses of PFOS in photo imaging have included film (including negative, colour reversal, cine and television and diagnostic X-ray), paper (colour reversal and positive) and reprographic plate (ESWI 2011). One report (DEFRA 2004) indicated 85% of the PFOS used in the EU photo-imaging industry was in X-ray film. It is not clear what proportion of PFOS is currently used in X-ray film. More recent information has not been provided by Parties or others. However, the acceptable purposes for use of PFOS in photo imaging which are currently registered by the EU under the Convention, are no longer required since alternatives are used by industry (European Commission, 2017).<sup>7</sup> This is in line with the submission from I&P Europe (2018) that indicated that PFOS is being rapidly phased out in Europe.

34. The PFOS-related compounds that have reported to have been used for this purpose, are tetraethylammonium perfluorooctanesulfonate (CAS No. 56773-42-3), used in the manufacture of photographic film (Defra, 2004), and FOSA quaternary ammonium iodide (CAS No. 1652-63-7), used in the manufacture of photographic film, paper and plates.<sup>8</sup>

35. PFOS, its salts and PFOSF are favoured in these photo imaging applications due to their lack photo-activity and ability to provide critical functionality (such as controlling surface tension, electrostatic charge, friction, and adhesion, and repelling dirt). Imaging materials that are very sensitive to light (e.g., high-speed films) benefit

<sup>6</sup> As indicated by BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention.

<sup>7</sup> [https://www.parlament.gov.at/PAKT/EU/XXV/EU/13/70/EU\\_137085/imfname\\_10705391.pdf](https://www.parlament.gov.at/PAKT/EU/XXV/EU/13/70/EU_137085/imfname_10705391.pdf).

<sup>8</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

particularly from these properties. The concentration of PFOS-related chemicals in coatings of films, paper and plates is in the range of 0.1 to 0.8 g/cm<sup>2</sup>.

36. Finding non-PFOS chemical alternatives for use in photo-imaging is therefore extremely challenging, as replicating the desired functionality is very difficult.

37. The submission from the Imaging and Printing Association (I&P Europe, 2018) reported that "a recent internal inquiry of I&P Europe, conducted in November and December of 2017, indicate that PFOS is forecasted to be completely phased out in 2018 or 2019 at the latest, i.e. that as of then PFOS is foreseen to be no longer used by its member companies". This would indicate that the photo-imaging industry has developed viable alternatives for the uses of PFOS in this sector in Europe, and probably other areas as well.

## 2.2.2 Availability of alternatives

### 2.2.2.1 Chemical alternatives

38. A number of alternative chemical substances have been identified for the photographic industry. Detail of these alternatives, as outlined in UNEP/POPS/POPRC.12/INF/15/Rev.1 are summarised in Table 1 below.

**Table 1 Overview of alternatives to PFOS for use in the photo imaging sector.**

Alternative	CAS No	Trade Names	Manufacturers	Class*	Source	Additional details
<b>Chemical alternatives</b>						
Telomer-based products of various perfluoroalkyl chain length C <sub>3</sub> - and C <sub>4</sub> perfluorinated compounds.	N/A	Information gap	Information gap	N/A	UNEP/POPS/POPRC.12/INF/15/Rev.1	Short-chain perfluorocarboxylic acids (PFCAs) have been assessed as being of lower overall concern to the environment based on the available information (NICNAS, 2015a).
Hydrocarbon surfactants	N/A	Information gap	Information gap	N/A	UNEP/POPS/POPRC.12/INF/15/Rev.1	
Silicon products <sup>9</sup>	N/A	Information gap	Information gap	N/A	UNEP/POPS/POPRC.12/INF/15/Rev.1	
PFOA and PFOA-related compounds <sup>10 11 12</sup>	N/A	Information gap	Information gap	N/A	UNEP/POPS/POPRC.12/INF/15/Rev.1	reduced >90% since 2000
<b>Non-chemical / alternative technologies</b>						
Digital techniques	N/A	Information gap	Information gap	N/A	UNEP/POPS/POPRC.12/INF/15/Rev.1	Digital techniques have substantively reduced photographic and X-ray film use.

\* Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: 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 for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

<sup>9</sup> A NICNAS (2018a) assessment was carried out for six cyclic polyorganosiloxanes, D3 (hexamethylcyclotrisiloxane), CAS 541-05-9 ; D4 (octamethylcyclotetrasiloxane cyclomethicone), CAS 556-67-2 ; D5 (Decamethylcyclopentasiloxane cyclomethicone), CAS 541-02-6 ; D6 (Dodecamethylcyclohexasiloxane cyclomethicone), CAS 540-97-6; D7 (tetradecamethylcycloheptasiloxane), CAS 107-50-6; Cyclomethicone polydimethyl cyclic siloxanes. All shown to be persistent, and D4, D5 shown to be bioaccumulative. The specific uses of these substances was not specified. D4 and D5 were assessed in the previous alternatives assessment report (UNEP/POPS/POPRC.10/INF/7/Rev.1).

<sup>10</sup> At its fourteenth meeting in 2018, in accordance with paragraph 9 of Article 8 of the Convention, the POPRC recommended to the Conference of the Parties that it consider listing perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds in Annex A to the Convention with specific exemptions (UNEP/POPS/POPRC.14/6)

<sup>11</sup> PFOA is included on the REACH Candidate List of substances of very high concern (SVHC) for Authorisation, based on an assessment concluding that PFOA is PBT according to REACH Article 57(d) and classified as toxic for reproduction category 1B in accordance with the CLP Regulation

<sup>12</sup> A NICNAS (2018b) assessment established that PFOA and octanoic acid, pentadecafluoro-, ammonium salt (APFO) are PBT substances according to domestic environmental hazard criteria.

39. No specific trade names or other product specific details have been reported according to the BAT/BEP expert guidance. I&P Europe (2018) indicate that detailed information on alternatives for PFOS identified and used in imaging products cannot be provided because it is considered confidential business information.

40. The presence of commercial products on the market would suggest that these chemical alternatives are readily available for photoimaging applications. However, the lack of available information of specific products and formulation means the level of availability and accessibility of alternatives, and potential difference in different locations remains unclear.

#### **2.2.2.2 Non-chemical / technological alternatives**

41. In terms of non-chemical alternatives, it has been observed that digital techniques have substantively reduced photographic and X-ray film use of PFOS, its salts and PFOSE. Estimates for 2010 for Europe published in ESWI (2011) report a 70% decrease in demand for coating solutions because of that shift. No further information on the impact of digital technology on the use of PFOS in photo-imaging has been supplied. The I&P Europe (2018) submission indicates that PFOS use in the photo-imaging sector is being rapidly phased out in Europe. It is indicated that this is predominantly the result of both a technology shift towards digital techniques replacing conventional photographic coatings, and a continued search for alternatives in the few remaining conventional photo-graphic materials where PFOS has been used.

42. The BAT/BEP experts guidance also outlines Best Environmental Practices for manufacturing of photographic materials, finishing operations, photo-processing operations (wet film processing), and recycling X-ray pictures, including the appropriate collection, treatment and disposal of wastes to reduce exposure and environmental release.<sup>13</sup>

#### **2.2.3 Suitability of alternatives**

43. The I&P Europe (2018) indicate that for a substance to be considered a viable alternative in photographic coatings, they require properties inherent to the manufacture of imaging materials, e.g., lack photoactivity and thus do not interfere with the imaging process, and further do not interfere with a number of other intrinsic properties of conventional photographic coating solutions such as colloidal stability.

44. I&P Europe (2018) indicate that the search towards alternatives for perfluorinated C<sub>8</sub> substances or fluorotelomer-based C<sub>8</sub> substances typically involved a “preferred replacement hierarchy” favouring non-fluorinated hydrocarbon alternatives, followed by non-perfluorinated substances, further followed by per-fluorinated substances with shorter chain lengths (C<sub>3</sub> or C<sub>4</sub>).

45. I&P Europe (2018) consider that some known possible alternatives for PFOS that have been identified in other areas e.g. silicone products and siloxane compounds, are in practice not usable as alternatives in the manufacture of conventional photographic products. The PFOA Risk Management Evaluation<sup>14</sup> suggests that developing chemical alternatives that are viable replacements in this sector is very challenging and requires significant R&D investment. In practice, the most effecting alternative approach to using PFOS in photo imaging is the technological shift to digital photography.

46. IPEN (2018) further note that the switch to digital technologies also includes developing countries, who report a rapid implementation of digital imaging technology for healthcare, citing examples of this use in Gabon, South Africa, Kenya and Kazakhstan.

47. The IAEA and WHO (2015) consider the rapid adoption of digital technology in healthcare results from “efficiencies inherent in digital capture, storage and display and the competitive cost structures of such systems when compared to alternatives involving film.”

#### **2.2.4 Implementation of alternatives**

48. The I&P Europe (2018) note that their member organisations have pursued further elimination of PFOS where possible, suggesting that industry is further utilising available alternatives.

49. I&P Europe (2018) noted, based on the results of a recent internal inquiry, that they forecast PFOS to be completely phased out in their member companies by 2019 at the latest. As discussed above, they suggest that this will predominantly be a result from the combined effects of a continued technology shift towards digital techniques replacing conventional photographic coatings and a continued search for alternatives in the few remaining conventional photo-graphic materials that still required PFOS.

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<sup>13</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>14</sup> UNEP/POPS/POPRC.13/7/Add.2.

50. As the spread of digital cameras has reduced film use, the use of PFOS in this area is not expected to grow.<sup>15</sup> World consumption of PFOS for colour film production fell from 23 t in 2000 to 8 t in 2004.<sup>16</sup> More recent data on the volumes of PFOS use in this sector is not available. The EU (2018) indicate declining volumes of PFOS use for photoimaging uses (for which data are available), including: a) for film from 4.75 t in 2000 to 0.27 t in 2010, b) for paper from 0.73 t in 2000 to 0 t in 2005 and c) for plates from 0.40 t in 2000 to 0 t in 2010, indicating alternatives are available and have been widely implemented in Europe (ESWI, 2011).<sup>17</sup> However these figures are not updated.

51. Canada (2018) suggested that product changes to remove PFOS and major shifts in the photographic industry have led to very low quantities of PFOS still being used in that sector globally, and it is expected that the use of PFOS in the photographic sector is declining rapidly as users move towards digital imaging.

52. Japan's photographic industry reported that PFOS is no longer used for photographic processing in Europe, Japan, North America or elsewhere.<sup>18</sup>

53. 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.<sup>19</sup> Volumes of PFOS use for these uses, and the feasibility/barriers for implementing alternatives to PFOS are unknown.

54. To summarise, despite a lack of quantitative information on the reduction in PFOS use attributed to the switch to digital technology, the above discussion indicates that the widespread technological switch in the photography industry has led to a significant decline in the use of PFOS in this sector, with a number of Parties indicating they have phased out the use of PFOS in photo imaging completely. Industry has confirmed the complete phase out of PFOS use in this sector can be expected by 2019 in Europe at least, which is attributed to the combined technology switch to digital techniques, and the implementation of non-PFOS alternatives.

### 2.2.5 Data gaps and limitations

55. The following key information gaps have been identified from the above discussion:

- (a) No specific information has been provided for chemical alternatives in terms of their identity, availability, accessibility, technical and economic feasibility, environmental and health effects etc.;
- (b) The trade names and chemical composition of alternatives in this sector are not available;
- (c) There are considerable data gaps relating to the technical feasibility of siloxane compounds used on the market for photographic application (see UNEP/POPS/POPRC.8/INF/17/Rev.1);
- (d) There are information gaps around the levels of PFOS still used globally for this application.

### 2.2.6 Concluding remarks

56. Industry predicts the complete phase-out of PFOS from photoimaging applications by 2019 in Europe. Also, industry reported PFOS is no longer used in this sector in Japan, North America and other areas. This phase-out is attributed largely to the rapid transition towards digital imaging. The remaining few uses of PFOS in photoimaging are niche and low quantities uses, requiring high R&D input, which is increasingly hard to justify. The continued rapid switch towards digital technology, for example through the wide use of digital techniques for medical imaging in developing and transitional countries, as well as the development of chemical alternatives, is likely to lead to further reduction in use of PFOS in this sector.

57. Based on the assessment of the use of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) for photographic coatings applied to film, paper and printing plates, the Committee recommends that the acceptable purpose for the use of PFOS, its salts and PFOSF for photo-imaging no longer be available under the Convention.

<sup>15</sup> See UNEP/POPS/POPRC.9/INF/11.

<sup>16</sup> See UNEP/POPS/POPRC.9/INF/11/Rev.1.

<sup>17</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>18</sup> See UNEP/POPS/POPRC.9/INF/11.

<sup>19</sup> See UNEP/POPS/POPRC.9/INF/11.

## 2.3 Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)

### 2.3.1 Introduction and background

58. The Semiconductor Industry Association (SIA, 2018) reported that the semiconductor industry globally has successfully completed the phase-out of PFOS, and therefore the industry no longer has a need for use exemptions for this set of applications. This would indicate that alternatives to PFOS and related compounds in this sector are available and being implemented globally.

59. PFOS has been used in the semi-conductor industry for applications including photo-resists, and anti-reflective coatings (ARCs) for semiconductors and etching agent for compound semi-conductors and ceramic filters, which are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of acceptable purposes, as of May 2018, the following Parties are registered for these uses: Canada, China, Czech Republic (photo-resists only), European Union, Japan, Norway, Switzerland, Turkey and Vietnam. Those uses are not considered as open applications.

60. PFOS is used as a component of a photo-resist substance, including photo acid generators or surfactants; or in ARCs, used in a photo microlithography process to produce semiconductors or similar components of electronic or other miniaturised devices. Semiconductor manufacturing comprises up to 500 steps, involving four fundamental physical processes:<sup>20</sup> a) Implant; b) Deposition; c) Etch/polish; and d) Photolithography.

61. As discussed in previous POPRC documents,<sup>21</sup> photolithography enables and defines the level of sophistication and performance of the electronic devices and is considered integral for the miniaturisation of semiconductors (Defra, 2004).<sup>22</sup> Formation of such small circuit features are enabled by so-called photo-resists, which are light sensitive polymer coatings on the silicon wafer. Light exposure changes the solubility of the photo-resist enabling it to 'etch' the small circuit features. Photo-resists require the use of so called photo-acid generators (PAGs) to increase their sensitivity to allow etching images smaller than the wavelength of visible light. ARCs are used in this application to avoid disturbance during photolithographic processes.

62. Historically, the acidic counter-ion was PFOS or a PFOS-related substance. PFOS is added to the photo-resist agent to make photo-resist soluble in water and to give surface activity. PFOS reduces the surface tension and reflection of etching solutions, properties that are important for achieving the accuracy and precision required to manufacture miniaturised high-performance semiconductor chips.<sup>23</sup> The exact PFOS derivative used is not publicly known and has not been disclosed by industry. Amec Foster Wheeler and Bipro (2018) noted that PFOS is still reportedly used in a number of European countries in this sector. The Netherlands (2018) noted<sup>24</sup> that, according to industry, without these fluorinated compounds the required properties cannot be obtained.

63. A key advantage of using PFOS is that very small amounts of PFOS-based compounds are required in the photolithographic process. The PFOS or PFOS-related substance concentration was in the range of 0.02 wt/wt% to 0.1 wt/wt% for photo-resists. It is not clear whether PFOS directly or a PFOS-related substance was used in older ARC formulations but the typical concentration of PFOS or PFOS-related substances was ~0.1 wt/wt% for ARC formulations.<sup>25</sup>

64. Photo-resist and anti-reflectant products are either water-based or solvent-based solutions. For example, DOW™ Photo-resists and Anti-Reflectants (Non-PFOS) are liquid formulations containing high-purity solvents, acrylic or other polymer resins, and cross-linking agents, stabilizers, or surfactants.<sup>26</sup>

65. PFOS has also been used as a surfactant in etching processes in the manufacture of compound semiconductors.<sup>27</sup> PFOS-related compounds are favoured because the use of relatively small amounts reduces the surface tension and reflection of etching solutions, properties that are important for accurate and precise photolithography required to manufacture miniaturized high-performance semiconductor chips e.g., for LCD displays. PFOS was part of an etching agent and rinsed out during the subsequent washing treatment.

<sup>20</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>21</sup> UNEP/POPS/COP.7/INF/21; UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>22</sup> See also 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

<sup>23</sup> See UNEP/POPS/POPRC.9/INF/11/Rev.1.

<sup>24</sup> Submission on PFOS, its salts and PFOSF and sulfluramid according to the POPRC-13 follow up.

<sup>25</sup> UNEP/POPS/COP.7/INF/21.

<sup>26</sup> [http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh\\_08fb/0901b803808fb120.pdf?filepath=productsafety/pdfs/noreg/233-00827.pdf&fromPage=GetDoc](http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08fb/0901b803808fb120.pdf?filepath=productsafety/pdfs/noreg/233-00827.pdf&fromPage=GetDoc).

<sup>27</sup> BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

66. For example, PFOS has been used in the etching process of piezoelectric ceramic filters which are used as a bandpass filter at intermediate frequency in two-way radios for police radios, FM radios, TV, remote keyless entry systems for cars, etc.<sup>28</sup>

### 2.3.2 Availability of alternatives

67. A number of alternative chemical substances have been identified for the semi-conductor industry. These include fluorinated substances and non-fluorinated phosphate compounds, e.g. perfluorobutanesulfonic acid, perfluoropolyethers or telomers according to KEMI (2015).<sup>29</sup>

68. It is reported that by 2015 the semi-conductor industry in Austria has replaced PFOS by using a PFOS-free photo-resists. However, no specific details of the composition of the used alternative were provided based on the claim of business confidentiality.

69. IPEN (2018) noted that patent literature also indicates active work in this area. For example, patents describe fluorine-free photo-resist compositions as an alternative to PFOS/PFAS use. Substitutes do exist for non-critical uses, and the semiconductor industry has phased out these uses, for examples, Fuji describes photo-resists that are “PFOS & PFAS free”.<sup>30</sup> Other companies offer PFOS-free photo-resists and ARCs (see Table 2 below).

70. Technology within the industry is improving to avoid/reduce the level of photo-resist required or the volume of PFOS needed. It is noted that new photolithography technologies use less photo-resist per wafer than older technologies, and the new photo-resist formulations contain much lower concentrations of PFOS.<sup>31</sup>

71. Swerea (2015) stated that replacement of PFOS is ongoing or has been achieved through a variety of means including the use of shorter-chain compounds (C<sub>4</sub> to C<sub>1</sub> carbon chains), the use of nonfluorinated substitutes and the elimination of the surfactant function within the photo-resist.

72. Where successful substitution has occurred, information on alternatives is limited (often based on confidential business information). Trade names and producers are known and an overview of the known alternative products available is provided in Table . Photo-resists and anti-reflective products without the use of PFOS are commercially available but information on the type and chemical class of alternatives has not been disclosed in detail.

**Table 2 Overview of known manufacturers and producers of PFOS alternatives for photo-resist and anti-reflective coatings for semi-conductors<sup>32</sup>**

Use	Product	Producer	Reference
Photo-resist	GKR Series KrF	Fujifilm Holdings America	<a href="http://www.fujifilmusa.com/products/semiconductor_materials/photo-resists/krf/index.html">http://www.fujifilmusa.com/products/semiconductor_materials/photo-resists/krf/index.html</a>
Photo-resist	Various Product Names	TOKYA OHKA KOGYO	<a href="http://tok-pr.com/catarog/Deep-UV_Resists/#page=1">http://tok-pr.com/catarog/Deep-UV_Resists/#page=1</a> )
ARCs	ARC® Coatings	Brewer Science Inc.	<a href="http://www.brewerscience.com/arc">http://www.brewerscience.com/arc</a>
ARCs	AZ® Aquatar®-VIII Coating	EMD Performance Materials	<a href="http://signupmonkey.ece.ucsb.edu/wiki/images/b/bb/AZ_Aquatar_VIII-A_45_MSDS.pdf">http://signupmonkey.ece.ucsb.edu/wiki/images/b/bb/AZ_Aquatar_VIII-A_45_MSDS.pdf</a>
Photo-resist and ARCs	Dow™ Photo-resists and Anti-Reflectants (non-PFOS)	The Dow Chemical Company	<a href="http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08fb/0901b803808fb120.pdf?filepath=productsafety/pdfs/noreg/233-00827.pdf&amp;fromPage=GetDo">http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_08fb/0901b803808fb120.pdf?filepath=productsafety/pdfs/noreg/233-00827.pdf&amp;fromPage=GetDo</a>

73. For etching agents used for compound semiconductors, it is indicated that non PFOS-based surfactants are in use for this application (WSC 2011).<sup>33</sup> According to information provided by the World Semiconductor Council short-chain perfluoroalkyl sulfonates are alternatives in use today (WSC 2011). The BAT/BEP guidance indicated there is no information available for alternative technologies for this use.

74. For etching agents for ceramic filters, non PFOS-based surfactants are in use for etching application (WSC 2011), as also noted by EU (2018).

<sup>28</sup> Japan, 2007, Annex F submission.

<sup>29</sup> See UNEP/POPS/COP.7/INF/21.

<sup>30</sup> [http://www.fujifilmusa.com/products/semiconductor\\_materials/photo-resists/krf/index.html](http://www.fujifilmusa.com/products/semiconductor_materials/photo-resists/krf/index.html).

<sup>31</sup> See UNEP/POPS/COP.7/INF/21.

<sup>32</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>33</sup> [http://www.semiconductorcouncil.org/wsc/uploads/WSC\\_2011\\_Joint\\_Statement.pdf](http://www.semiconductorcouncil.org/wsc/uploads/WSC_2011_Joint_Statement.pdf).

75. The BAT/BEP guidance indicated the availability of alternatives, but there is no information available for alternative substances or technologies used. IPEN (2018) have noted that alternative methods using dry etching (including plasma etching) are available in place of wet etching processes.

76. The chemical identity of a number of PFOS alternatives used in photo-resists and ARCs, as marketed by Dow™ (see Table 2) include Amyl Acetate (CAS No: 628-63-7) ; Anisole (CAS No: 100-66-3); n-Butyl Acetate (CAS No: 123-86-4); Ethyl acetate (CAS No: 97-64-3); Methyl 3-methoxypropionate (CAS No: 3852-09-3); Propylene glycol methyl ether acetate (CAS No: 108-65-6). These chemical alternatives are further investigated in Chapter 3.

### 2.3.3 Suitability of alternatives

77. Industry had previously indicated that identifying and qualifying alternatives for all critical uses in the semiconductor sector is extremely complex and is process-, technology-, and company-specific (UNECE, 2005). Industry has previously considered that while alternatives are commercially available, no chemical alternatives currently available that would allow for the comprehensive substitution of PFOS in essential applications.<sup>34</sup> No alternative substances have been commercialized for existing uses in PAG and ARCs that would allow for the comprehensive substitution of PFOS in these critical applications.

78. Despite the challenges noted above, a SIA (2018) announcement that the semiconductor industry has successfully completed the phase-out of PFOS, as noted above, would suggest the alternatives developed (chemical or non-chemical) are technically and economically feasible and there are no major barriers to their implementation. It is reported that, in the US, the cost of developing a new photo-resist represents 0.3 % of annual sales, indicating that cost is not a barrier to develop a new photo-resist system.<sup>35</sup>

79. The 2017 BAT/BEP guidance noted that it is not possible to definitively determine if it is feasible to replace PFOS and related compounds technically, due to a lack of information about the alternatives.

80. There may be one additional specialized application for which, according to industry sources, there is currently no substitute for PFOS, i.e. use in liquid etchant in the photo mask rendering process.<sup>36</sup> For photo mask etching with strong acids, it is considered that the non-fluorosurfactants available are not stable enough, and shorter-chain fluorosurfactants do not have sufficiently low surface tensions to be considered viable alternatives.<sup>37</sup>

81. IPEN (2018) reported that plasma etching is currently used commercially using low-pressure plasma systems. Plasma etching does not cause photo-resist adhesion problems; uses small amounts of chemicals; lowers cost of disposal of reaction products; and can be used in automated processes. Its disadvantages include use of complex materials and the possibility of poor selectivity and residues left on the wafer. However, according to plasma etching system manufacturers, controlled plasma etching removes all unwanted organic residues from the metal surface unlike acid etchants; adheres to surfaces better than acid etchants; improves the physical properties of the etched material; and is less risky and less costly.

82. A new dry etch technology now being commercially introduced is atomic layer etch (ALE), which selectively removes materials at the atomic scale. These can be plasma or thermal based systems or a hybrid of both. Suppliers of these technologies include Applied Materials, Hitachi High-Technologies, Lam Research, and TEL. Information on the relative performance has not been made available, this will need to be assessed in order to determine the suitability of this technique in practice.

83. The SIA (2018) evidence would suggest that to a large extent, the challenges facing industry in terms of developing suitable alternatives have been met and PFOS has been almost entirely phased out. However, it is not clear precisely what alternative approaches have been utilised to achieve this. This section has highlighted a number of aspects where development of alternative is indicated to be very challenging. From the available information, it is not clear what substances or techniques are being used to address these aspects.

### 2.3.4 Implementation of alternatives

84. The Semiconductor Industry Association (SIA, 2018) reported that the semiconductor industry globally has successfully completed the phase-out of PFOS, and therefore the industry no longer has a need for use exemptions for this set of applications. It should be noted that this applies to only member organisations of the SIA, so it may not mean that all use of PFOS has been eliminated globally. However, the World Semiconductor Council<sup>38</sup> has association

<sup>34</sup> See UNEP/POPS/COP.7/INF/21.

<sup>35</sup> See UNEP/POPS/COP.7/INF/21.

<sup>36</sup> See UNEP/POPS/POPRC.3/20/Add.5

<sup>37</sup> See UNEP/POPS/COP.7/INF/21.

<sup>38</sup> [https://www.semiconductors.org/clientuploads/directory/DocumentSIA/International%20Trade%20and%20IP/21st%20WSC%20Joint%20Statement%20May%202017%20Kyoto%20\(Final\).pdf](https://www.semiconductors.org/clientuploads/directory/DocumentSIA/International%20Trade%20and%20IP/21st%20WSC%20Joint%20Statement%20May%202017%20Kyoto%20(Final).pdf)

members of companies located in many countries including the top four global semiconductor manufacturers: Intel, Samsung, TSMC, and Qualcomm. In addition, members of the World Semiconductor Association which announced the phase-out at its 2017 meeting in Japan include industry associations from China, Chinese Taipei, Europe, Japan, South Korea, and USA.<sup>39</sup>

85. The SIA (2018) evidence indicated that PFOS has been mostly eliminated from this use already with the availability of alternative substances or techniques likely to lead to the remaining uses being phased out in the foreseeable future.

86. As a further example of this, IPEN (2018) note that IBM began PFOS/PFOA phase-out in 2003 and eliminated PFOS and PFOA in its wet etch processes in 2008 and went on to eliminate PFOS/PFA in all its photolithography processes in 2010.

87. In the EU, it is reported that the use of PFOS in the semi-conductor industry declined from 470 kg per annum in 2000 to 9.3 kg in 2015, with further decline likely after this date.<sup>40</sup> This indicates that alternative substances and formulations have been successfully implemented, leading to a relatively rapid decline in PFOS use.

88. In the case of photo-resists, the BAT/BEP Group of Experts, 2017, stated that for best practice “the use of PFOS, its salts and PFOSF for formulations that were introduced into the market before 2011 should be phased out and alternative/non PFOS-based and non PFOS-related substances should be used for formulations that were introduced into the market after 2011”.

89. EU (2018) indicated that, for photo-resist and anti-reflective coatings, in non-critical uses (e.g. developing agents) substitution of PFOS has already taken for photo-resist and anti-reflective coatings for semi-conductors’ alternative formulations are only recently available on the market.

90. In the photolithography industry, it is considered that few chemical alternatives are available that would allow for the comprehensive substitution of PFOS in critical applications (i.e., PAGs and ARCs). Therefore, the declining use of PFOS and ultimate phase-out can be attributed more strongly to new photolithography technologies, use of less photo-resist per wafer, and the new photo-resist formulations that contain much lower concentrations of PFOS.<sup>41</sup>

91. This demonstrates that through a combination of implementing new chemical alternatives to replace PFOS, and new technologies that minimise the levels of PFOS needed, the use of PFOS in the semiconductor industry can be eliminated.

### 2.3.5 Data gaps and limitations

92. The following key information gaps have been identified from the above discussion:

(a) The semi-conductor industry has indicated that a successful global phase-out of PFOS has been completed in this sector. However, it is noted that the SIA (2018) input does not specify the composition of the alternatives predominantly used in this industry, or details about process or technique changes to eliminate PFOS use;

(b) Within the semi-conductor industry, it is not clear what alternative substances and approaches have been utilised largely due to confidentiality of trade secret information. Industry claims that they need more time to develop a full range of qualitatively comparable alternatives.<sup>42</sup>

### 2.3.6 Concluding remarks

93. The semiconductor industry globally has successfully completed the phase-out of PFOS, indicating that PFOS has been mostly eliminated from this use already with the availability of alternative substances/techniques likely to lead to the remaining uses being phased out in the foreseeable future.

94. Based on the steadily declining use of PFOS, its salts and PFOSF for semi-conductors (photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters) and the commercially availability of alternatives, the Committee recommends that the acceptable purpose for the use of PFOS, its salts and PFOSF for photo-resist and anti-reflective coatings for semi-conductors and as etching agent for compound semi-conductors and ceramic filters no longer be available under the Convention.

<sup>39</sup> <http://www.semiconductorcouncil.org/about-wsc/members>

<sup>40</sup> Information submitted through National Implementation Plans available for EU Member States and information contained related to PFOS production and use; COP 5; 04.06.2015).

<sup>41</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>42</sup> Based on submission by Netherlands for UNEP/POPS/COP.7/INF/11.

## 2.4 Aviation hydraulic fluids

### 2.4.1 Introduction and background

95. Aviation hydraulic fluids are listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of acceptable purposes, as of May 2018, the following Parties are registered for this use: Canada, China, Czech Republic, Switzerland, Vietnam, and Zambia. This use is considered as an open application according to document UNEP/POPS/POPRC.7/INF/22/Rev.1. Fire-resistant hydraulic fluids based on phosphate ester chemistry (e.g., Skydrol® 7000 developed by Monsanto) were initially developed in the late 1940s (Skydrol, 2003). Hydraulic fluids are used in applications with performance demands that “oil-based” hydraulic fluids cannot match (e.g., fire resistance and very good low temperature properties). Hydraulic fluids actuate moving parts of the aircraft such as wing flaps, ailerons, the rudder and landing gear. It was discovered that localized corrosion occurs in the valves of the hydraulic system over time affecting their efficiency causing premature overhaul of mechanical parts.

96. Aviation hydraulic fluids based on fire resistant alkyl or aryl phenyl phosphate esters may contain additives such as cyclohexanesulfonic acid, decafluoro(pentafluoroethyl), potassium salt (CAS No. 67584-42-3) and different chain-length homologs (SDS Hyjet®) in concentrations of about 0.05% (Defra 2004).

97. In the manufacturing process for aviation hydraulic fluids, PFOS-related compounds such as potassium perfluorethylcyclohexyl sulfonate (CAS 67584-42-3), was used as an additive to the aviation hydraulic fluids. It was noted that the potassium salt of PFOS was used in such a small quantity that it was not listed on the MSDS at Boeing (Boeing, 2001).<sup>43</sup>

98. The presence of the fluorinated surfactant inhibits corrosion of mechanical parts of the hydraulic system by altering the electrical potential at the metal surface, thereby preventing the electrochemical oxidation of the metal surface under high pressure (Defra 2004).

### 2.4.2 Availability of alternatives

99. EU (2018) reported that overall the knowledge about alternatives in this sector is very limited.

100. It is noted that the hydraulic fluids existed before PFOS was industrially available and the oil-based fluids might potentially be an alternative.<sup>44</sup> A key factor in the switching to non-PFOS alternatives in this sector may therefore be the level to which the hydraulic system will need to be adapted or refitted to accommodate new fluid formulations.

101. It is reported that the fire-resistant aviation hydraulic fluids on the market principally contain tri-alkyl phosphates, tri-aryl phosphates, and mixtures of alkyl-aryl-phosphates, but the products only provide rough descriptions of their chemical composition such as “contain phosphate esters”. The precise composition of these products is not clear.

102. Fluorinated phosphate esters (that may contain other fluorinated additives) are used alternatives but no detailed information concerning their performance, chemical composition of the aviation hydraulic oils or environmental and health impacts is available.

103. As noted in UNEP/POPS/POPRC.8/INF/17/Rev.1, there is no available information on: health and environmental effects including toxicological and ecotoxicological information, cost-effectiveness, efficacy, variability, accessibility and socio-economic considerations of alternatives to the use of PFOS-related compounds in aviation hydraulic fluids.

104. 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.<sup>45, 46</sup>

105. 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 LD-4.<sup>47</sup>

106. The 2017 BAT/BEP Group of Experts guidance document noted that no information is available on alternative substances or technologies in this sector.

<sup>43</sup> <http://www.boeing-suppliers.com/environmental/TechNotes/TechNotes2001-02.pdf>.

<sup>44</sup> See UNEP/POPS/COP.7/8.

<sup>45</sup> National report from Spain to the Stockholm Convention on PFOS, 2014.

<sup>46</sup> PFOS\_Norway\_8 Jan 2016\_HYJET V Data sheet (003).pdf.

<sup>47</sup> <http://www.atsdr.cdc.gov/toxprofiles/tp99-c3.pdf>.

107. A review of publicly available information from the companies or commercially available products listed above identified a number of chemical substances used in 'alternative' hydraulic fluids. These chemical substances or commercial products, and their potential POP characteristics, are discussed in Chapter 3.

108. The BEP noted for this use focus on the minimisation of emissions to the environment, through appropriate down-cycling and handling of spent aviation hydraulic fluids, physical chemical treatment and incineration in specialised treatment facilities that operates at high enough temperatures to thermally mineralize the fluorinated substances.

#### 2.4.3 Suitability of alternatives

109. It is not possible to make a detailed assessment of the technical or economic feasibility of alternatives due to the very limited information available, largely due to confidentiality of trade secret information.

110. The potassium salt of perfluoroethylcyclohexyl sulphonate (CAS No: 67584-42-3) is not a PFOS precursor, but a PFOS related substance, and it has been used in hydraulic oils instead of PFOS in the past. However, like other C<sub>8</sub> compounds it is likely to be persistent.<sup>48</sup> 3M which formerly produced this chemical has ceased to do so.

111. It is noted that phosphate esters 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. This factor could impact the overall feasibility of using these compounds as alternatives in aviation hydraulic fluid.

112. However, no specific information of the chemical composition of alternatives was made available so it is not possible to comment on their potential feasibility and impact to health and environment in a comprehensive way.

#### 2.4.4 Implementation of alternatives

113. Canada (2018) indicated that no PFOS is intentionally added to aviation hydraulic fluids and aviation hydraulic fluids containing PFOS have been prohibited in Canada since 2016.

114. It is noted that the EU and Norway withdrew their notification for acceptable purposes for this use in 2017, which indicates the viability and feasibility of alternatives. Both Vietnam and Zambia noted that they are conducting an inventory of PFOS use and they may be able to withdraw acceptable purposes for this use based on their outcomes.

115. These observations suggest that alternatives are commercially available and have been implemented, leading to the successful phase out of PFOS from this use.

116. IPEN (2018) commented that the POPRC requested Parties and Observers to provide information on whether PFOS was still used in aviation hydraulic fluids. It was noted that there are a large number of products (see trade names above) but very little information about what they actually contain.

#### 2.4.5 Data gaps and limitations

117. The following key information gaps have been identified from the above discussion:

- (a) The identity of specific chemical alternatives to PFOS in aviation hydraulic fluids is unknown;
- (b) Lack of data available to assess technical and economic feasibility, environmental and health impacts etc.;
- (c) Lack of information on the volumes of PFOS still in use for this sector.

#### 2.4.6 Concluding remarks

118. A complete assessment of availability, suitability and implementation of alternatives in aviation fluids is not possible due to a lack of available data. Aviation hydraulic fluids without fluorinated chemicals but based on, for example, phosphate esters exist and are on the market through a range of different products. No updated information on the usage of a PFOS-related substance, cyclohexanesulfonic acid, decafluoro(pentafluoroethyl), potassium salt that has been used (rather than PFOS) in hydraulic fluids and an assessment on health or environmental effects is available. Given the significant information gaps, it is difficult to draw definitive conclusions. A number of Parties have reported they no longer use PFOS for this acceptable purpose and /or have withdrawn their notification, indicating viable alternatives are available and there may be no further need for the use of PFOS in aviation hydraulic fluid.

<sup>48</sup> A NICNAS (2015b) assessment categorized perfluoroethylcyclohexyl sulphonate as persistent (P) according to domestic environmental hazard criteria. The bioaccumulation potential and toxicity are categorised as 'uncertain'.

119. Based on the assessment and the availability of alternatives and the withdrawal of a number of Parties from the register of acceptable purposes, the Committee recommends that the acceptable purpose for the use of PFOS, its salts and PFOSF for aviation hydraulic fluids no longer be available under the Convention

## **2.5 Metal-plating (Metal plating (hard metal plating) only in closed-loop systems; Metal plating (hard metal plating); Metal plating (decorative plating))**

### **2.5.1 Introduction and background**

120. 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 of May 2018, according to register of acceptable purposes, ongoing production and use has been indicated for China, EU and Vietnam. Ongoing use (only) is reported in Canada, Czech Republic, Norway, Switzerland and Turkey.

121. Metal plating (hard metal plating) and metal plating (decorative plating) are listed as specific exemptions for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of specific exemptions, China is registered for those uses, although it is noted that the expiry date has not been provided. Registered exemptions for all other countries have either expired or been withdrawn. These uses are considered as open applications, unless used in closed loop process, according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

122. In practical terms, the difference between hard and decorative metal plating is the thickness, hardness and deposition of the chrome layer on the plated object. The two techniques have different overall aims, for hard metal plating, the function is to provide resistance against corrosion, abrasion etc, while for decorative metal plating, the main function is primarily a decorative surface finish.<sup>49</sup>

123. The term “hard” plating refers to the process of electrodepositing a thick layer (0.2 mm or more) of certain types of metal directly onto substrates. The deposited chrome layer provides desirable properties, such as hardness, wearability, corrosion resistance, lubricity, and low corrosion of friction. Examples of hard metal plated parts include, hydraulic cylinders and rods, railroad wheel bearings and couplers, moulds for the plastic and rubber industry, tool and die parts.

124. In “decorative” plating only a thin layer (0.05 to 0.5µm) of metal is deposited onto substrates, the deposited chrome layer providing desirable properties such as aesthetically pleasing appearance, non-tarnishing etc. Examples of decorative chrome plated parts include, car and truck pumpers, motorcycle parts, kitchen appliances, smart phones and tablets. Metal plating is an electrolytic process with a significant amount of gases released from the process tank. This causes bubbles and mist to be ejected from the plating bath causing aerosols, consisting of process liquids containing e.g. chromic acid, to be dispersed into outdoor ambient air unless controlled, for example with chemical fume (mist) suppressants. In chrome plating, the plating bath typically consists of chromic acid (Cr(VI) acid). Cr(VI) is a known human carcinogen and therefore minimising or eliminating its use or controlling emissions to prevent occupational and environmental exposure is essential.

125. Chemical fume (mist) suppressants are surfactants that lower the surface tension of the plating solution. By controlling the surface tension, the process gas bubbles become smaller and rise more slowly than larger bubbles. Slower bubbles have lower kinetic energy so that when the bubbles burst at the surface, mist is less likely to be emitted into the air and the droplets fall back into the plating bath.

126. PFOS salts are or have been commonly used as a surfactant, wetting agent and mist suppressing agent for chrome metal plating processes to create protective foam and decrease aerosol emissions. PFOS has been favoured because, in the chromic acid solution, other mist suppressants degrade more rapidly under the prevailing, strongly acidic and oxidizing conditions. Fluorinated surfactants (including PFOS) are not reported to be used in other metal plating applications (e.g. copper plating, nickel plating, tin plating, zinc and zinc alloy plating, electroplating of polymers) besides metal plating with chromium (VI).

127. PFOS is effective in metal plating as it lowers the surface tension of the plating solution and forms a single foam 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) to the atmosphere.

128. 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). The concentration of the PFOS in the mist suppressant chemical formulation can range between 1-15 % depending on the formulation (supplier). The price is dependent on the concentration of PFOS in the chemical, with cheaper products typically containing about 2-3 % PFOS and more expensive products containing 3-7 % PFOS. The

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<sup>49</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

potassium, lithium, diethanolamine and ammonium salts of PFOS may also be used.<sup>50</sup> The typical use rate of PFOS-salts in these applications was 30 mg/l to 80 mg/l (0.03 wt% to 0.08 wt%) (Blepp et al. 2015). The calculated process lifetime for PFOS ranged from 0.41 years to 0.70 years.<sup>51</sup>

129. The consideration of alternatives in the metal plating sector is focussed predominantly on the hard metal plating only in closed-loop systems. However, EU (2018) noted that currently, there is no harmonised definition of closed loop systems and the definition of ‘closed loop’ can vary dependent on different understanding. The 2017 BAT/BEP expert guidance states that “a closed loop system needs to be utilized when using PFOS as mist suppressants”. The document has includes nine criteria to achieve “closed loop performance”, which can collectively result in a 98% efficiency to recover chromic acid. However the mist suppressant recovery efficiency of these measures is unclear. These measures include:

- (a) Removal of remaining chromic acid and mist suppressants from plating bath, and rinse plated articles directly above the plating bath;
- (b) Closely control the mass balance of the mist suppressant;
- (c) Transport exhaust air and aerosols above the plating bath via an exhaust to an evaporator;
- (d) Treat the remaining exhaust air further in a 2-stage wet air scrubber;
- (e) Utilize multi-step counter-current rinse cascades to further clean the finished parts and recycle the electrolyte solution;
- (f) Utilize evaporators to concentrate the rinse solution to be recirculated into the plating bath.
- (g) Remove contamination of Cr(III) and other metal ions in the plating bath by circulating the most diluted rinsing cascade through a double cation exchange resin;
- (h) Treatment of waste water through ion exchange resins to remove metal ions and through granulated activated carbon filters to remove mist suppressant residues;
- (i) Collect and reprocess chromium hydroxide sludge generated during the plating process to reclaim chromium.

130. It is noted that 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), commonly achieved with the use an evaporator is required to regain the electrolyte from the rinse water.<sup>52</sup> Multi-step criteria defining the characteristics of a closed loop system have been provided by Blepp et al. (2015) and the UNEP (2017) BAT/BEP expert guidance, which will lead to a ca. 98% efficiency to recover chromic acid. However, no information is available on mist suppressant recovery efficiency. Blepp et al. (2015) includes as a characteristic of largely closed loop also the treatment of PFOS containing waste water with PFOS specific ion exchangers. Since the mist suppressant is solved in the chromic acid solution, the recovery efficiency is assumed to be directly related to the recovery ration of Cr(VI), or at least in the same order of magnitude, neglecting specific adsorption or concentration effects.

### 2.5.2 Availability of alternatives

131. 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.<sup>53</sup>

132. It is indicated that a range of chemical alternatives (both fluorinated and non-fluorinated), and non-chemical or alternative process approaches are available for use in chrome metal plating applications. An overview of these different alternatives is provided in Table 3 below.

<sup>50</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>51</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>52</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>53</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

Table 3 Overview of alternatives to PFOS for use in the metal plating sector.

Composition	CAS No	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
<b>Fluorinated alternatives</b>							
6:2 Fluorotelomer sulfonate (6:2 FTS)  (Hard metal)	27619-97-2	Yes	No	<ul style="list-style-type: none"> <li>• Capstone (Chemours)</li> <li>• FS10 Proquel OF (Kiesow)</li> <li>• ANKOR® Dyne 30 MS (Enthone)</li> <li>• ANKOR® Hydraulics (Enthone)</li> <li>• ANKOR® PF1 (Enthone)</li> <li>• Fumetrol® 21 (Atotech)</li> <li>• Fumetrol® 21 LF 2 (Atotech)</li> <li>• HelioChrome® Wetting Agent FF (Kaspar Walter)</li> <li>• Maschinenfabrik GmbH &amp; Co. KG)</li> <li>• PROQUEL OF (Kiesow Dr. Brinkmann)</li> <li>• Wetting Agent CR (Atotech)</li> </ul>	UNEP/POPS/POPRC.10/INF/7/Rev.1  BAT/BEP Expert Guidance  Poland (2018)  Germany (2018)	3	Some of the products listed are not resistant in chrome sulfuric acid pickling and hard chrome baths.
6:2 Fluorotelomer sulfonate (6:2 FTS)  (Decorative)	27619-97-2	No	Yes	<ul style="list-style-type: none"> <li>• ANKOR® Dyne 30 MS (Enthone)</li> <li>• Cancel ST-45 (Plating Resources, Inc.)</li> <li>• FS-600 High Foam (Plating Resources, Inc.)</li> <li>• FS-750 Low Foam (Plating Resources, Inc.)</li> <li>• Fumetrol 21 (Atotech)</li> <li>• SLOTOCHROM CR 1271 (SchlötterGalvanotechnik)</li> <li>• UDIQUE® Wetting Agent PF2 (Enthone)</li> <li>• Wetting Agent CR (Atotech)</li> </ul>	UNEP/POPS/POPRC.10/INF/7/Rev.1  BAT/BEP Expert Guidance	3	
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt	754925-54-7	Yes	No	<ul style="list-style-type: none"> <li>• F-53 (China product)</li> </ul>	UNEP/POPS/POPRC.10/INF/7/Rev.1 BAT/BEP Expert Guidance	3	Available in China
2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate	73606-19-6	Yes	No	<ul style="list-style-type: none"> <li>• F-53B (China product)</li> </ul>	UNEP/POPS/POPRC.10/INF/7/Rev.1 BAT/BEP Expert Guidance	3	Available in China

Composition	CAS No	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane	N/A	Yes	No	No information	UNEP/POPS/POPRC.10/INF/7/Rev.1	3	
Other fluorinated alternatives	N/A	Yes	Yes	<ul style="list-style-type: none"> <li>Chromnetzmittel LF (CL Technology GmbH)</li> <li>Netzmittel LF (Atotech)</li> <li>RIAG Cr Wetting Agent (RIAG Oberflächentechnik AG)</li> </ul>	BAT/BEP Expert Guidance	N/A	No information on chemical identity is known:
<b>Fluorine-free alternatives</b>							
Alkane sulfonates	N/A	Yes	Yes	<ul style="list-style-type: none"> <li>TIB Suract CR-H (TIB Chemicals AG))</li> </ul>	BAT/BEP Expert Guidance		Not resistant to hard chromium plating, less effective in decorative chromium plating
Oleo amine ethoxylates	26635-93-8	No	Yes	<ul style="list-style-type: none"> <li>ANKOR® Wetting Agent FF (Enthone))</li> <li>Antispray S (Coventya)</li> </ul>	BAT/BEP Expert Guidance	N/A	(Z)-Octadec-9-enylamine, ethoxylated (Oleylamine thoxylat)
Other non-fluorinated alternatives,	N/A	Yes	Yes	<ul style="list-style-type: none"> <li>CL-Chromeprotector BA (CL Technology GmbH)</li> <li>Antifog V4 (Chemisol GmbH &amp; Co. KG)</li> <li>Non Mist-L (Uyemura)</li> </ul>	BAT/BEP Expert Guidance	N/A	No information on chemical identity
<b>Non-chemical / alternative processes</b>							
Physical covers (netting, balls) for metal plating baths (chromium (VI))	N/A	Yes	Yes	Information gap	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1 BAT/BEP Expert Guidance	N/A	E.g. Mesh or blankets (Composite Mesh Pads) placed on top of bath  Not recommended or considered BEP
Add-on air pollution control devices	N/A	Yes	Yes	Information gap	BAT/BEP Expert Guidance	N/A	E.g. Packed Bed Scrubbers
Novel plating processes	N/A	Yes	Yes	Topocrom <a href="http://www.topocrom.com">www.topocrom.com</a>	BAT/BEP Expert Guidance	N/A	E.g. HVOF (High Velocity Oxygen Fuel) Process
Trivalent chromium or Cr(III) plating.	N/A	No	Yes		BAT/BEP Expert Guidance	N/A	

\*Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: 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 for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

### 2.5.2.1 *Chemical alternatives in metal plating*

133. Germany (2018) indicated that the available chemical alternatives to PFOS can be divided into two main categories:

(a) Fluorinated substitutes: As to their uses, these substances are comparable with PFOS, and they can be used in almost all processes including chromo-sulfuric acid etchant, bright chromium and hard chromium electrolytes. The fluorinated substitutes can be divided into three sub-groups:

- (i) Short-chain fluorinated surfactants;
- (ii) Polyfluorinated surfactants;
- (iii) Polyfluorinated compounds;

(b) Fluorine-free substances: These have already been partially used in bright chrome electrolytes in decorative plating. According to some suppliers of process chemicals, their use in hard chromium electrolytes is also possible. According to the current state of knowledge, the use of such substances should be considered on a case-by-case basis.

134. Chemical alternatives are currently available for hard metal plating and decorative plating.<sup>54</sup> The industry association FluoroCouncil (2018) indicated that short-chain fluorosurfactant alternatives such as 6:2 fluorotelomer sulfonate and potassium perfluorobutane sulfonate have been reviewed globally and approved by regulators and have been commercially available from numerous suppliers worldwide for over a decade. Poland (2018) and Germany (2018) indicated 6:2 fluorotelomer sulfonate compounds are commercially available in those countries. A large number of commercially available products containing non-PFOS alternatives are listed in Table 4.

135. Non-fluorinated alternatives are also available in this sector. It is indicated<sup>55</sup> that non-fluorinated alternatives for hard metal plating are available on the European market but are new, and some are still being tested. The chemical description and CAS numbers of these products have not been released by the industry. For example, IPEN (2018) cited a study by the Danish Ministry of Environment, which identified several non-fluorinated alternatives for use in hard chrome plating (as shown in Table 4). Canada (2018) indicated that PFOS-free fume suppressants are now already in use, and that PFOS is no longer allowed for this application in Canada.

136. The German electroplating industry association (ZVO, 2018) indicated the availability of PFOS-free alternative products from 10 German suppliers. It is noted that information is lacking regarding the exact identity and composition of these chemical compounds, however it is indicated that three are fluorinated and seven are non-fluorinated.

137. One chemical alternative to PFOS, as identified in the BAP/BAT Guidance document, are oleo amine ethoxylates (CAS 26635-93-8). This substance was not covered in the previous alternates assessment and will be considered in more detail in Chapter 3.

### 2.5.2.2 *Non-chemical alternatives / alternative processes*

138. A number of alternative approaches have been outlined, with the intention of either replacing the use of Cr(VI) in the plating process completely, altering the technique used in the plating/coating process, or providing alternative means of preventing the release of Cr(VI) during the process. These are described below.

139. For decorative plating, the BAT/BEP expert guidance (2017) noted that parts of the decorative chrome plating industry have adopted the use of trivalent chromium, Cr(III) in plating, which is intrinsically less toxic than Cr(VI). The use of Cr(III) represents the BAT for the applications in which it is feasible, and it is indicated that, where used, it has eliminated the use of PFOS as mist suppressant. It is also suggested that the use of trivalent chromium (Cr(III)) could also be applied in hard metal plating in some applications. In principle, the use of PFOS would not be strictly necessary if Cr(VI) was not used, however it is noted that Cr(III) has been shown to oxidise to Cr(VI) under environmental conditions. For example Apte et al. (2006) indicated a 17% conversion in sludge samples. The potential for conversion of Cr(III) to Cr(VI) during the plating process is unclear and will require further investigation.

140. Novel plating techniques for hard chrome plating have been developed. For example, the High Velocity Oxygen Fuel (HVOF) process, is known to be globally available and is considered effective and with low costs

<sup>54</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>55</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

(Mehta et al., 2017). Depending on the substrate and coating powder used, Mehta et al. (2017) noted that the HVOF method displays high deposition efficiency and good quality finish (high density, low porosity), but has the disadvantage of requiring high temperature application.

141. Another alternative process has also been developed where no surfactants are required<sup>56</sup> e.g. in processes where surfaces are coated in a closed coating reactor, thereby significantly reducing the chromic acid aerosols are emitted in the room air.

142. Several physical alternative techniques are being developed. IPEN (2018) cited the results of a study by the Danish Ministry of Environment, which noted that physical methods can be effective by promoting condensation of the aerosol close to the electrolyte surface using, for example, a mesh solution and avoiding the transportation of aerosol from the surface of the electrolyte with a cover that prevents ventilation.

143. Germany (2018) outlined a number of alternative technologies for the prevention of Cr(VI) release during plating processes, including the use of PTFE-coated balls on top of bath, and mesh or blanket covers for plating baths.<sup>57</sup> However, the effectiveness of this approach relative to mist suppressants has been questioned (see Section 2.5.3). The use of control devices, such as Composite Mesh Pads (CMP) or Packed Bed Scrubbers (PBS), to catch aerosols from chromium plating are considered as alternatives to the use of PFOS-based control devices.<sup>58</sup> It has been indicated that there are no factors limiting the accessibility of these control devices, and they are commercially available in Canada.<sup>59</sup>

### 2.5.3 Suitability of alternatives

144. ZVO (2018) noted that, multi- and polyfluorinated alternatives have substituted PFOS and its salts in most cases. They have displayed similar technical feasibility with respect to quality and process stability. However, 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 due to its extremely persistent properties.<sup>60</sup>

145. It is noted that numerous products, for example, based on short chain fluorosurfactants, have been tried for the application in hard metal plating, but all alternatives have proven to be less effective and less stable than PFOS under the harsh conditions of this process.<sup>61</sup> 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.<sup>62</sup>

146. As outlined in a report by Amec Foster Wheeler and Bipro (2018) a number of limitations have been noted for the use of PFOS-free alternatives in metal plating:<sup>63</sup>

- (a) The performance is not equal to PFOS based suppressants, particularly for fluorine-free alternatives;<sup>64</sup>
- (b) Plating baths may need to be dosed at higher concentrations than the PFOS salts to meet specific surface tension requirements and might be less stable and therefore may have to be replenished more frequently.<sup>65</sup> This may have significant cost implications;
- (c) Use of alternatives may cause corrosion of lead anodes that will then need to be replaced more frequently. This may have significant cost implications;
- (d) Products can reduce Cr(VI) to Cr(III) in the chromium electrolyte which can lead to serious faults in the chromium coating;
- (e) Short chain fluorinated alternatives could pose similar risks to the environment like PFOS and that use of shorter chain fluorinated alternatives leads to the occurrence of very persistent degradation products in the environment (e.g. PFHxA in water bodies; see current Germany submission 2018; POPRC 13 follow-up); PFOS can be retained more easily than alternatives by activated carbon techniques or the use of ion exchangers, so there is a danger of higher levels of environmental release;

<sup>56</sup> [http://www.topocrom.com/content/pdf/Artikel\\_Verfahren\\_k\\_muell.pdf](http://www.topocrom.com/content/pdf/Artikel_Verfahren_k_muell.pdf).

<sup>57</sup> <http://www.subsport.eu/case-stories/179-de/?lang=de>.

<sup>58</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs

<sup>59</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>60</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>61</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>62</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>63</sup> See also BAT/BEP Group of Experts 2017; (UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>64</sup> BAT/BEP Group of Experts 2017; (UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>65</sup> BAT/BEP Group of Experts 2017; (UNEP/POPS/POPRC.12/INF/15/Rev.1.

(f) Fluorinated alternatives to PFOS could potentially have similar properties to PFOS and could therefore lead to regrettable substitutions.

147. Germany (2018) has indicated that the partially fluorinated substance- 6:2 fluorotelomer sulfonate (6:2 FTS) is not considered a viable alternative due to environmental concerns relating to degradation to become the stable perfluorohexanoic acid (PFHxA).

148. The BAT/BEP expert guidance reports that 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) should not be considered viable alternatives due to negative impacts on human health and the environment. No information is available on the shorter chain alternatives developed in China. Current BAT/BEP for PFOS means that PFOS is used in closed loop so that hardly any emissions occur. By selecting suitable activated carbon, or ideally ion exchangers, and optimized flow rates, up to 99% of PFOS can be removed from wastewater by adsorption onto the activated carbon. ZVO (2018) express concern that alternatives may be able to pass such filters significantly, which would lead to higher rates of environmental release, if processes are adapted for closed loop also concerning PFOS emissions. This factor would need to be considered against the relative differences in the PBT properties and other environmental impacts of alternatives compared to PFOS.

149. ZVO (2018) considered there are no other reliable alternatives on the market at the moment. Non-fluorinated alternatives are not economically viable because their use causes additional risks with respect to safety, process stability and device preservation. ZVO (2018) note that non-fluorinated alternatives tested were not stable enough in the hard chrome plating bath, but could be used for decorative chrome plating, for which alternative chromium (III) processes seem to exist already.

150. ZVO (2018) suggest that most companies and local authorities in Germany indicate they would prefer returning to PFOS with the constraint of implementing activated carbon filters, that may hold back all PFOS and prevent it from being disseminated to environment.

151. Fluorocouncil (2018) considered that the technical feasibility of the alternatives is specific to the industrial metal plating process in practice. Users have adopted alternatives that meet their industrial use requirements. No one substance has provided a universal solution as a replacement for PFOS. According to the current state of knowledge, noted in the BAT/BEP guidance, the use of fluorine-free alternative substances should be considered on a case-by-case basis.

152. In terms of the non-chemical or process based approaches, it is indicated by Germany (2018) that regarding PTFE-coated balls on top of bath, the state of knowledge is that this alternative will not reduce chromium emission from the chroming bath but, in contrast, chromium emissions appear to increase, as compared to emissions released in cases where no mist suppression is applied at all. Germany (2018) also indicate that the use of mesh or blanket covers requires further research before this can be considered an effective control measure.

153. Germany (2018) noted that, as reported in German Environment Agency (2017), in one company it has been estimated that in around 20% of applications the HVOF methods of spraying chromium layers can replace hard chromium layers deposited by electroplating<sup>66</sup>. However, layers deposited using this method may be more porous and less resistant to corrosion (German Environment Agency, 2017).

154. Oosterhuis et al. (2017) provided cost estimate data for the substitution of persistent organic pollutants, including PFOS, to safer alternatives. It was indicated that for metal plating, alternatives appeared to be available at limited additional cost, in some cases close to zero or even negative but always less than \$1000 per kilogram.

#### 2.5.4 Implementation of alternatives

155. The UNEP (2017) BAT/BEP expert guidance stated that “Non PFOS-based mist suppressants should be used for this application and all measures of a “closed loop” system should be implemented in the plating process”. This indicates that alternatives should be implemented as best practice. For some applications, the alternative technology “Cr(III) Plating” represents the BAT. This alternative process does not require the use of mist suppressants, hence where this technique is used as best practice, the switch to a non-PFOS alternative process should also take place.

156. The use of chromium (III) instead of chromium (VI) for certain decorative chrome plating processes has made PFOS use in decorative chrome plating obsolete.<sup>67</sup> For example, Norway has reported the industry phase out of the use of PFOS-containing wetting/anti-mist agent by using the chromium (III) process instead of the chromium (VI) process where possible.

157. It is reported that Canada and Japan discontinued this use of PFOS in hard metal plating processes, in favour of using alternatives. In the European Union, it is reported that the annual PFOS use for metal plating declined from

<sup>66</sup> See also [https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2017-11-01\\_texte\\_95-2017\\_pfos\\_en\\_0.pdf](https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2017-11-01_texte_95-2017_pfos_en_0.pdf).

<sup>67</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

about 10 tonnes in 2003 to around 4 tonnes in 2010, suggesting a transition towards alternative substances and processes

158. National Implementation Plans (2017, 2018) indicate that PFOS is currently still in use in hard metal plating in the EU, at least in the Czech Republic, Germany and the UK. Netherlands and Germany reported the use for PFOS in hard metal plating (POPRC 11 follow-up). This indicates the continued use of PFOS in this sector, and that the switch to alternatives has not been fully implanted in these countries. Continued use of PFOS as a Chrome mist suppressant in China has also been indicated by a CAFSI Survey (Huang et al., 2013).

159. The UK (2018) evidence submitted reports that the total volume of PFOS used in the UK was 131 kg in 2015, 63 kg in 2016 and 120 kg in 2017. It is noted that all of the volume used in 2017 is for use in metal plating. This would indicate that PFOS is still being used in relatively large quantities in this sector and there has not been a full switch to non-PFOS alternatives.

160. IPEN (2018) noted that Vietnam and Zambia are conducting an inventory of PFOS use and they may be able to withdraw acceptable purposes for this use based on their outcomes. At COP7, Canada reported declining use of PFOS in hard metal plating in closed loop systems until 2014 when the use was 0 kg. This suggests that Canada can withdraw its acceptable purpose for this use.

### 2.5.5 Data gaps and limitations

161. The following key information gaps have been identified from the above discussion:

- (a) Lack of harmonised definition of 'closed loop' process. This is required in order to establish a common understanding among industry stakeholders and competent authorities to enable harmonised conditions for this use;
- (b) Information is lacking at present regarding the processes suitable for use of the identified alternatives, as well as processes where they cannot be used and why;
- (c) A more detailed understanding of the degradation products of potential alternatives is required to fully establish the environmental performance of different alternatives;
- (d) Knowledge gaps exist concerning new novel plating practices, including details of the processes themselves, identity of chemicals used, best practices and levels of market acceptance.

### 2.5.6 Concluding remarks

162. Continued need for PFOS in metal plating (both hard metal and decorative) is indicated by some Parties, while others have indicated the use of PFOS is either declining or has been completely phased out, indicating the viability and feasibility of alternatives.

163. Fluorinated alternatives, fluorine-free alternatives and alternative technologies in hard metal plating and decorative plating are globally available. However, depending on the substance/process a number of limitations to the use of alternatives have been identified, including potentially poor performance, higher costs and possible environmental concerns. Fluorine-free products are not considered equally effective in all applications and more information about their areas of application and their limitations is required. PFOS alternatives in metal plating need to be considered on a case-by-case basis. Fluorinated alternatives or their degradation products might be very persistent.

164. Based on the availability of alternatives for PFOS, its salts and PFOSF for hard metal plating (only in closed-loop systems) and their assessment, the fact that some Parties indicated the use of PFOS is either declining or has been completely phased out, while others indicated the continued need, the Committee recommends that the use of PFOS, its salts and PFOSF for hard metal plating (only in closed-loop systems) be converted from an acceptable purpose to a specific exemption.

165. For metal plating (hard metal plating) and metal plating (decorative plating), it is noted that for a number of Parties, the notification has expired or been withdrawn. While there is uncertainty over the potential for conversion of Cr(VI) to Cr(III), based on the availability of viable alternatives, and the use of Cr(III) techniques in the case of decorative plating the Committee recommends that the specific exemptions for the use of PFOS its salts and PFOSF for metal plating (hard metal plating) and metal plating (decorative metal plating) no longer be available under the Convention.

## **2.6 Certain medical devices (such as ethylene tetrafluoroethylene copolymer (ETFE) layers and radio-opaque ETFE production, in vitro diagnostic medical devices, and CCD colour filters)**

### **2.6.1 Introduction and background**

166. 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. According to the register of acceptable purposes, as of May 2018, the following Parties are registered for those uses: China, Japan, and Vietnam. This use is not considered as an open application.

167. PFOS is or has been reportedly used in charge-coupled device (CCD) colour filter used in video endoscopes. The CCD is part of technology enabling capturing digital images.<sup>68</sup> Video endoscopes are used to examine and treat patients at hospitals. The exact levels of use of PFOS for this use is not known (EU, 2018). It is estimated that around 70% of the video endoscopes used worldwide, or about 200,000 endoscopes, contain a CCD 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.<sup>69</sup>

168. Another use of PFOS described is as a dispersant of contrast agents that are incorporated into an ethylene-tetrafluoroethylene (ETFE) copolymer layer that is used in radio-opaque catheters. 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).

### **2.6.2 Availability of alternatives**

169. Very little information is available on potential alternatives to PFOS for uses in medical devices, either in previously published sources or the recent evidence submissions by Parties and Observers.

170. For use in ethylene-tetrafluoroethylene (ETFE) copolymer layers, the BAT/BEP guidance noted that PFBS may have replaced PFOS as a dispersant of contrast agents in ETFE layers for radio-opaque catheters. However, no information was available for alternatives to PFOS for use in production of radio-opaque ETFE or use in certain in-vitro diagnostic devices.

171. 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.

172. Canada (2018) indicated that that use of alternative substances in medical devices has been implemented, for example Poly-para-xylene (Parylene).

173. IPEN (2018) reported that Clariant produces fluorine-free lubricants for catheters to reduce friction and they are incorporated into the polymer to reduce the possibility of migration into the body. No information on the specific composition or relative performance of these products relative to PFOS-containing products has been made available.

### **2.6.3 Suitability of alternatives**

174. It is considered that it is technically possible to produce PFOS-free CCD filters for use in new equipment.<sup>70</sup>

175. IPEN (2018) suggested that alternatives are available noting that chlorodifluoromethane is used in ETFE synthesis in a pyrolysis step under high temperature. Chlorodifluoromethane is also known as HCFC-22 or R22 – the most commonly used refrigerant gas subject to the Montreal Protocol and a substance which must be completely phased out by 2030. This has implications for the potential overall environmental performance of this alternative.

### **2.6.4 Implementation of alternatives**

176. There are an estimated 200,000 existing endoscopes that use PFOS-containing filters.<sup>71</sup> A gradual phase-out of existing endoscopes will be required to establish completely PFOS-free equipment. It is not indicated how feasible it will be to achieve this, nor what timescales.

177. IPEN (2018) noted that Japan stated in 2008 that to make all CCDs in video endoscope PFOS-free, it will take at least several years. It could be indicated, therefore, that sufficient time has now passed for this phase out to have taken place. Japan plans to cancel the exemptions in domestic laws in April 2018 because substitution is completed

<sup>68</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>69</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>70</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>71</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

for the use of certain medical devices which are registered as acceptable purposes (Japan, 2018)<sup>72</sup>. Vietnam noted that they are conducting an inventory of PFOS use and they may be able to withdraw acceptable purposes for this use based on their outcomes.

178. A survey of Parties' PFOS use reported in 2015 at COP7 did not indicate any use of this acceptable purpose" (IPEN submission 2016). Japan (2018) indicated that the manufacture and use of PFOS was banned in April 2018, with the exception of use in research and development. If Parties have no further need for the use of PFOS in this use, they should be encouraged to withdraw their notification, allowing the acceptable purpose for this use to be eliminated or a timetable established that might permit moving this use to a specific exemption.

### 2.6.5 Data gaps and limitations

179. The following key information gaps have been identified from the above discussion:

- (a) Current levels of use/continued need for PFOS in registered countries (China, Vietnam) and development of alternatives is unclear;
- (b) The steps in place to control the potential release chlorodifluoromethane in the production of ETFE are unclear;
- (c) No information was available for alternatives to PFOS for use in production of radio-opaque ETFE or use in certain in-vitro diagnostic devices.

### 2.6.6 Concluding remarks

180. From the above discussion it is indicated that alternatives to the use of PFOS in medical devices have been developed and are commercially available. There is very limited information on the composition, technical and economic feasibility as well as the environmental and health impacts of these alternatives.

181. Only three Parties maintain registrations for this acceptable purpose (China, Japan and Vietnam), suggesting that PFOS-free medical devices are implemented in most other parts of the world. The status of phasing out PFOS use for this acceptable purpose in China and Vietnam, and the development and implementation of alternatives in these countries is unclear. Japan has indicated that it no longer uses PFOS, suggesting there is no further need to maintain their notification.

182. Based on the assessment, the Committee concluded that alternatives for the use of PFOS, its salts and PFOSF for certain medical devices are available and therefore recommends that the use of PFOS, its salts and PFOSF for 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 longer be available under the Convention.

## 2.7 Fire-fighting foam

### 2.7.1 Introduction and background

183. Fire-fighting foam is listed as acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As of May 2018, according to register of acceptable purposes,<sup>73</sup> the following Parties are registered for this use – Cambodia, Canada, China, Switzerland,<sup>74</sup> Vietnam and Zambia. This use is considered as an open application according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

184. Aqueous film-forming foam (AFFF), sometimes referred to as aqueous fire-fighting foam, is a generic term for fire-fighting or vapour suppression products. The performance of fire extinguishing foams is improved by the aqueous film and hence by the property determining surfactant.<sup>75</sup> 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. The formation of the water film is exclusively provided by polyfluorinated surfactants.

185. Fire-fighting foams with fluorosurfactants have been specifically developed and widely used due to their particular effectiveness in extinguishing liquid fuel fires at airports and oil refineries and storage facilities (Class B

<sup>72</sup><http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC13/POPRC13Followup/PFOSInfoSubmission/tabid/6176/Default.aspx>.

<sup>73</sup><http://chm.pops.int/Implementation/Exemptions/AcceptablePurposes/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx>.

<sup>74</sup> According to Swiss law ([www.admin.ch/opc/en/classified-compilation/20021520/](http://www.admin.ch/opc/en/classified-compilation/20021520/)) fire-fighting foams containing PFOS that were placed on the market before 1 August 2011 may be used in fire safety installations, including use in any functional tests required for such installations until 30 November 2018.

<sup>75</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

fires).<sup>76</sup> In the past industry has favoured the use of C<sub>8</sub>-based perfluorinated compounds, including those containing PFOS, which are developed specifically for use on liquid (Class B) fires.<sup>77</sup> As discussed in subsequent sections, industry indicates that C<sub>8</sub>-based foams have been largely displaced by C<sub>6</sub>-based foams, as well as other non-fluorinated substances.

186. Historically, the perfluorinated substances (such as PFOS) used in AFFFs have been produced using electrochemical fluorination (ECF), with hydrogen fluoride used as a feedstock alongside organic material (Swedish Chemicals Agency, 2015). The Swedish Chemicals Agency (2015) comments that C<sub>6</sub> technologies (i.e. C<sub>6</sub> fluorotelomer based AFFF) are not based on ECF but rather telomerisation, beginning with perfluoroalkyl iodide as the raw material. Where telomerisation reactions involve perfluorinated compounds it is possible to form C<sub>8</sub> perfluorinated compounds, including PFOA, as a contaminant within C<sub>6</sub> species. The Swedish Chemicals Agency (2015) noted that studies exist demonstrating that goods marketed as C<sub>6</sub> fluorotelomer products still contain concentrations of C<sub>8</sub> (including PFOA/PFOS) significantly above trace residual concentrations, in some cases at concentrations with equal amounts of C<sub>6</sub> and C<sub>8</sub>. Regulation (EC) No 850/2004 of the European Parliament and of the Council on Persistent Organic Pollutants sets a concentration limit of PFOS and PFOS derivatives in preparations of 10 mg/kg (0.001%).

187. AFFFs are typically formulated by combining synthetic hydrocarbon surfactants with fluorinated surfactants. This combination has been preferred, as this is considered by the industry to be more cost-effective and performs better than either surfactant separately. The concentration of perfluorinated compounds in fire-fighting foams is relatively low (0.9–1.5%) (Pabon and Corpart, 2002). When mixed with water, the resulting solution achieves a relatively low surface tension, allowing the solution to produce an aqueous film that spreads across a hydrocarbon fuel surface.<sup>78</sup> The performance of fire extinguishing foams is improved in several ways by the aqueous film and hence by the presence of the fluorosurfactant. 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.

188. Fluorosurfactants are therefore considered a key ingredient in AFFFs, providing unique performance attributes, enabling them to be effective in preventing and extinguishing fires, particularly Class B flammable liquid fires, for example at chemical plants, fuel storage facilities, airports, underground parking facilities and tunnels.<sup>79</sup> 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).<sup>80</sup>

189. Canada (2018) noted that the use of PFOS is permitted “in aqueous film forming foam (AFFF) present in a military vessel or military fire-fighting vehicle contaminated during a foreign military operation and the use of AFFF at a concentration less than or equal to 10 ppm” but no data on volume of PFOS used in this application is reported. The major suppliers of AFFF in Canada (90-100% of the firefighting foam market) indicated they no longer use C<sub>8</sub> fluorosurfactants in their production process.

190. This section discusses the availability, suitability and implementation of PFOS-free alternatives for fire-fighting foams, with particular emphasis on the relative merits of fluorinated vs. non-fluorinated. The available information previously presented on the availability, suitability and implementation of alternatives to PFOS, is updated based on recently submitted information. Further to information previously published, information on the use of PFOS in fire-fighting foams and potential alternatives has been provided by Norway, Switzerland, Canada, EU, the FFFC and IPEN.

## 2.7.2 Availability of alternatives

191. It was noted over a decade ago<sup>81</sup> that a number of alternatives to the use of PFOS-based fluorosurfactants in fire-fighting foams are now available, including non-PFOS-based fluoro-surfactants; silicone based surfactants; hydrocarbon based surfactants; fluorine-free fire-fighting foams; and other developing fire-fighting foam technologies that avoid the use of fluorine.<sup>82</sup>

<sup>76</sup> Internationally fires are classified into groups based on the nature of the fire. This in turn defines what kind of fire-fighting media is most appropriate to be used. Class B fires relate to flammable liquids, where fire-fighting foams may be needed to suppress the fire (e.g. oil-based fires). <http://surreyfire.co.uk/types-of-fire-extinguisher/>.

<sup>77</sup> See UNEP/POPS/POPRC.13/7/Add.2.

<sup>78</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>79</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>80</sup> See UNEP/POPS/POPRC.8/INF/17/Rev.1.

<sup>81</sup> See UNEP/POPS/POPRC.3/20/Add.5 - Risk management evaluation on perfluorooctane sulfonate.

<sup>82</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

192. Non-PFOS based AFFFs are now widely commercially available from all major suppliers of fire-fighting equipment and have been in use for several years.<sup>83</sup> For example, suppliers in North America and Norway include but are not limited to, Ansul and Chemguard (both Tyco companies), Chemours, Kidde, and Solberg.

193. There are two key categories of alternatives to consider in this section, a) Short-chained fluorinated alternatives, and b) non-fluorine containing alternatives. An overview of available alternatives is presented in Table 4 below.

**Table 4 Overview of alternatives to PFOS for use in fire-fighting foams**

Composition	CAS No	Trade Names	Manufacturer	Information Source	Class*	Additional details
<b>Fluorinated alternatives</b>						
Dodecafluoro-2-methylpentan-3-one	756-13-8	NOVEC 1230	3M	UNEP/POPS/POPRC.10/INF/7/ Rev.1	3	Replacement of Halon-based fire extinguishant
C <sub>6</sub> fluorotelomer sulfonamide compounds	Information gap	C <sub>6</sub> fluorotelomer sulfonamide compounds	Chemours	<a href="https://www.chemours.com/Capstone/en_US/products/Index.html">https://www.chemours.com/Capstone/en_US/products/Index.html</a>		
Perfluorohexane ethyl sulfonyl betaine	N/A	Capstone™ products	Chemours	UNEP/POPS/POPRC.10/INF/7/ Rev.1  <a href="https://www.chemours.com/Capstone/en_US/products/Index.html">https://www.chemours.com/Capstone/en_US/products/Index.html</a>	3	Perfluorohexane ethyl sulfonyl betaine and C <sub>6</sub> -fluorotelomers often used in combination with hydrocarbons
Carboxymethyl-dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]propylammonium hydroxide <sup>84</sup>	34455-29-3	Information gap	Information gap	UNEP/POPS/POPRC.10/INF/7/ Rev.1	3	
A fluorosynthetic versatile AR foam concentrate containing 5-10% 2-(2-butoxyethoxy) ethanol	11234-5	BIO HYDROPOL 6	Bio Ex	UNEP/POPS/POPRC.12/INF/15/Rev.1	Not screened	
Sodium p-perfluorooctylbenzene sulfonate (OBS)	70829-87-7	Information gap	Information gap	Bao et al. (2017)	N/A	Commercially available in China
Others (unidentified)	Information gap	See Table 5	See Table 5			See Table 5
<b>Non-fluorinated alternatives</b>						
Protein-based foams	N/A	Sthamex F-15	Dr. Sthamer	UNEP/POPS/POPRC.12/INF/15/Rev.1	N/A	
Hydrocarbon surfactants, water, solvent, sugars, a preservative, and a corrosion inhibitor	N/A	RE-HEALING™ Foam (RF)	Solberg	UNEP/POPS/POPRC.12/INF/15/Rev.1	N/A	S. Presidential Green Chemistry Challenge award winner. <a href="https://www.epa.gov/greenc">https://www.epa.gov/greenc</a>

<sup>83</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>84</sup> A NICNAS (2015b) assessment considered the environmental risks associated with the industrial uses of nine per- and poly-fluorinated organic chemicals which are indirect precursors to short-chain perfluorocarboxylic acids (PFCAs). Insufficient data are presented in this assessment to categorise the parent chemicals in this group according to domestic environmental hazard thresholds or the aquatic hazards of chemicals in this group according to the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS). Available data indicate that chemicals in this group have the potential to degrade to PFHxA, PFPeA and PFBA. Therefore, the principal risk posed by the chemicals in this group is assumed to result from cumulative releases of these short-chain perfluorocarboxylic acid degradation products. The specific uses of these substances was not specified in the assessment.

Composition	CAS No	Trade Names	Manufacturer	Information Source	Class*	Additional details
						hemistry/presidential-green-chemistry-challenge-2014-designing-greener-chemicals-award.
Products that contain glycols	N/A	Hi Combat ATM, "Trainol"	AngusFire	UNEP/POPS/POPRC.12/INF/15/Rev.1	N/A	Synthetic detergent foams, often used for forestry, high-expansion applications and for training e.g. marine uses
2-6% Hexylene glycol (CAS No: 107-41-5, EC 203489-0); hydrolysed protein [70-80%], metallic salt: NaCl+MgCl <sub>2</sub> [8-15%]; FeSO <sub>4</sub> *7H <sub>2</sub> O[0-2%]	N/A	PROFOAM 806G	Gepro Group	UNEP/POPS/POPRC.12/INF/15/Rev.1	N/A	
Others (unidentified)	N/A	See Table 6	See Table 6			See Table 6
Non-chemical alternative						
None identified	N/A	N/A	N/A	N/A	N/A	

\* Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: 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 for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

### 2.7.2.1 Short-chained fluorinated alternatives

194. As previously reported, over the past several years, a widely adopted approach in industry has been to replace PFOS-based long-chain fluorosurfactants used in AFFFs with shorter-chain fluorosurfactants such as perfluorohexylethanol [6-2 FTOH] derivatives.<sup>85</sup> The FFFC (2018) indicate that most foam manufacturers have now transitioned to the use of only short-chain (C<sub>6</sub>) fluorotelomer surfactants. DuPont (now Chemours), for example, have previously commercialised two AFFFs based on 6:2 fluorotelomer sulfonamidealkylbetaine (6:2 FTAB) or 6:2 fluorotelomer sulfonamideaminoxide (Wang et al., 2013).<sup>86</sup> Chemours currently market eight fluorosurfactant-based firefighting foams on their website.<sup>87</sup>

195. As discussed in the previous section, the Swedish Chemicals Agency (2015) comments that C<sub>6</sub> technologies are not based on ECF but rather telomerisation, beginning with perfluoroalkyl iodide as the raw material. Where telomerisation reactions involve perfluorinated compounds it is possible to form C<sub>8</sub> perfluorinated compounds, including PFOS, as a contaminant within C<sub>6</sub> species.<sup>88</sup>

196. Alternative fluorosurfactants based on perfluorobutane sulfonate (PFBS) and related substances have also been considered but this has never been applied or successfully used in fire-fighting foams due to its non-dispersive properties. Perfluorohexane sulfonate (PFHxS)<sup>89</sup> is currently considered as a long chain PFCAs according to the OECD definition, however biomonitoring measurements in fire-fighters have shown equal levels of PFHxS and PFOS, which suggests the use of PFHxS and/or PFHxS-related substances in some fire-fighting foams (Dobraca et al., 2015).

<sup>85</sup> See UNEP/POPS/POPRC.8/INF/17/Rev.1.

<sup>86</sup> Note that Chemours has now replaced DuPont on the market ([https://www.chemours.com/Capstone/en\\_US/uses\\_apps/fire\\_fighting\\_foam/index.html](https://www.chemours.com/Capstone/en_US/uses_apps/fire_fighting_foam/index.html)).

<sup>87</sup> [https://www.chemours.com/Capstone/en\\_US/products/Index.html](https://www.chemours.com/Capstone/en_US/products/Index.html).

<sup>88</sup> UNEP/POPS/POPRC.13/7/Add.2.

<sup>89</sup> PFHxS is currently under review by the POPRC as a potential POP.

197. There is relatively little publicly available information on the chemical structure or properties of the AFFF products containing fluorinated alternatives. Canada (2018) noted that the actual C<sub>6</sub> (or below) fluorosurfactants contained in AFFF formulations are considered proprietary by AFFF manufacturers.

198. A number of manufacturers and commercial products have been identified, where the details of the precise formulations are not divulged due to trade secrets (see Table 5 below).

**Table 5 Commercially available fluorinated alternatives for fire-fighting foams, chemical composition not disclosed.<sup>90</sup>**

Commercial product	Manufacturer
ARCTIC™ foam concentrates	Solberg
NOVEC 1230	3M
STHAMEX AFFF 3%	Dr. Sthamer
Fomtec AFFF 3% and 6%	Dafo Formtec
Ansulite 3x3 low viscosity AFFF	Ansul Inc.
Hydral AR 3-3	Sabo-Foam
BIO HYDROPOL 6	Bio-Ex
Platinum AFFF 3% LT	Tyco Fire Integrated Solutions
FS- series	Chemguard
DX- series	Dynax

199. EU (2018) noted that fluorinated chemicals, in addition to those used in the commercial products detailed above, include, for example polyperfluorinated alkyl thiols and for class B fires mainly 6:2 fluorotelomer based (6: 2 FTSAS (fluorotelomermercaptoalkylamido sulfonate) 6:2 FTAB (fluorotelomer sulfonamide alkylbetaine).

200. Bao et al. (2017) reported that the aromatic compound sodium p-perfluorooxynonenoxybenzene sulfonate (OBS) (CAS no. 70829-87-7), belonging to the group of PFASs, is considered a cost-effective surfactant, and is widely used in China as co-formulant of fluoro-protein fire-fighting foams. The study indicated OBS may be a desirable alternative to PFOS as it can be readily treated by H<sub>2</sub>O<sub>2</sub>/UV.

#### 2.7.2.2 Fluorine-free alternatives

201. Since 2000, significant developments have been made to produce a new generation of fire-fighting foams, consisting of water-soluble non-fluorinated polymer additives and increased levels of hydrocarbon detergents<sup>91</sup> i.e. formulations that do not use any fluorine-based chemistry, including as surfactants or other components.

202. For example, Wang et al. (2015) investigated the surface tension and foam property of a variety of fluorine-free surfactants. The fire extinguishing performance of 2.5% alkyl glucose amide and 2% organosilicone surfactant containing foam extinguishing agent met the national standard requirements and it was indicated that alkyl glucose amide and organosilicone surfactant can replace fluorocarbon surfactant in foam extinguishing agent.

203. It has been indicated that non-fluorinated foams now exist and are available commercially in the market.<sup>92</sup> The FFFC (2018) note that most foam manufacturers also produce fluorine-free foams. For example, fluorine-free foams certified to different ICAO levels,<sup>93</sup> required for use at civilian airports, are available on the market and are already introduced at airports in practice (FFFC, 2018).

204. Fluorine-free fire-fighting foams are based on the following compositions:<sup>94</sup>

- (a) Silicone-based surfactants;
- (b) Hydrocarbon-based surfactants;
- (c) Synthetic detergent foams, often used for forestry and high-expansion applications and for training (“Trainol”); new products with glycols (Hi Combat ATM from AngusFire);

<sup>90</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1 (Annex 5)

<sup>91</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1

<sup>92</sup> See UNEP(2017) BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs

<sup>93</sup> International Civil Aviation Organisation specifications – see <http://www.firefightingfoam.com/knowledge-base/international-standards/icao/>

<sup>94</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

(d) 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. It is noted that protein based foams were commonly used until the 1960s/70s before being replaced in favour of fluorinated surfactants.

205. There is relatively little publicly available information on the chemical structure or properties of the AFFF products containing non-fluorinated alternatives. A number of manufacturers and commercial products have been identified, where the details of the precise formulations are not divulged due to trade secrets (see Table 6 below). However, in some cases safety data sheets (SDSs) may provide information the chemical identity of foam ingredients, for example the SDS of Moussol APS 3% does list its chemical ingredients.<sup>95</sup>

**Table 6 Commercially available non-fluorinated alternatives for fire-fighting foams, chemical composition not disclosed (as of July 2018)**

Commercial product	Manufacturer
Freedol	3F
Freefor SF	3F
Hyfex SF	3F
RE-HEALING Foams : RF3x6 ATC Foam ; RF6 Foam ; RF3 foam	Solberg
F3	Aberdeen Foams
AR-F3	Aberdeen Foams
HS-100	Chemguard
UNIPOL-FF	Auxquimia
BIO FOR C	Bio-Ex
BIO T	Bio-Ex
BIO FOAM 5	Bio-Ex
ECOPOL foams : ECOPOL, ECOPOL F3 HC, ECOPOL Premium	Bio-Ex
Eco-Safe*	Kerr Fire
HotFoam Meteor P+ Foam	Tyco
Moussol APS 3%	Dr. Sthamer
Sthamex k-1%, Sthamex IAF 2%, Sthamex-class A, Sthamex class A-Classic	Dr. Sthamer
Foamusse 3%	Dr. Sthamer
Moussol FF 3/6	Dr. Sthamer
Enviro 3x3 Plus	Fomtec
Solberg foam HI-EX	Solberg
Respondol ATF	Angus Fire
JetFoam	Angus Fire
HS-series	Chemguard

\* Training foams

206. The FFFC (2018) noted that the Solberg Company developed Re-Healing Foam™ RF,<sup>96</sup> a high-performance fluorine-free foam concentrate for use on Class B hydrocarbon fuel fires. Airservices Australia now reportedly use the Solberg Re-Healing RF6 6% foam as the preferred operational fire-fighting foam at the 23 capital and major regional city airports (out of 260 national hangars, airports and aerodromes) throughout Australia. When stored correctly, the Re-healing foam has a shelf-life of 10 20 years (Solberg, 2014). In Norway, a number of sectors, including the offshore oil industry have reported to phase-out of PFOS containing fire-fighting foam. with fluorine-free foam using the Solberg Re Healing foam. Emission of PFAS from firefighting foam from the off-shore sector has been reduced by 50% from 2014 to 2016 (from 4 tonnes in 2014 to 2 tonnes in 2016). Furthermore, both civil airports and military properties are phasing in/ or has switched to fluorine-free foam from Solberg (Re-Healing). For example, it is indicated that at Copenhagen Airport, fluorine-free Solberg RF Re-Healing Foam has been used to replace AFFF (FFFC, 2018).

<sup>95</sup> <https://files.chubbfiresecurity.com/chubb/en/uk/contentimages/CFAR6%20MOUSSOL%20APS.pdf>.

<sup>96</sup> <https://www.solbergfoam.com/getattachment/41e509c4-63cd-4b7a-b734-fda67d7642f9/SOLBERG-Expands-Product-Certifications-on-Foam-1.aspx>.

207. Clearly, there has been considerable action within the industry to produce PFOS-free alternatives in fire-fighting foams. While there is uncertainty around the precise chemical composition of products currently on the market, beyond the content of SDSs, the available information indicates the industry standard for fire-fighting foams has largely switched to the use of short-chained PFAS and fluorinated telomers and use of fluorine-free alternatives is also being developed in this sector.

### 2.7.2.3 Reducing the environmental impacts of using AFFFs

208. One key aspect of fire-fighting foam usage that has been highlighted previously<sup>97</sup> due to concerns over potential release of PFOS to the environment, is the issue of the use of fire-fighting foams during training or testing operations. The UNEP (2017) BAT/BEP guidance document states that “surrogate, non-fluorinated foams should be used for training purposes as well as for testing and commissioning of fixed systems and vehicle proportioning systems. Non-PFOS fluorinated surfactants based on short-chain fluorotelomers should be used for Class B fire-fighting foam concentrates”.

209. The FFFC (2018) indicated that industry is actively working to prevent fire-fighting foams from entering the environment when they are used for training exercises, or when a discharge takes place during foam system testing, fire-fighting operations, inadvertent discharge or leakage, or disposal following decommissioning of a fire-fighting system, and that new methods have been developed to test foam systems and equipment without releasing foam to the environment, and non-fluorosurfactant foams are now available for training and other uses.

210. As reported in the PFOA Risk Management Evaluation (RME) addendum,<sup>98</sup> the FFFC provided details of best practice for use of Class B fire-fighting foams, which includes AFFF (PFOA/PFOS and C<sub>6</sub> telomers) and fluorine-free types of product. The guidance focuses on measures which can be grouped into one of three categories:

(a) Selection of when to make use of Class B fire-fighting foams - Class B fire-fighting foams should only be used when the most significant flammable liquid hazards are identified. [For land-based facilities and other non-land-based facilities, such as ships, that have potential liquid flammable risks, hazard assessments should be used in advance to investigate whether other non-fluorinated techniques can achieve the required extinguishment and burn back resistance.] This includes consideration of the potential shortfalls that alternative methods may have. Furthermore, training exercises should not use fluorinated fire-fighting foams due to concerns over environmental pollution;

(b) Containment of environmental release during use of Class B fire-fighting foams for live incidents. The FFFC (2016) notes the variability of potential incidents and highlights that it is not possible to contain and collect fire runoff in all situations. However, the FFFC (2016) also highlight that runoff from liquid flammable fires will contain a mixture of water, residual hydrocarbon products, fire-fighting foam and therefore loss to environment should be avoided. For facilities that make use of flammable liquids (such as fuel farms and petroleum/chemical processing, airport operations, specific rail transportation, marine and military storage and industrial facilities) the FFFC (2016) best practice guidance states that a firewater collection plan should be developed in advance, and for fixed systems with automatic release triggers containment should be built into the system design. However, it is not clear how many facilities have done this in practice, and to what extent these best practices effectively control releases;

(c) Disposal of contaminated runoff and foam concentrate - Class B fire-fighting foam concentrates (which include PFOS-containing foams) do not carry expiry dates, but generally have a service life of 10–25 years. It is also possible to have testing completed routinely to assess whether the foam in stock still meets requirements. Destruction of Class B fire-fighting foam concentrate should be through thermal destruction and according to provisions of the Stockholm Convention to destroy POPs in an environmentally sound manner. For contaminated firewater from use of foams the FFFC (2016) guidance highlights that the solution will contain a mixture of chemicals and that thermal destruction is the preferable option. Other options include a combination of coagulation, flocculation, electro-flocculation, reverse osmosis, and adsorption on granular activated carbon (GAC).

211. The UNEP (2017) BAP/BEP guidance emphasises the need “to follow best environmental practices to minimize releases to the environment and to collect all waste with following incineration at high enough temperatures to thermally mineralize the fire-fighting foam ingredients”. This includes:

- (a) Use of training foams that do not contain fluorinated surfactants;
- (b) Containment, treatment, and proper disposal of any foam solution;
- (c) Collection, containment, treatment, incineration of firewater runoff.

212. It is indicated that there is no available information on alternative technology for this use.<sup>99</sup>

<sup>97</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>98</sup> See UNEP/POPS/POPRC.13/7/Add.2.

<sup>99</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

213. A review of information pertaining to the alternative products (both fluorinated and non-fluorinated) outlined in Tables 4, 5, and 6 has been conducted to identify, where possible, the key chemical constituents of these alternatives e.g. through chemical safety sheets and commercial websites. In many cases, information on the chemical identity of alternatives is lacking due to the commercial sensitivity of this information. The key chemical components (by mass) identified in products, particularly those reported in multiple different products by several different manufacturers, and their potential POPs characteristics, have been assessed in Chapter 3.

### 2.7.3 Suitability of alternatives

214. As noted by the industry body, the Fire Fighting Foam Coalition Inc. (FFFC) (2018), fluorotelomer-based fire-fighting foams have played an important role in combating flammable liquid fires in applications such as aviation, military, and oil/gas production. The alternatives to PFOS in this sector should achieve an adequate level of technical performance to ensure that foams produced meet the required level of fire safety in these key applications.

215. The available testing information indicates that both C<sub>6</sub>-fluorinated and fluorine-free fire-fighting foams can be as effective as PFOS-based firefighting foams, although variability in efficacy of these non-PFOS foams is noted across different testing studies.

216. As presented in the discussion below, and previously,<sup>100</sup> there is some conflicting evidence and opinion regarding the relative efficacy of foams based on short-chained PFAS and fluorinated telomers against fluorine-free alternatives. In a number of tests, fluorine-free foams are shown to display the level performance to comply with required standards, however it is also indicated in some cases that the performance of fluorine-free foams can have some drawbacks relative to fluorinated foams.

217. The FFFC (2018) indicated that PFOS-based and fluorosurfactant or fluorotelomer-based fluorosurfactant based foams and firefighting foams can meet material specifications of the International Standards Organization (ISO Standard 7203), Underwriters Laboratories (UL Standard 162), European Standard (EN-1568) and the US military (Mil-F-24385). Similarly, manufacturers of fluorine-free foams, such as Norwegian producer Solberg Scandinavian AS indicate that fluorosurfactant- and fluoropolymer-free fire-fighting foam have shown to perform the same ability to extinguish Class B fires (liquid fuel fires) as traditional AFFF and have been approved for the control and extinguishing of class B flammable liquid hydrocarbon and polar fuel fires.<sup>101</sup>

218. The EU (2018) indicated that PFOS-free fire-fighting foams are available but non-fluorinated alternatives often cannot achieve the stringent performance requirements. Similarly, Canada (2018) noted that some manufacturers and end-users consider that fluorine-free fire-fighting foams do not have comparable extinguishing effects as foams with fluorosurfactants. The UNEP (2017) BAP/BEP guidance states that “non-PFOS fluorinated surfactants based on short-chain fluorotelomers should be used for Class B fire-fighting foam concentrates”.

219. Castro (2017) reported the results of testing data on fluorine-free foams that indicate there are significant differences in the performance between AFFFs and non-fluorinated foams depending on the type of fire. It was noted that, for heptane and diesel fires, the time required for fluorine-free foams to control the fires relative to AFFF was 5-6% slower, but for Jet A1 fuel and gasoline it was 50-60% slower. It was noted that for fluorine-free fire-fighting foams, the application rate to control a fire is higher than for AFFFs but application rate had no impact on the extinguishing rate. The authors attributed these observations to the AFFFs having good foam repellence against hydrocarbons when applied in forceful application. It was suggested the lack of good oil-repellence properties for fluorine-free foams could mean, even if the fuel is covered with the foam blanket, some fuel may still be picked up and becomes contaminated, impeding full rapid extinguishment and potentially increasing the risk of re-ignition. It was concluded that that fires on fuels with lower flash points are more difficult to control with fluorine-free foams.

220. One key aspect of relative suitability of fluorinated and non-fluorinated foams alternatives, is the relative performance in terms of foam degradation. Non-fluorine alternatives have been indicated to break down more quickly, which may have important implications in terms of volumes of use (and associated costs) as well as the risk of re-ignition. Also, as noted in the PFOA RME some fluoro-surfactants foam manufacturers indicate that fluorine-free fire-fighting foams may offer less protection against re-ignition, which makes it impossible to apply this alternative for some operations. It was also previously noted that some of the new foams have high viscosity that makes it hard to use with the same equipment as for PFOS-foam.

221. As noted in the PFOA RME<sup>102</sup> fire test data provided by the United States Naval Research Laboratories (NRL, 2016) indicating that AFFF agents achieved extinguishment in 18 seconds compared to 40 seconds for the fluorine-free foam, and that AFFF agents displayed slower degradation (35 minutes) compared to fluorine-free foams (1-2

<sup>100</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>101</sup> <https://www.solbergfoam.com/Technical-Documentation/Technical-Bulletins.aspx>.

<sup>102</sup> See UNEP/POPS/POPRC.13/7/Add.2.

minutes)<sup>103</sup>. In another study, fluorine-free foam and PFAS-containing foams met displayed similar levels of performance, but neither achieved the 30-second standard in US Navy tests.<sup>104</sup> Additional data on relative degradation rates of different foam compositions is required to draw definitive conclusions on the relative performance of fluorinated vs. non-fluorinated foams. It is indicated that modern development in fluorine-free foams has substantially decreased any difference in performance levels (IPEN, 2018).

222. However, a number of sources indicate that fluorine-free fire-fighting foams can meet the same performance and technical criteria as fluorosurfactant-based AFFFs. For example, in 2012, a testing programme led by the UK Civil Aviation Authority notes that fluorine-free foams are ICAO Level B approved and indicated that a new generation of fluorine-free firefighting foams using compressed air foam systems (CAFS),<sup>105</sup> proved to be as effective and efficient as the currently used AFFFs.<sup>106</sup> Similarly, independent fire tests conducted by the Southwest Research Institute found that Solberg's Re-Healing RF3 foam was effective in extinguishing Jet A fuel, meeting the Performance Level B testing requirements of ICAO Fire Test Standard (Huczek, 2017).

223. As noted in the PFOA RME<sup>107</sup> the Institute for Fire and Disaster Control Heyrothsberge in Germany tested six fluorine free alcohol resistant fire-fighting foams and one PFAS containing foam for their ability to extinguish fires of five different polar liquids (Keutel and Koch, 2016). The authors conclude that there are fluorine-free foams available which show a similar performance compared with PFAS containing foams. Also noted in the PFOA RME, the State of Queensland (2016) in Australia, report that many fluorine-free foams are acknowledged as meeting the toughest fire-fighting standards and exceeding film-forming fluorinated foam performance in various circumstances and that fluorine-free foams are widely used by airports and other facilities including oil and gas platforms.

224. In terms of economic viability, the FFFC (2018) note that fluorotelomer-based foams have been manufactured and sold for more than 40 years with numerous companies that sell fluorotelomer-based foams worldwide, representing a significant percentage of the fire-fighting foam used worldwide. Canada (2018) expressed concern that, for the extinguishing of liquid fires, approximately twice as much water and foam concentrate are needed when using fluorine-free foams, compared to when fluorosurfactant-based foams are used (as indicated by Castro, discussed above).

225. It should be noted, however, that the potential practical environmental advantages of using fluorine-free foams instead of fluorinated compounds, for instance, resulting from the avoidance of remediation costs, loss of reputation, damage to the organisation's brand image, class actions, and potential loss of operating licenses (Klein, 2013) should be taken into consideration. The environmental performance and characteristics of each foam formulation will need to be carefully evaluated and compared before a definitive conclusion can be drawn in this respect.

226. The above discussion highlights that both fluorinate and fluorine-free alternatives are shown to be viable as replacements for PFOS-based foams, although variability in available evidence on the performance of alternatives for fire-fighting foam applications is noted. For example, more data is needed to fully assess the effectiveness of fluorine-free foams on large-scale liquid fires.

227. As discussed by IPEN (2018), it is considered that no new generation foam (either fluorinated or fluorine-free) can be considered as a straightforward 'drop in' replacement for any formulation previously in use. The consideration of the viability of alternatives needs to consider both fire-fighting performance and compatibility with existing system control and application methods. It is suggested that performance capability of alternative foams will be specific to a particular formulation and the type of application equipment used. Hence it is not possible to definitively state if all C<sub>6</sub>-fluorinated alternatives perform better than all fluorine-free alternatives and vice versa.

228. The FFFC (2018) noted that fluorotelomer-based foams can meet the same required material specifications as PFOS-based foams and can be used interchangeably in the same equipment and at the same concentration levels by military and industrial users in North America, Europe, Asia and many other parts of the world. A variety of fluorine-free Class B foams are reported to be on the Swedish and Norwegian market indicating the viability of this as an alternative for certain applications including aviation and military use and are widely used in the oil and gas industry, including offshore platforms.

229. It should be noted that Dodecafluoro-2-methylpentan-3-one - manufactured and sold by 3M should generally not be considered a viable alternative to PFOS AFFF, since technically it is used as a fire protection fluid.

<sup>103</sup> Note, the addendum to the PFOA RME is at draft stage and has not yet been formally accepted or published. Information referred to here citing UNEP/POPS/POPRC.13/7/Add.2 may therefore be revised based on the final version of the PFOA RME addendum.

<sup>104</sup> <https://theintercept.com/2018/02/10/firefighting-foam-afff-pfos-pfoa-epa/>

<sup>105</sup> Simple systems in which high pressure air is injected into the water/foam solution before leaving the piping leading to the turret or hose line.

<sup>106</sup> <https://www.internationalairportreview.com/article/11655/ensuring-a-safer-future-for-the-aviation-industry/>

<sup>107</sup> See UNEP/POPS/POPRC.13/7/Add.2.

230. It is noted that environmental concerns have been raised relating to both long- and short-chain PFAS. For example, Cousins (2016) argues that all PFASs entering groundwater, irrespective of their perfluoroalkyl chain length and bioaccumulation potential, will result in poorly reversible exposures and risks as well as further clean-up costs. The overall suitability of non-fluorinated alternatives for fire-fighting foam applications is less clear. However, Cousins (2016) and Hetzer (2014) comment that encouraging progress has been made, with some foam manufacturers stating that AFFF is no longer needed.

231. Oosterhuis et al. (2017) provided cost estimate data for the substitution of persistent organic pollutants, including PFOS, to safer alternatives. It was indicated that for fire-fighting foam, alternatives appeared to be available at limited additional cost, in some cases close to zero or even negative but always less than \$1,000 per kilogram. However, it is indicated that the cost of remediation could be well over \$10,000 per kilogram.

#### 2.7.4 Implementation of alternatives

232. The existing evidence suggests that over the past 20 years, the use of PFOS in fire-fighting foams has declined substantially, with the use of non-PFOS containing foams now widespread across Europe, North America, Norway and Australia. For example, all commercial airports in Sweden and Norway have replaced PFAS-based fire-fighting foams with fluorine-free foams because of environmental safety concerns.

233. The Estimated Inventory of PFOS-based AFFF by FFFC (2011) in the USA reported that the volumes of use in this sector had declined from 4.6M gallons in 2004 to less than 2M gallons in 2011, indicating a substantial switch to the use of non-PFOS based fire-fighting foams.<sup>108</sup>

234. Canada (2018) indicated that foams containing PFOS have not been manufactured in the U.S. or Europe since 2002. However, it is noted that, 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.<sup>109</sup>

235. The FFFC (2018) indicate that over the past few years most manufacturers have transitioned to only short-chain (C<sub>6</sub>) fluorosurfactants and that fluorotelomer-based foams are available on the market and accessible by foam users anywhere in the world.

236. As discussed in Section 2.7.3, airports in a number of counties (including Norway and Denmark) as well as Australia are reportedly phasing out the use of PFOS-containing firefighting foams in favour of fluorinated and fluorine-free alternatives.

237. A number of Parties indicated they may no longer have a requirement for the acceptable purpose for PFOS in this sector. IPEN (2018) notes that Switzerland has indicated that remaining stocks can be used in cases of emergency by fire brigades until 2014 and in stationary uses until 2018.<sup>110</sup> This suggests that Switzerland can withdraw its acceptable purpose for this use. Vietnam and Zambia note that they are conducting an inventory of PFOS use and they may be able to withdraw acceptable purposes for this use based on their outcomes.

238. Continued use of PFOS as surfactants in AFFF in China has been indicated by a CAFSI Survey (Huang et al., 2013).

239. The FFFC (2018) concluded that safe and effective alternatives to the use of PFOS, its salts, PFOSF and related compounds in fire-fighting foams are readily available worldwide, and therefore a specific exemption for the use of PFOS-based fire-fighting foams is no longer needed. Information received from other Parties and previously published information would seem to support this conclusion.

#### 2.7.5 Information gaps and limitations

240. The following key information gaps have been identified from the above discussion on:

(a) Technical performance of fluorine-free alternatives – need for more information on the capabilities and limitations of these alternatives; continued R&D effort required to improve the performance and capability of fluorine-free alternatives;

(b) Lack of available information concerning PFOS alternatives used in composition of commercial fire-fighting foams to be able to assess environmental/health risks;

(c) Assessment and full screening of the toxicological properties of potential alternatives against POPs criteria, where data is available (see Section 3 discussion).

<sup>108</sup> Estimated Inventory Of PFOS-based Aqueous Film Forming Foam (AFFF). 2011 update to the 2004 report entitled “Estimated Quantities of Aqueous Film Forming Foam (AFFF) In the United States”. Prepared for the Fire Fighting Foam Coalition, Inc.

<sup>109</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>110</sup> see Chemical Risk Reduction Ordinance, Annex 1.16 ([www.admin.ch/opc/en/classified-compilation/20021520/#app18](http://www.admin.ch/opc/en/classified-compilation/20021520/#app18)).

## 2.7.6 Concluding remarks

241. The assessment indicated that alternatives to PFOS-based fire-fighting foam are readily available in many countries and have been demonstrated to be technically feasible and economically viable but some have potential negative environmental and health impacts. On that basis, the Committee recommends that the acceptable purposes for the production and use of PFOS, its salts and PFOSF for fire-fighting foam be amended to a specific exemption for the use of fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) already in installed systems, including both mobile and fixed systems, and with the same conditions specified in paragraphs 2 (a)-(d) and 3 of the annex to decision POPRC-14/2 on perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds.

242. The Committee recognized that a transition to the use of short-chain per- and polyfluoroalkyl substances (PFASs) for dispersive applications such as fire-fighting foam is not a suitable option from an environmental and human health point of view and that some time may be needed for a transition to alternatives without PFASs.

## 2.8 Insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*

### 2.8.1 Introduction and background

243. Insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.* are listed as an acceptable purpose for the production and use of PFOS, its salts and PFOSF in Annex B. As of May 2018, according to register of acceptable purposes,<sup>111</sup> the following Parties are registered for this use: Brazil and Vietnam. This use is considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1. It should be noted that, according to the Convention text, the acceptable purpose is for the production and use of PFOS-F as an intermediate in the production of sulfluramid, to produce insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*

244. Leaf cutting ants of the genera *Atta spp.* and *Acromyrmex spp.* are found only in a large part of Latin America and the southern part of the United States. They are the dominant species in both natural and human-disturbed settings where they occur, and can cause significant harm in agricultural, forest, and livestock agronomic ecosystems.<sup>112</sup>

245. Leaf cutting ants are also noted for their important ecological role,<sup>113</sup> contributing to environmental diversity, productivity, and nutrient and energy flow, improving drainage and root penetration, increasing organic matter and mineralization, as well as improving 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 control method might be chosen. It has also been indicated that leaf cutting ants can also develop anti-fungal bacteria, which could be used in the development of new treatment of fungal infections, cancer and parasitic diseases.<sup>114</sup>

246. Leaf-cutting ants can cut around 29% to 77% of plants in natural environments (De Britto et al., 2016). They are a non-specific pest of cultivated plants that can cause significant economic damage in agriculture (grains, oilseeds, fruit, vegetables, tuberous roots, stimulant plants, sugarcane and ornamental), forestry (*Eucalyptus*, *Pinus*, *Hevea brasiliensis*, *Gmelina arborea*, etc.) and livestock (grasses in general). Colonies persist and grow despite the numerous control strategies to which they are subject.

247. It is estimated that the leaf-cutting ants compete with cattle for grass and can consume 255-639 kg of grass per ant colony per year, which is equivalent to 870,000 head of cattle per year in São Paulo (De Britto et al., 2016). For sugarcane, losses due to leaf cutting ant species can amount to 3.2 tons/hectare of sugarcane for each ant colony, corresponding to 5.3% loss of productivity (De Britto et al., 2016). The Government of Brazil describes the control of leaf-cutting ants as “essential for Brazilian agribusiness”, referring to these two species of ants as “the main pest of forest plantations, agriculture and livestock” (De Britto et al., 2016), mentioning in particular eucalyptus and pine plantations, grass for livestock, sugar cane, grains, and fruit.

248. The use of chemical control with toxic baits containing N-Ethyl perfluorooctane (sulfluramid) is considered a practical, economical and operational approach to controlling leaf cutting ants.<sup>115</sup> Sulfluramid 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.<sup>116</sup> Insect baits typically contain sulfluramid active ingredient in relatively low concentration in the form of pellets. A review by PAN (2018) of existing products for use on ant species currently advertised for purchase and/or available in retail outlets noted the concentration of active ingredient ranged from 0.01% to 0.3%.

<sup>111</sup><http://chm.pops.int/Implementation/Exemptions/AcceptablePurposes/AcceptablePurposesPFOSandPFOSF/tabid/794/Default.aspx>.

<sup>112</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>113</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>114</sup> <https://hms.harvard.edu/news/ants-antifungals>.

<sup>115</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>116</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

249. Sulfluramid is noted as a potential precursor to PFOS, and this has led to concern regarding the formation of PFOS and/or PFOA in the environment from the use of insect baits containing sulfluramid (PAN, 2018; POPRC-12/6) and the potential of exposure routes to humans via crops (IPEN, 2018).

250. A study by Zabaleta et al. (2016) investigated the potential biodegradation products of sulfluramid in soils and uptake in in soil–carrot (*Daucus carota ssp sativus*) mesocosms. PFOS yields of up to 34% using a technical sulfluramid standard and up to 277% using Grão Forte, a commercial sulfluramid bait formulation containing 0.0024% sulfluramid were noted. Formation of other breakdown products including perfluorooctane sulfonamide acetate (FOSAA), perfluorooctane sulfonamide (FOSA), and perfluorooctanoic acid (PFOA) was also observed. However, it should be noted that formation of PFOA was attributed to the presence of perfluorooctanamide impurities. The authors note that, a significant fraction of PFOS observed appears to be associated with one or more unidentified PFOS-precursors in the commercial bait.

251. The results of the Zabaleta et al. (2016) study provided evidence for that the application of sulfluramid baits can lead to the occurrence of PFOS in soils, crops and in the surrounding environment, potentially leading to human exposure to PFOS. Brazil (2018) noted that, for soils from Brazil and tropical environments, information on the environmental formation of PFOS from use of sulfluramid-containing insect baits is lacking, and more conclusive information on the possible formation of PFOS from the insect baits with sulfluramid in regions where these are used is required.<sup>117</sup> The industry association ABRAISCA (2018) report that research is currently ongoing to evaluate with the insect bait with sulfluramid may degrade into PFOS in Brazilian soils.

252. A study by Nascimento et al. (2018) investigated the occurrence of sulfluramid, PFOS, PFOA and other PFASs in various environmental samples (leaves, water, soil, sediment) from an agricultural region of Brazil, where sulfluramid is suspected to be applied on eucalyptus plantations. The measured profiles of PFAS were shown to be dominated by PFOS and perfluorooctane sulfonamide (FOSA) for each environmental matrix. The mean  $\Sigma$ PFOS concentration measured in soils and eucalyptus leaves was 1490 pg g<sup>-1</sup>. The authors suggested, based on their observations, that sulfluramid can be considered indirect source of PFAS including PFOS to the Brazilian environment.

253. It is also noted that sulfluramid ant baits and gels are also widely advertised and sold in urban Brazil for ants other than the leaf-cutting ants listed as an acceptable purpose (PAN 2018).

254. In this section we update the available information previously presented on the availability, suitability and implementation of alternatives to sulfluramid, based on recently submitted information from Parties and others. Further to information previously published, information on the use of sulfluramid in the control of leaf-cutting ants, and potential alternatives has been provided by Brazil, ABRAISCA, PAN, and IPEN.

## 2.8.2 Availability of alternatives

255. Both chemical and non-chemical alternatives have been developed for use in insect baits to control leaf cutting ants. An overview of the available alternatives, both chemical and non-chemical, is presented in Table 7. This compiles information from previously published sources (e.g. UNEP/POPS/POPRC.12/INF/15; BAT/BEP Experts guidance documents) and more recent submissions from Parties and observers.

### 2.7.2.1 Chemical alternatives

256. A number of chemical alternatives have been previously tested as alternatives to sulfluramid, including chlorpyrifos, cypermethrin, a mixture of chlorpyrifos and cypermethrin, fipronil, imidacloprid, abamectin, deltamethrin, fenitrothion, and a mixture of fenitrothion and deltamethrin. It is noted that fipronil and chlorpyrifos are considered more acutely toxic to humans and the environment than sulfluramid, and the effectiveness of these substances has been questioned, thus new alternatives are being studied in Brazil. It is indicated that due to severe toxicological and environmental characteristics, chlorpyrifos use in insect baits is no longer used in insect baits in Brazil for control leaf cutting ants (Brazil, 2018).

257. The reported chemical alternatives to sulfluramid currently considered as pesticides for leaf cutting ants are: fipronil, deltamethrin, fenitrothion and hydramethylnon (see Table 7). In principle these pesticides are available on the world market, but it is noted that they are not all freely available everywhere.<sup>118</sup> It has been indicated that they are all available as commercial products on the Argentinean market. Deltamethrin, fenitrothion and permethrin are registered and used in Brazil in complementary forms, in very specific applications for the control of leaf-cutting ants.

258. There are two alternative chemical methods that have been developed as a complementary form insect bait to the control of leaf-cutting ants:<sup>119</sup>

<sup>117</sup> UNEP-POPS-POPRC13FU-SUBM-PFOS-Brazil-20180209.En.

<sup>118</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>119</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

(a) Thermonebulizable solutions (thermal fogging) – generation of ultra-fine droplets in a range of 1 µm - 50 µm using thermo-pneumatic energy. Via controlled flow through a nozzle, the pesticide solution is injected into the hot exhaust gas stream near the outlet of the resonator causing it to be atomized forming ultra-fine fog droplets. The active ingredient permethrin (CAS No. 52645-53-1) is mixed with diesel or kerosene as a vehicle;

(b) Dried powder formulations – deltamethrin is mixed in a talcum powder vehicle and manually applied via hand-held equipment (called “dusters”) into the ant hill holes.

259. The use of dried powder formulations is limited to a few regions of the country and far from being used widely. These are recommended only for use as a complementary form in very specific situations, for example, to control some species of *Acromyrmex* colonies and initial colonies of *Atta*.

#### 2.7.2.2. Non-chemical alternatives / alternative technologies

260. A wide range of non-chemical methods have also been developed with the aim of controlling leaf cutting ants. It is noted that Brazil has studied a number of mechanical, cultural, and biological methods since the early 1950s. These are briefly summarised below, and the viability and effectiveness of these approaches is discussed in the following sections:

- (a) Biodiversity measures – e.g., through introduction of different and more varied plant species;
- (b) Cultural control – conventional soil preparation by ploughing and harrowing leading to the mortality of newly formed *Atta* nests;
- (c) Physical / mechanical controls – i.e., physically excavating the ant nests for queen ant removal;
- (d) Barriers – i.e. plastic tape coated with grease, plastic cylinders and strips of aluminium, plastic or metal fastened around the tree trunks;
- (e) Natural plant extracts – for example the product Bioisca was registered in Brazil in 2011, based on saponins and flavones extracted from the plant *Tephrosia candida*;
- (f) Biological controls using fungi– e.g., using the pathogenic fungi *Escovopsis sp.*, and *Syncephalastrum sp.* to control leaf cutting ants has been suggested, as well as the entomopathogenic *Metarrhizium anisopliae* and the entomopathogenic fungi *Beauveria bassiana* and *Aspergillus ochraceus*; and
- (g) Integrated Pest Management – an integrated approach involving improvements in on-farm diversity in conjunction with biological controls such as the pathogenic fungi described above, to minimise damage above economic thresholds.

261. Developing effective biological and physical controls is challenging because leaf-cutting ants have mechanical and chemical defences that help them to counterbalance the effect of some control measures. For example, exocrine glands and symbiotic bacteria are the main sources of antimicrobials in leaf-cutting ants and are used to counter biological control agents. The combination of multiple methods, such as those that limit the growth of bacteria together with biological control agents could therefore be a promising approach in certain settings.

#### 2.8.3 Suitability of alternatives

262. According to De Britto et al. (2016), to be considered an adequate insecticide used to formulate bait for the control of leaf-cutting ants, the substance should fulfil the following criteria: lethal (to ants) at low concentrations or otherwise to prevent the ant from feeding or reproducing; act by ingestion; present a delayed toxic action; be odourless and non-repellent; and paralyze the plant cutting activities, in the first days after application.

263. Brazil (2018) consider that chemical control with toxic baits remains the only approach that has technology available to control leaf-cutting ants genus *Atta sp.* and *Acromyrmex sp.* with technical, economic and operational viability.<sup>120</sup> It was also suggested that two active ingredients, dechlorane<sup>121</sup> and sulfluramid have displayed full efficiency in the control of leaf-cutting ants, wherein the first is no longer used. Currently, Brazil (2018) consider sulfluramid to be the only active ingredient registered for the control of leaf-cutting ants, efficient for all species, that fulfils all of the technical criteria outlined above.

264. Brazil (2018) indicated that there are no available alternatives for this use, taking into account technical feasibility, humans and environment effects, cost/effectiveness, availability and viability. (According to Guidance on General Considerations Related to Alternative and Substitutes for Persistent Organic Pollutants Listed and Candidate Chemicals-UNEP/POPS/ POPRC.5/10/Add.1).

<sup>120</sup> UNEP-POPS-POPRC13FU-SUBM-PFOS-Brazil-20180209.En (submitted for UNEP/POPS/POPRC.12/INF/15/Rev.1).

<sup>121</sup> Dechlorane is a candidate for Annex D evaluation.

265. According to Brazil,<sup>122</sup> fenoxycarb, pyriproxyfen, diflubenzuron, teflubenzuron, silaneafone, thidiazuron, tefluron, prodrone, abamectin, methoprene, hydramethylnon, boric acid, some insecticides from the group of neonicotinoids insecticides, pyrethroids, spinosyns, have been tested for controlling leaf-cutting ants, but they were not found to be effective for all species and settings. De Britto et al. (2016) note that that fipronil and other phenylpyrazoles used in the toxic bait formulation, do not show potential for replacing the sulfluramid.

**Table 7 Overview of alternatives to sulfluramid for use in insect baits for the control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.***

Composition	CAS No	Trade name	Manufacturer	Class*	Source(s)	Additional details
<b>Chemical alternatives</b>						
Fipronil	120068-37-3	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC. 10/INF/7/Rev.1 UNEP (2017) BAP/BEP guidance	
Fenitrothion (thermal fogging)	122-14-5	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC. 10/INF/7/Rev.1 BAT/BEP Group of Experts, 2017	
Deltamethrin (dried powder)	52918-63-5	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC. 10/INF/7/Rev.1 BAT/BEP Group of Experts, 2017	
Hydramethylnon	67485-29-4	Amdro® Ant Block	Information gap	4	Brazil (2018) UNEP/POPS/POPRC. 10/INF/7/Rev.1	For further information, see for example, <a href="http://www.cdpr.ca.gov/docs/risk/rcd/hydrameth.pdf">http://www.cdpr.ca.gov/docs/risk/rcd/hydrameth.pdf</a> and <a href="http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/hydmthn.pdf">http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/hydmthn.pdf</a> .
<b>Non-chemical / Alternative Technology</b>						
Biodiversity	N/A	N/A	N/A	N/A	PAN (2018) UNEP/POPS/POPRC. 8/INF/17/Rev.1 UNEP/POPS/POPRC. 9/INF/11/Rev.1	Can cause the decline and ultimate death of small colonies
Cultural control	N/A	N/A	N/A	N/A	IPEN (2018) Abraisca (2018) BAT/BEP Group of Experts, 2017 UNEP/POPS/POPRC. 8/INF/17/Rev.1	
Physical / mechanical controls	N/A	N/A	N/A	N/A	IPEN (2018) Abraisca (2018) BAT/BEP Group of Experts, 2017 UNEP/POPS/POPRC. 8/INF/17/Rev.1	
Barriers	N/A	N/A	N/A	N/A	IPEN (2018) Abraisca (2018) BAT/BEP Group of Experts, 2017	
Natural plant extracts	N/A	Bioisca	Cooperativa De Cafeicultores e Agropecuaristas	N/A	PAN (2018) IPEN (2018) Abraisca (2018) BAT/BEP Group of Experts, 2017	

<sup>122</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

Composition	CAS No	Trade name	Manufacturer	Class*	Source(s)	Additional details
Biological controls using fungi	N/A	N/A	N/A	N/A	PAN (2018) IPEN (2018) Abraisca (2018) BAT/BEP Group of Experts, 2017	

\* Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: 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 for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

266. The BAT/BEP Group of Experts guidance (2017) noted that assessment of BAT is difficult because the two species of ants are very different, and more information is available on ways to control the genus *Atta* whereas little information is available on the need of and ways to control the genus *Acromyrmex*. The guidance states that “alternative technologies are only effective and efficient in specific situations and require specific equipment and different labour skills that those needed to apply toxic bait”. The combination of technologies overall is considered more labour intensive and costly.

267. In Brazil, fipronil is only registered for use in baits to control certain *Atta* species and is suggested this might not be as efficient and seems to display broader toxicity to other animals.<sup>123</sup> There is insufficient available data to determine the overall feasibility of this substance as a replacement for sulfluramid.

268. A special formulation of hydramethylnon, sold under the trade name Amdro® Ant Block, is currently the only widely available bait product labelled for control of leaf cutting ants in the USA.<sup>124</sup> De Britto et al. (2016) notes that this product has several drawbacks, including a 30% efficiency, the requirement for multiple applications, and a relatively short useful lifetime. This product has not been registered or used in Brazil for leaf-cutting ants. This product may not be used in agricultural sites (e.g., livestock pastures, gardens, cropland) and may not be suitable to treat large any colonies.

269. In terms of alternative techniques for leaf cutting ant control, dried-powder dusting with deltamethrin, is noted to have a number of limitations, including:

- (a) Cannot be applied to moist/wet soil that will cause clogging and clumping of the powder making it ineffective in reaching far into the nests;
- (b) Before application, loose soil needs to be removed from the ant hill;
- (c) Not effective in eradicating large nests because the powder will not reach into the depth of all the tunnels.

270. Dried-powder dusting with deltamethrin is therefore recommended for complementary use to control initial nests of *Atta* species and some *Acromyrmex* species (De Britto et al., 2016).

271. Thermo-nebulization (thermal fogging) is also noted to display some limitations, including:

- (a) Use of specialised equipment and associated high costs;
- (b) Greater work force needed (at least three operators per application);
- (c) Equipment operational problems and maintenance;
- (d) Increased exposure of equipment operators and their colleagues to the insecticides;
- (e) Potential contamination of soil and water.

272. This technique can be applied to control *Atta spp.* in mature nests but cannot be used to control *Acromyrmex spp.* It is being utilized in specific situations, such as very high infestation rates and initial land preparation for cultivation.<sup>125</sup>

273. For mechanical controls, the 2017 BAT//BEP guidance states that excavation of the young nests and capturing the ant queens is an effective way to control the leaf-cutting ants in smaller areas. Excavation is recommended only during the third and fourth months after the nuptial flight, when the queens are about 20 cm deep in the soil (Zanetti et al. 2014). Brazil (2018) indicate that mechanical control by excavating their nests for queen ant removal is no longer recommended for leaf-cutting colonies that are more than 4 months old, this is when the queen will be lodged at

<sup>123</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>124</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>125</sup> BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

depths exceeding 1 meter, thus rendering the technique unviable. It is considered that, in practice, mechanical control will be unviable in areas used for commercial plantations, in reforestation projects and grazing systems.

274. Barriers are noted as being one of the oldest and most cost-effective control methods used for these ants, but only in small orchards (Zanetti et al. 2014). However, constant inspections and repairs are necessary to protect the trees. This control mechanism is not applicable to agricultural and forest crops because of the high maintenance requirements.<sup>126</sup>

275. From the discussion above, it can be concluded that there is no single chemical or process alternative approach that will cover all applications. With the variety of different scales of application, differences in the effectiveness against the different ant species, as well as other considerations, a variety of approaches is required. The 2017 BAT/BEP Group of Experts report outlines different best available techniques based on a number of different specific situations (see Table ).

276. A number of biological controls have been investigated and show potential for controlling leaf cutting ants (Zabaletti et al., 2014). For example, IPEN (2018) cite laboratory studies that suggest the entomopathogenic fungi *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. However, it should be that while displaying some promising results, these techniques are still at the R&D stage and tests have not resulted in conclusive results on the efficiency or consistency of this approach.

**Table 8 The UNEP (2017) BAT/BEP Group of Experts recommend the following best practice for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.***

Situation	BAT
For initial large area land preparation and high infestation rate on mature <i>Atta</i> nests	Thermo-nebulization with permethrin
For small areas, such as small orchards and residential uses	Mechanical Control: Excavation of the young nests and capturing the ant queens
	Barriers <sup>27</sup> fastened around tree trunks, such as plastic tape coated with grease, plastic cylinders and strips of aluminium
To control nests no larger than 5m <sup>2</sup>	Dried-powder dusting with deltamethrin
To control young <i>Atta</i> colonies and certain <i>Acromyrmex</i> species	Dried-powder dusting with deltamethrin
To control certain <i>Acromyrmex</i> species	Dried-powder dusting with deltamethrin
All other	Baits containing sulfluramid

277. PAN (2018) indicate that there is evidence to suggest that biological control agents such as using strains of *Escovopsis* parasitic fungi (Meirilles et al., 2015) or the pathogenic fungus *Syncephalastrum sp.* (Barcoto et al., 2017), could be promising alternatives for the control of leaf cutting ants. At present this is not considered a viable alternative approach as uncertainties over the long-term potential remain. More research is required to establish the potential for this approach in different settings at operational level. The feasibility and potential risks of biological controls, with reference to the use of potentially invasive species and wider ecological impacts need to be carefully considered if proposed approaches involve species that are not already widespread in the local environment.

278. As noted by PAN (2018) the plant extract product Bioisca, based on an extract of the leguminous plant *Tephrosia candida* (white hoarypea) is currently being used, for instance, in organic farmers in Brazil to control the ant species *Atta sexdens rubropilosa* (*saúva-limão*) and *Atta laevigata* (*saúva cabeçade-vidro*). The product is certified as an organic product by Biodynamic and the efficacy of the product has been validated in various regions of Brazil (PAN, 2018). However, this approach is not currently recommended for large-scale use such as in agriculture, forestry and livestock farming, and the wider operational potential of these products requires further investigation and development.

279. The potential for baits produced from other natural resources has also been reported (PAN, 2018). Other plant extracts which have shown promise include limonoids extracted from the roots of the South Brazilian endemic plant *Raulinoa echinata*, neem and sesame oil. Baits prepared with neem oil (azadirachtin) have been reported to reduce ant foraging by 75.5% for *Atta spp.* and 83.5% for *Acromyrmex spp.* in a field trial in Brazil. Baits prepared with sesame oil reduced ant foraging by 55.9% and 67.6% of *Atta spp.* and *Acromyrmex spp.*, respectively. Baits prepared with neem and sesame do not kill leaf-cutting ant colonies but reduce forage activity and hence leaf-loss. It is noted that further research is required into the wider technical feasibility and operational consistency of control methods

<sup>126</sup> BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

using natural plant extracts before these can be recommended for widespread use and be considered viable alternatives.

280. For cultural controls, De Britto et al. (2016) indicated that that approaches such as crop rotation, ploughing and harrowing, the use of fertilizers and limestone, the digging of nests, and the use of composting have been widely used but are not considered a feasible alternative to controlling leaf cutting ants in all situations. It is also noted that, with the practice of minimum cultivation adopted in several cultivars and reforestation projects, such control has been abandoned. It is also noted that the practice of minimum tillage, which reduces soil preparation throughout the area and adopted by many forest producers may increase the number of leaf-cutting ant nests (Zanetti et al., 2014).

281. As noted by PAN (2018), research in Costa Rica has indicated 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. De Britto et al. (2016) indicate that the presence of forest understory and native vegetation strips and the consequent bird populations in situ are factors that contribute in reducing the number of ant nests initially, but the need to be thoroughly tested before they can be recommended, and it is noted this is currently in the research phase.

282. De Britto et al. (2016) indicated that cultural management using resistant plants, plants toxic to ants, and applied biological management by manipulating natural enemies, including predators (birds, mammals, amphibians, reptiles, beetles, other ants), the parasitoids (*Phoridae flies*) and nematodes, is so far considered to have not provided consistent results so is not considered technically, economically, or operationally viable at this stage, although it is noted they occur in nature and contribute to reducing the mortality of the ant queens and consequently the foundation of new colonies. This is an ongoing area of research.

283. There is uncertainty and contradictory opinion on the potential for integrated pest management to control leaf cutting ants, and further research and development is clearly required in this area. According to Della Lucia et al. (2013), a lack of economic thresholds and sampling plans focused on the main pest species preclude the management of leaf-cutting ants; such management would facilitate their control and lessen insecticide overuse, particularly the use of insecticidal baits.

#### 2.8.4 Implementation of alternatives

284. According to the BAT/BEP Group of Experts guidance (2017) sulfluramid-containing pellet bait represents 95% of the formicide bait market in Brazil. This would suggest that the level of replacement from sulfluramid to non-sulfluramid control agents has been minimal.

285. Brazil (2018) report that recent trends in the production, use and export of sulfluramid from PFOSF for the production of insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.*:

- (a) Production – increase from 28.684 kg in 2013 to 35.090 kg in 2017 (22% increase);
- (b) Use – increased from 27 165 kg in 2013 to 33 186 kg in 2017 (16% increase);
- (c) Export – increase from 859 kg in 2013 1064 kg in 2017 (24% increase).

286. The evidence submitted by Brazil (2018) indicates that insect baits containing sulfluramid are exported to several other South American and Central American countries. The time trend (2013-2017) in the volumes of sulfluramid exported is variable between countries but there is a lack of downwards trend in the volumes exported to these countries over this time.

287. The above observations would suggest that sulfluramid continues to be used in relatively significant quantities and none of the chemical or non-chemical alternatives outlined in this section are being widely implemented in Brazil or other South or Central American countries. This is consistent with position stated by Brazil (2018) that there are no available alternatives for this use (see above).

288. While innovative chemical, biological and physical methods are available and/or being developed, it appears none of these are currently widely implemented. This should be the focus of continued research, testing and, where demonstrated to be technically and operationally feasible, the implementation of alternative approaches.

#### 2.8.5 Information gaps and limitations

289. The following key information gaps have been identified from the above discussion:

- (a) Further scientific research and development, and implementation of suitable alternatives where feasible should be undertaken to reduce and eliminate the use of sulfluramid where possible;
- (b) In particular – demonstration of non-chemical measures such as plant extracts and other biological and cultural controls in field studies are needed to develop and demonstrate feasibility as widespread control measures;
- (c) Data on conversion rate of sulfluramid to PFOS in the environment under natural conditions.

## 2.8.6 Concluding remarks

290. Brazil is continuing to use PFOSF to produce sulfluramid which is used for control of leaf-cutting ants from the species of *Atta* spp. and *Acromyrmex* spp. The data provided by Brazil on levels of production, use and export of sulfluramid suggest there has not been a significant switch to any alternative substances or techniques for this acceptable purpose.

291. The BAT/BEP expert guidance notes a number of alternative chemicals and approaches are available and are considered best practice for a number of specific applications.

292. The assessment of the use of alternatives to PFOS, its salts and PFOSF showed dissenting views on the need to use sulfluramid for combatting leaf cutting ants, the availability of alternatives, technical and economic feasibility and operational effectiveness of these alternatives.

293. The Committee discussed both the lack of clarity in the text of the Annex listing PFOS, its salts and PFOSF, as sulfluramid is not explicitly mentioned in the use entry, and the current wide-spread use of sulfluramid. Based on these discussions, the Committee suggests including the word “sulfluramid (CAS Number 4151-50-2)” in the entry for the listed acceptable purpose and specifying that the current acceptable purpose is meant for agricultural use only.

294. The Committee therefore recommends that the acceptable purpose be maintained and that the text of the use entry in the Annex be clarified as follows: “insect baits with sulfluramid (CAS Number 4151-50-2) as an active ingredient for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. for agricultural use only.”

295. The Committee encourages additional research and development of alternatives and, where alternatives are available, that they be implemented.

296. The Committee further encourages Parties to consider monitoring activities for sulfluramid, PFOS and other relevant degradation products in the different environmental compartments (soil, ground water, surface water) of the application sites

## 2.9 Photo masks in the semiconductor and liquid crystal display (LCD) industries

### 2.9.1 Introduction and background

297. Photo masks are an essential part of the photolithography process of semiconductor and LCD production. They are used to transfer the desired geometric pattern via light to the photo-resist carrying silicon wafer. The pattern on the photomask that will be transferred to the photo-resist on the silicon wafer is being created by an etching process that requires the use of a surfactant to reduce patterning defects. In this wet etching process, PFOS was used as a surfactant in the etching solution to enhance surface wettability by reducing the surface tension of the solution.<sup>127</sup>

298. Photo masks in the semiconductor and liquid crystal display (LCD) industries is listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of specific exemptions, as of May 2018, China is the only Party registered for this use. The expiry date for this registration is ‘not provided’. All other registrations for this specific exemption have now expired.

### 2.9.2 Availability, suitability and implementation of alternatives

299. The World Semi-Conductor Council (WSC) reported in 2011 that the use of PFOS in etchants has been eliminated (WSC 2011).<sup>128</sup>

300. It has been indicated that information on alternatives is available but chemical identities, properties, and trade names and producers were not identified. According to industry information this use has been eliminated.

301. No information on available alternative substances has been provided in recent submissions by Parties or Observers. A dry process exists and is practiced for some specific cases for photo masks for the semiconductor industry (Japan, 2007 Annex F submission).

### 2.9.3 Information gaps and limitations

302. The following information gaps have been identified:

(a) Very little information on the specific identity, technical or economic feasibility or implementation of alternatives, either chemical or non-chemical (process-based);

(b) No data on continued level of use or level of need for this use in China, or estimated timescale for a phase-out.

<sup>127</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>128</sup> [http://www.semiconductorcouncil.org/wsc/uploads/WSC\\_2011\\_Joint\\_Statement.pdf](http://www.semiconductorcouncil.org/wsc/uploads/WSC_2011_Joint_Statement.pdf).

## 2.9.4 Concluding remarks

303. It is indicated that industry has largely phased out the use of PFOS from this use, with China the only party maintaining a notification for this specific exemption.

304. Industry has largely phased out the use of PFOS, its salts and PFOSF from this use. Therefore, the Committee recommends that the specific exemption for the use of PFOS, its salts and PFOSF for photo masks in the semiconductor and liquid crystal display (LCD) industries no longer be available under the Convention.

## 2.10 Electric and electronic parts for some colour printers and colour copy machines

### 2.10.1 Introduction and background

305. Electrical and electronic equipment often requires hundreds of parts and thousands of processes to make them. For example, parts from the semiconductor industry might find uses in colour printers and colour copy machines.

306. Electric and electronic parts for some colour printers and colour copy machines is listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of specific exemptions, as of May 2018, China is the only Party registered for this use. The expiry date for this registration is 'not provided'. All other registrations for this specific exemption have now expired. This use is considered an open application according to document UNEP/POPS/POPRC.7/INF/22/Rev1.

307. PFOS-based chemicals are used in the manufacturing of digital cameras, cell phones, printers, scanners, satellite communication systems, and radar systems, amongst others. The PFOS-related compounds are used as process chemicals, and the final products are considered as mostly PFOS-free. It has been reported that 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  $8 \times 10^{-4}$  ppm PFOS.

308. 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.

### 2.10.2 Availability, suitability and implementation of alternatives

309. It is indicated that PFOS-related chemicals are no longer used on colour printers and colour copy machines.<sup>129</sup> While the specific identities of replacements or substitutes for PFOS, PFOS-related chemicals and mixtures are not publicly available due to trade secrets restrictions, these substances and mixtures have included short-chain PFAS and various fluorinated telomers.<sup>130</sup>

310. There is no further information available on PFOS alternatives for these uses, either in previously published POP RC documents or the recently submitted information from Parties and Observers.

### 2.10.3 Information gaps and limitations

311. There is currently no detailed information available on alternatives, chemical identify and properties and trade names and producers, the technical feasibility or environmental impacts of PFOS alternatives in this sector.

### 2.10.4 Concluding remarks

312. PFOS, its salts and PFOSF for these uses has been largely phased out. This indicates that alternatives to PFOS are available and widely implemented. Therefore, the Committee recommends that the specific exemption for the use of PFOS its salts and PFOSF for electric and electronic parts for some colour printers and colour copy machines no longer be available under the Convention.

## 2.11 Insecticides for control of red imported fire ants and termites

### 2.11.1 Introduction and background

313. Red imported fire ants (RIFAs) are native to South America but have become a pest in the southern United States, Australia, the Caribbean, Taiwan, Hong Kong, and several southern Chinese provinces.<sup>131</sup> RIFAs are a threat to human activity because of their painful stings, which may cause severe allergic reactions in venom sensitive people. The RIFA are therefore a threat to pets, new-born chicks and calves, wildlife, and sleeping or bed-ridden individuals,

<sup>129</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>130</sup> <http://chm.pops.int/tabid/2467/Default.aspx> (submission by USA).

<sup>131</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

and cause damage to electrical equipment and their mounds interfere with cutting and harvesting machinery in cattle operations and other landscape and agricultural functions.<sup>132</sup>

314. Termites become a problem when they damage timber and other materials in structures. Damage may extend to household furniture, paper products, many synthetic materials and food items. Each year hundreds of thousands of structures (bridges, dams, decks, homes, retaining walls, roads, utility poles, and underground cables and pipes) require treatment for the management of termites.

315. Insecticides for control of RIFAs and termites is listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of specific exemptions, as of May 2018, China is the only Party registered for this use. The expiry date for this registration is ‘not provided’. All other registrations for this specific exemption have now expired. This use is considered an open application according to UNEP/POPS/POPRC.7/INF/22/Rev1.

316. A common method to control RIFA is with baits consisting of pesticides on processed corn grits coated with soybean oil. N-Ethyl perfluorooctane sulfonamide (EtFOSA; CAS No. 4151-50-2), also called sulfluramid, has been used as a pesticide for this application. 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.<sup>133</sup>

### 2.11.2 Availability, suitability and implementation of alternatives

317. It is indicated that alternative substances and (non-chemical) technologies to sulfluramid for the control of RIFAs and termites are commercially available on the market and have been implemented globally. The UNEP (2017) BAT/BEP guidance<sup>134</sup> states that for best practice, ‘alternative substances to sulfluramid should be used to control RIFA effectively’.

318. The alternative chemical substances and mixtures developed have included short-chain PFAS and various fluorinated telomers. An overview of identified alternatives to sulfluramid is provided in Table 9. It is noted that several of the alternative substances listed here are also included in the list of alternatives for use as insect baits for control of leaf-cutting ants from *Atta spp.* and *Acromyrmex spp.* (see Table 9 below). In China, for example, 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.

319. Huang et al. (2013) noted the existence of three registered products for termite control in China, using either hexaflumaron or chlorofluazuron as the active ingredient.

320. It should be noted that some of the chemistries of these alternatives have been part of the assessment of alternatives to endosulfan.<sup>135</sup>

321. The “delayed action” pesticides are effective after a time period ranging from a few days to up to 6 months. Baits can be 80-90% effective in controlling RIFA because foraging ants carry the poison back to the colony. Granules containing contact insecticides might be less effective because they only control foraging ants but not the colony. Spraying ants or individual mounds might be less effective since this method does not control the colony but might cause the colony to disperse.

322. 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.

**Table 9 Examples of reported alternatives to sulfluramid for the treatment of RIFAs and termites, as identified in the BAP/BEP guidance document**

Alternative	CAS No.	RIFA	Termites	Pesticide Action	Class	Information source
<b>Chemical alternatives</b>						
Abamectin	71751-41-2	Yes	No	Delayed Action	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
Acephate	30560-19-1	Yes	No	Contact Insecticide	Not screened	BAT/BEP Guidance

<sup>132</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>133</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>134</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>135</sup> See UNEP/POPS/POPRC.8/INF/12.

Alternative	CAS No.	RIFA	Termites	Pesticide Action	Class	Information source
Alpha-Cypermethrin (Pyrethroid)	67375-30-8	Yes	No	Contact Insecticide	4	POPRC-8/6: Assessment of alternatives to endosulfan
Bifenthrin (Pyrethroid) <sup>1</sup>	82657-04-3	Yes	Yes	Contact Insecticide	4	POPRC-8/6: Assessment of alternatives to endosulfan
Carbaryl	63-25-2	Yes	No	Contact Insecticide	Not screened	BAT/BEP Guidance
Chlorpyrifos (Organophosphate)	2921-88-2	Yes	Yes	Contact Insecticide	2	UNEP/POPS/POPRC.10/INF/7/Rev.1
Cyfluthrin (Pyrethroid)	68359-37-5	Yes	Yes	Contact Insecticide	Not screened	BAT/BEP Guidance
Cypermethrin (Pyrethroid)	52315-07-8	Yes	Yes	Contact Insecticide	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
Deltamethrin (Pyrethroid)	52918-63-5	Yes	No	Contact Insecticide	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
D-Limonene (citrus oil extract)	5989-27-5	Yes	No	Contact Insecticide	Not screened	BAT/BEP Guidance
Fenitrothion	122-14-5	No	Yes	Contact Insecticide	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
Fenvalerate	51630-58-1	No	Yes	Contact Insecticide	Not screened	BAT/BEP Guidance
Fipronil	120068-37-3	Yes	No	Delayed Action	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
Hydramethylnon	67485-29-4	Yes	Yes	Delayed Action	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
Indoxacarb	144-171-61-9	Yes	No	Delayed Action	4	POPRC-8/6: Assessment of alternatives to endosulfan
Imidacloprid	138261-41-3, 105827-78-9	Yes	Yes	Contact Insecticide	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
Metaflumizone	139968-49-3	Yes	No	Delayed Action	Not screened	BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs
Methoprene	40596-69-8	Yes	No	Delayed Action	Not screened	BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs
Permethrin (Pyrethroid)	52645-53-1	No	Yes	Contact Insecticide	Not screened	BAT/BEP Guidance
Pyriproxyfen	95737-68-1	Yes	No	No info	4	UNEP/POPS/POPRC.10/INF/7/Rev.1
<b>Non-chemical alternatives</b>						
Biological controls, including phorid flies	N/A	Yes	No	N/A	N/A	UNEP/POPS/POPRC.8/INF/17/Rev.1

Alternative	CAS No.	RIFA	Termites	Pesticide Action	Class	Information source
( <i>Pseudacteon spp.</i> ), the microsporidian protozoan ( <i>Thelohania solenopsae</i> ) and the fungus <i>Beauveria bassiana</i> , the endoparasitic fungi <i>Myrmecomyces annellisae</i> and <i>Myrmecinosporidium durum</i> , and the parasite <i>Mattesia spp.</i>						UNEP/POPS/POPRC.9/INF/11/Rev.1
Biological controls, including <i>Beauveria bassiana</i> and <i>Metarhizium anisopliae</i> .	N/A	No	Yes	N/A	N/A	BAT/BEP Guidance
Viruses, SINV-1, SINV-2, SINV-3	N/A	Yes	No	N/A	N/A	BAT/BEP Guidance

323. In terms of non-chemical alternatives, biological controls are considered promising for RIFA control, including the potential use of phorid flies (*Pseudacteon spp.*), the microsporidian protozoan (*Thelohania solenopsae*) and the fungus *Beauveria bassiana*, the endoparasitic fungi *Myrmecomyces annellisae* and *Myrmecinosporidium durum*, and the parasite *Mattesia spp.*<sup>136</sup>

324. 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. Natural enemies, such as parasitic decapitating flies from South America have been successful in areas where they have been released but they are not available to the general public.<sup>137</sup> Biological control options for termites include *Beauveria bassiana* and *Metarhizium anisopliae*.

325. It has been indicated that 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. This suggests that viable alternatives are readily available and effective for these uses. Continued use of PFOS as a bait for cockroach and termite control in China has also been indicated by a CAFSI Survey (Huang et al., 2013).

326. It is noted that eight of the insecticides identified in Table 9 were not included in the previous PFOS alternatives assessment report. These include Acephate (CAS No : 30560-19-1); Carbaryl (CAS No: 63-25-2); Cyfluthrin (Pyrethroid) (CAS No: 68359-37-5); D-Limonene (citrus oil extract) (CAS No: 5989-27-5); Fenvalerate (CAS No: 51630-58-1); Metaflumizone (CAS No: 139968-49-3); Methoprene (CAS No: 40596-69-8); Permethrin (Pyrethroid) (CAS No: 52645-53-1). These substances, and their potential POPs characteristics are considered in more detail in Chapter 3.

### 2.11.3 Information gaps and limitations

327. The following information gaps have been identified:

- (a) Information on levels of use and need for continued use in China is lacking;
- (b) A number of chemical alternatives listed in Table have not been previously screened for POPs criteria in previous studies;
- (c) Limited information is available on the effectiveness of chemical methods (i.e. biological controls) and consistency of these methods.

<sup>136</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>137</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

## 2.11.4 Concluding remarks

328. Use of PFOS in the control of RIFAs and termites appears to be no longer used in most countries, with only China maintaining a registration for a specific exemption. A range of chemical alternatives have been identified and it is indicated these are widely available and technically feasible. These alternatives have been widely implemented. There is a strong case to remove this specific exemption. However, there are a number of chemical alternatives identified, for which POPs screening is required. The suitability of biological controls should also be further investigated.

329. A range of chemical and non-chemical alternatives have been identified and it is indicated these are widely available and technically feasible. These alternatives have been widely implemented by Parties. The Committee recommends that the specific exemption for the use of PFOS, its salts and PFOSF for insecticides for control of red imported fire ants and termites no longer be available under the Convention.

## 2.12 Chemically driven oil production

### 2.12.1 Introduction and background

330. PFOS, its salts and PFOSF have been used as surfactants in the oil and gas sector to enhance oil or gas recovery in wells (for example, to recover oil trapped in small pores between rock particles), and as evaporation inhibitors for gasoline, such as jet fuel and hydrocarbon solvents.<sup>138</sup>

331. Chemically driven oil production is listed as a specific exemption for the production and use of PFOS, its salts and PFOSF in Annex B. According to the register of specific exemptions, as of May 2018, China is the only Party registered for this use. The expiry date for this registration is 'not provided'. All other registrations for this specific exemption have now expired.

332. Very limited information is available on the use of PFOS and the development of alternatives for this use. The UNEP (2017) BAP/BEP guidance document<sup>139</sup> notes that obtaining detailed information on this use proved to be challenging.

### 2.12.2 Availability, suitability and implementation of alternatives

333. The EU (2018) noted that information on alternatives, on chemical identity/properties and trade names/producers is available but quite limited.

334. Chemical alternatives to PFOS have been identified and it is indicated these are readily available. An overview of these alternatives is presented in Table 10 below.

**Table 10 Overview of alternatives to PFOS for use for chemically driven oil production**

Composition	CAS No	Trade Names (Manufacturer)	Information Source	Class*	Additional Comments/Details
Perfluorobutane sulfonate (PFBS) <sup>140</sup>	29420-49-3	Gas Well Stimulant WS 1200 (3M)	UNEP/POPS/POPRC.8/INF/17/Rev.1 BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs	3	See SDS at: <a href="http://multimedia.3m.com/mws/mediawebsserver?mwsId=SSSSSuUn_zu8l00xmxtd=G58mvlv70k17zHvu9lxtD7SSSSSS--">http://multimedia.3m.com/mws/mediawebsserver?mwsId=SSSSSuUn_zu8l00xmxtd=G58mvlv70k17zHvu9lxtD7SSSSSS--</a>
6:2-Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	Information gaps	UNEP/POPS/POPRC.8/INF/17/Rev.1	3	None

<sup>138</sup> See UNEP/POPS/COP.7/INF/26.

<sup>139</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>140</sup> A NICNAS (2015c) assessment, indicated that this perfluorinated organic anion is highly persistent and mobile and, as a result, has the potential to become globally distributed. Nevertheless, currently available data indicate that PFBS is not expected to be highly bioaccumulative or toxic to aquatic organisms. PFBS was assessed in the previous alternatives assessment report (UNEP/POPS/POPRC.10/INF/7/Rev.1).

Composition	CAS No	Trade Names (Manufacturer)	Information Source	Class*	Additional Comments/Details
PFBS derivatives, fluorotelomer-based fluorosurfactants, perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids. <sup>141</sup>	N/A	Information gaps	UNEP/POPS/POPRC.8/INF/17/Rev.1 UNEP/POPS/POPRC.9/INF/11/Rev.1	N/A	None
Sodium <i>p</i> -perfluorous nonenoxybenzene sulfonate (OBS)	70829-87-7	Various (incl. 3F)	Bao et al. (2017)	N/A	Potential concern over environmental toxicity.

\* Based on UNEP/POPS/POPRC.10/INF/7/Rev.1: 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 for classification due to insufficient data); Class 4 (Substances that are not likely to meet all Annex D criteria).

335. The principal PFOS alternatives identified in oil and mining industries include perfluorobutane sulfonate (PFBS) based substances and short-chain telomer-based fluorosurfactants, as well as perfluoroalkyl-substituted amines, acids, amino acids, and thioether acids.<sup>142</sup>

336. Sodium *p*-perfluorous nonenoxybenzene sulfonate (OBS) has also been reported as a potential alternative to PFOS as an oil production agent in China, however concerns have been raised regarding the potential degradation and toxicity of OBS to the environment (Bao et al., 2017).

337. In most parts of the world where oil exploration and production are 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

338. The UNEP (2017) BAP/BEP guidance states that 'non-PFOS-related compounds should be used for this application'. The BAP/BEP guidance document also notes that 'oil and gas production were reportedly carried out without the use of PFOS, its salts and PFOSF in other countries, including developing countries, thus indicating the existence of alternative processes that did not require PFOS'.<sup>143</sup>

### 2.12.3 Information gaps and limitations

339. The following information gaps have been identified:

- (a) Available information on the relative availability, technical and economic feasibility, environmental viability and implementation of identified alternatives is lacking;
- (b) Very few products on the market have been identified.

### 2.12.4 Concluding remarks

340. Use of PFOS-related compounds in this sector is only reported in China, with indication it has been phased out in favour of alternatives everywhere else. However, the levels of PFOS still used, and the necessity of its continued use are unclear. The assessment showed that alternatives are widely available. Given the use of alternatives to PFOS, its salts and PFOSF in most oil-producing areas, the Committee recommends that the specific exemption for the use of PFOS, its salts and PFOSF for chemically driven oil production no longer be available under the Convention.

<sup>141</sup> A NICNAS (2014) assessment indicated that The principal risk posed by the chemicals in this group if emitted to the environment has been assumed to result from the cumulative releases of PFBS.

<sup>142</sup> UNEP/POPS/COP.7/INF/26.

<sup>143</sup> UNEP/POPS/COP.7/INF/26.

## 2.13 Expired specific exemptions (Carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, rubber and plastics)

### 2.13.1 Introduction and background

341. At its seventh meeting (2015), the Conference of the Parties noted, through Decisions SC-7/1, pursuant to paragraph 9 of Article 4, that as there are 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, no new registrations may be made with respect to them.

342. According to the register of specific exemptions,<sup>144</sup> any registrations for exemptions for use of PFOS in these applications expired in 2015. It was noted in UNEP/POPS/POPRC.12/INF/15/Rev.1 that 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 for these uses. It can therefore be assumed that alternatives to PFOS in these uses are readily available, technically and economically feasible, and have been widely implemented already.

343. A brief discussion is provided here, referring to recently submitted information from individual Parties or Observers, as well as previous information provided in UNEP/POPS/POPRC.12/INF/15/Rev.1 and the BAT/BEP Group of Experts guidance document.

### 2.13.2 Carpets, leather and apparel, textiles and upholstery

344. Side-chain fluorinated polymers have historically been used 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 and medical fabrics (e.g. woven or nonwoven surgical drapes and gowns) to repel water, oil and dirt (stains). 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).

345. PFOS-related chemicals are no longer used in these application<sup>145</sup> and a variety of alternative substances are widely available. Potential alternatives to PFOS for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles include both fluorinated and non-fluorinated substances. It is noted that in many cases, the specific identity of some of the developed alternatives have not been disclosed due to trade secrets.

346. The FluoroCouncil (2018) noted that both fluorinated and non-fluorinated alternatives are available and on the market, with two alternative fluorinated technologies in global use that provide oil- and water- repellent and -stain release properties in this sector:

(a) Short-chain fluorotelomer-based side chain (“C<sub>6</sub>”) fluorinated polymers, with high molecular-weight acrylic polymers that contain 6:2 fluorotelomer functionality to provide repellent performance. Examples of suppliers who offer these products commercially:

- (i) Daikin: <https://www.daikin.com/chm/products/fiber/index.html>;
- (ii) Asahi: <https://www.agc-chemicals.com/jp/en/fluorine/products/detail/use/index.html?pCode=JP-EN-F001>;
- (iii) Chemours: [https://www.chemours.com/Capstone/en\\_US/uses\\_apps/textiles/index.html](https://www.chemours.com/Capstone/en_US/uses_apps/textiles/index.html);
- (iv) Archroma: <http://www.bpt.archroma.com/products-services/finishing/repellency-soil-release/>;
- (v) Fuxin Heng Tong Fluorine Chemicals Co. Ltd: <http://www.htfluor.us/>;
- (vi) Nicca: [http://www.niccausa.com/product\\_data\\_sheet/ni-805/](http://www.niccausa.com/product_data_sheet/ni-805/);
- (vii) Jintex: [http://www.jintex.com.tw/en/product\\_unit.php?pid=1&uid=272](http://www.jintex.com.tw/en/product_unit.php?pid=1&uid=272);
- (viii) Rudolf Chemie: <http://www.rudolf.de/en/products/textile-auxiliaries/finishing/>;
- (ix) Maflon: Hexafor from Maflon: <http://www.maflon.com/images/maflon.pdf>;
- (x) Ruco-Coat® from Rudolf Group: <http://www.rudolf-duraner.com.tr/en/products/co-producer-b2b/10-water-oil-and-soil-repellent-agents/12-c6-based-fluorocarbon-polymers.html>;
- (xi) Theteguard and Thetapel from ICT: <http://www.ictchemicals.com/products/technical-platforms/fluorinated-specialty-polymers/>;

<sup>144</sup><http://chm.pops.int/Implementation/Exemptions/SpecificExemptions/ChemicalslistedinAnnexBRoSE/PFOSRoSE/tabid/4644/Default.aspx>.

<sup>145</sup> UNEP/POPS/POPRC.12/INF/15/Rev.1.

(b) Short-chain electrochemical fluorination-based side chain (“C<sub>4</sub>”) fluorinated polymers, high molecular-weight acrylic polymers that contain perfluorobutane sulfonyl functionality to provide repellent performance. Examples of suppliers who offer these products commercially: Scotchgard™ from 3M: [https://www.scotchgard.com/3M/en\\_US/scotchgard/built-in-protection/](https://www.scotchgard.com/3M/en_US/scotchgard/built-in-protection/).

347. It is also noted that perfluoropolyether technologies, such as Fluorolink® PFPE produced by Solvay<sup>146</sup> are available for the production of textiles and leather goods.

348. It is noted that short-chain fluorinated products, both short-chain fluorotelomer-based and perfluorobutanem sulfonyl-based, have been applied for manufacture, sale and use in carpets, textiles, leather, upholstery, apparel, and paper applications.<sup>147</sup> FluoroCouncil (2018) reported that short-chain fluorinated alternatives have been on the market and extensively used as efficient alternatives for over a decade. Fluorinated alternatives uniquely provide both oil and water repellence as well as water and oily stain protection. Short-chain alternatives have been adequately reviewed and approved by multiple competent regulatory authorities worldwide.

349. FluoroCouncil (2018) also reported large number of global suppliers are offering “non-fluorinated” alternatives, including:

- (a) Hydrocarbon wax-based repellents consisting of paraffin-metal salt formulations;
- (b) Hydrophobic modified polyurethanes (hydrophobic modified hyper-branched polyurethanes called dendrimers);
- (c) Polysiloxane-based products;
- (d) Resin-based repellents consisting of fatty modified melamine resins.

350. It is indicated that non-fluorinated alternatives provide durable water repellence due to hydrophobic properties, but do not provide oil repellence or soil and stain release so are not technically viable for all uses. These alternatives are used commercially on a global basis where the performance (water repellent) is suitable for the intended use of the consumer product.<sup>148</sup>

### 2.13.3 Paper and packaging

351. Fluorinated chemicals have previously been used in the paper industry to produce waterproof and greaseproof paper. 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.<sup>149</sup>

352. Two specific PFOS-related compounds have been used:

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

353. Chemical alternatives for this use have been developed and are indicated to be available, technically and economically feasible and widely implemented already. The FluoroCouncil (2018) indicate there are two principal alternatives for impregnation of paper and cardboard for that are in global use to provide oil- and grease repellent properties to paper and paper packaging. These include:

(a) Short-chain fluorotelomer-based side chain (“C<sub>6</sub>”) fluorinated polymers, with high molecular-weight acrylic polymers that contain 6:2 fluorotelomer functionality to provide repellent performance. Examples of suppliers who offer these products commercially:

- (i) Daikin: <https://www.daikin.com/chm/products/fiber/index.html>;
- (ii) Asahi: <https://www.agc-chemicals.com/jp/en/fluorine/products/detail/use/index.html?pCode=JP-EN-F001>;
- (iii) Chemours: [https://www.chemours.com/Capstone/en\\_US/uses\\_apps/textiles/index.html](https://www.chemours.com/Capstone/en_US/uses_apps/textiles/index.html);
- (iv) Archroma: <http://www.bpt.archroma.com/products-services/finishing/repellency-soil-release/>;
- (v) Fuxin Heng Tong Fluorine Chemicals Co. Ltd: <http://www.htfluor.us/>;

<sup>146</sup> <https://www.solvay.com/en/markets-and-products/featured-products/Fluorolink.html>.

<sup>147</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>148</sup> A recently completed multi-party project called SUPFES reported on this (<http://www.supfes.eu/ProjectInfo.aspx>).

<sup>149</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

(b) Perfluoropolyether-based oil- and grease repellent products. Examples of suppliers who offer these products commercially: Solvay <https://www.solvay.com/en/markets-and-products/featured-products/solvera.html>.

354. It is reported that these products have been evaluated by competent regulatory authorities responsible for their use in food contact paper and paper packaging. (e.g., Bundes Insitut fur Riskiobewertung, BfR and the U.S. Food and Drug Administration, FDA).

355. Fluorocouncil (2018) also notes that, in addition, users requiring oil- and grease-proof packaging have widely shifted to not-in kind alternative packaging materials and systems (e.g., polymers/plastics for example in chocolate wrappers). It is also reported that a Norwegian paper producer (Nordic Paper) is developing a non-chemical approach using mechanical processes to produce, without using any persistent chemical, extra-dense paper that inhibits leakage of grease through the paper.<sup>150</sup>

#### 2.13.4 Coatings and coating additives

356. Historically, PFOS derivatives have had several uses in coating, paint and varnishes to reduce surface tension, for example, for substrate wetting, for levelling, as dispersing agents and for improving gloss and antistatic properties, as well as additives in dyes and ink, as pigment grinding aids and as agents to combat pigment flotation problems.<sup>151</sup> PFOS was favoured due to the very low (<0.01% w/w) concentrations required.

357. PFOS-related fluorinated polymers containing up to 4% of fluorinated residuals have also been sold as coating materials, for example in printed circuit boards and hard disk drive components to provide protection against corrosion, contamination and grime as well as repellent properties leading to an improved manufacturing efficiency.<sup>152</sup>

358. Chemical alternatives for this use have been developed and are indicated to be available, technically and economically feasible and widely implemented already.

359. The FluoroCouncil (2018) and UNEP/POPS/POPRC.12/INF/15 provided details on the type of alternatives available in this sector:

(a) Short-chain fluorotelomer-based side chain fluorinated (“C<sub>6</sub>”) fluorinated polymers. Examples of suppliers who offer these products commercially;

(i) Chemgard: <http://www.chemguard.com/specialty-chemicals/product-applications/wetting-leveling.htm>;

(ii) Chemours: [https://www.chemours.com/Capstone/en\\_US/uses\\_apps/fluorosurfactants/index.html](https://www.chemours.com/Capstone/en_US/uses_apps/fluorosurfactants/index.html);

(iii) Dynax: <http://dynaxcorp.com/>;

(b) Short-chain electrochemical fluorination-based side chain (“C<sub>4</sub>”) fluorinated polymers e.g. C<sub>4</sub>-compounds based on perfluorobutane sulfonate. Examples of suppliers who offer these products commercially:

(i) 3M: [http://solutions.3m.com/wps/portal/3M/en\\_EU/EU-EAMD/Home/OurProducts/NovelFluorosurfactants/](http://solutions.3m.com/wps/portal/3M/en_EU/EU-EAMD/Home/OurProducts/NovelFluorosurfactants/);

(ii) Miteni: <http://www.miteni.com/index.htm>;

(c) Oxetane Fluorosurfactants;

(d) Fluorinated polyethers (PolyFox®);

(e) 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;

(f) Silicone polymers, such as polyether-modified polydimethyl siloxane, mixed with di-(2-ethylhexyl) sulfosuccinate in ethanol and water (WorléeAdd®);

(g) 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;

(h) Fatty alcohol polyglycol ether sulphate, sometimes together with a sulfosuccinate.

#### 2.13.5 Rubber and plastics

<sup>150</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>151</sup> See UNEP/POPS/POPRC.12/INF/15/Rev.1.

<sup>152</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

360. Because of good surfactant properties with extremely stable and non-reactive characteristics, perfluorocarbons, including PFOS are used in release agents for plastic and rubber products manufacture.<sup>153</sup> A release agent is a chemical, often wax, silicone or fluorocarbon fluid, used in moulding and casting, that aids in the separation of a mould from the material being moulded. It reduces imperfections in the moulded surface; it is also known as a parting agent, mould lubricant, mould release lubricant and de-moulding agent. PFOS, its salts and PFOSF have been previously used as mould release agents in rubber and plastics moulding applications

361. It is noted that perfluorobutane sulphonate (PFBS) derivatives or various C<sub>4</sub>-perfluorocompounds are used as alternatives to PFOS in rubber moulding defoamers in electroplating and as additives in plastics.

### 2.13.6 Information gaps and limitations

362. For alternatives developed in the paper and packaging industry, information required on alternatives used that provide dirt and stain repellent properties as it is indicated that the required functionality is not currently provided by the alternates described in this section.

### 2.13.7 Concluding remarks

363. There are no longer any Parties registered for specific exemptions for production or use in these sectors. It is indicated that alternatives to PFOS in most uses are widely available and technically viable and have been implemented globally.

## 3 Assessment of POPs characteristics of chemical alternatives to PFOS, its salts and PFOSF

### 3.1 Introduction and background

364. A report on the assessment of alternatives to PFOS, its salts and PFOSF, based on a screening to analyse whether or not the identified alternatives met the numerical thresholds in Annex D, was published in 2014 (UNEP/POPS/POPRC.10/INF/7/Rev.1). This assessment was a two-step process: I) prioritization to screen for those alternatives that had a potential to be POPs based on, bioaccumulation (B) and persistence (P) (i.e., criteria (b) and (c) of Annex D to the Convention, and ii) a more detailed assessment of the POPs characteristics of alternatives that had been identified as having a potential to be POPs. It should be noted that the assessment of POPs characteristics as part of this report is not intended to imply that the POPRC has fully considered whether alternative chemicals have met the Annex D criteria.

365. A 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 was published in 2012 (UNEP/POPS/POPRC.8/INF/17/Rev.1) based on the terms of reference and the outline of the technical paper agreed by the Committee as contained in its decision POPRC-7/5 and in document (UNEP/POPS/POPRC.7/INF/22/Rev.1).

366. This paper provided an initial assessment of the risks, associated with identified alternatives, taking into account the characteristics of potential persistent organic pollutants as specified in Annex D to the Convention, of identified alternatives to PFOS and associated compounds. The assessment of POPs characteristics as part of the previous alternatives assessment report was not intended to imply that the POPRC has fully considered whether alternative chemicals have met the Annex D criteria.

367. A total of 58 alternatives to PFOS were identified. From these 54 substances were subject to prioritization, (with a further four transformation products which were not assessed). One substance was selected as category I (potential persistent organic pollutants<sup>154</sup>), 13 substances as category II (candidates for further assessment), 34 substances were category III (candidates for further assessment with limited data) and 6 substances were selected as category IV (not likely to fulfil the criteria on persistence and bioaccumulation in Annex D).

368. Of the 14 substances identified during the first screening assigned to category I and II, three of these substances, the pesticides, Chlorpyrifos, Cypermethrin, Deltamethrin, had previously been considered during the assessment of alternatives to endosulfan. (UNEP/POPS/POPRC.8/INF/13) and two fluorinated substances, 6:2 FMA (in category I) and 1-chloro-perfluorohexyl phosphonic acid (in category II), it was considered that very incomplete data would prevent a thorough assessment.

369. Factsheets of information for the remaining nine screened PFOS alternative were subsequently prepared following the assessment (UNEP/POPS/POPRC.10/INF/8/Rev.1). The factsheets provide an analysis on a screening level as to whether or not the identified alternatives to PFOS, its salts and PFOSF meet the numerical thresholds in

<sup>153</sup> See BAT/BEP Guidance for use of PFOS and related chemicals under the Stockholm Convention on POPs.

<sup>154</sup> Note, this is based on a consideration of P and B characteristics only

Annex D and the factsheets summarise the evidence base for the conclusions regarding whether Annex D criteria are met.

370. Depending on the category in which they had been placed in the prioritization step, the alternatives to PFOS were further assessed and consequently assigned to one of the four classes based on their likelihood to meet all the criteria in Annex D to the Convention. The four classes are as follows:

- (a) Class 1: Substances considered met all Annex D criteria;
- (b) Class 2: Substances considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data;
- (c) Class 3: Substances that are difficult for classification due to insufficient data;
- (d) Class 4: Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e).<sup>155</sup>

371. An overview of the substances and products assessed in the previous assessment is provided in Appendix 2 to this report, and the results from the previous alternatives assessment, carried out in UNEP/POPS/POPRC.10/INF/7/Rev.1 are provided in Appendix 2 to the present report. It was noted that the UNEP/POPS/POPRC.10/INF/7/Rev.1 assessment is only a first screening indicating the likelihood and not a definite classification of the substances concerning their POP characteristics.

372. The purpose of the assessment carried out in the present report is to provide an assessment of the potential POP characteristics of 'additional' alternatives to those previously screened and assessed, that have been identified, based on submission of information by Parties and others, since the previous report was published.

### 3.2 Selection of chemical alternatives for the assessment of POPs characteristics

373. It is noted that many of the alternative substances previously screened (see Appendix 2) are discussed in the sections on individual uses in Chapter 2, i.e., many of the substances identified as potential alternatives were screened for POPs characteristics in the previous assessment conducted in 2014. The result of the previous assessment is set out in Appendix 3 to the present report (annex to decision POPRC-10/4).

374. With reference to the discussion in Chapter 2, the more recent submissions of information from Parties and others<sup>156</sup> have not identified a significant number of 'new' alternative chemical substances, and where additional alternatives to those previously assessed have been identified, the majority of these are commercial products, where the chemical composition has not been divulged due to trade secrets. Therefore, the assessment has not been able to consider the full range of sectors covered by the existing SEs and APs and the alternatives for PFOS developed for these. The assessment in the present study is limited to a select few sectors, for which information on the chemical identify and composition of alternatives was more readily available.

375. It is noted that the pesticide Permethrin was previously screened for the report on the assessment of chemical alternatives to endosulfan. This assessment assigned Permethrin as "not likely to fulfil the criteria on persistence and bioaccumulation in Annex D".<sup>157</sup> However, it is noted that Annex III of UNEP/POPS/POPRC.6/INF/12 considered permethrin as bioaccumulative. Furthermore, the Joint Research Centre (JRC, 2018) included permethrin in its consideration of chemicals for the Watch List under the Water Framework Directive. It was concluded that permethrin is a good candidate substance for environmental quality standard (EQS) derivation and consideration as potential priority substance or inclusion on the watch list. Indeed, experts were split between inclusion in the priority substances list or in the Watch list. Therefore, Permethrin has been included in the screening for the current assessment.

376. In this assessment, the principal source of information was a review of the inputs provided by Parties and observers<sup>158</sup> and any literature/ additional information sources referenced therein; including company websites and safety data sheets.

377. In identifying alternatives to POPs, the list of alternatives should include not only alternative chemicals that can be used without major changes in products or processes in which they are used, but also innovative changes in the design of products, industrial processes and other practices using non-chemical alternatives.<sup>159</sup> These alternatives are not further considered in this report since the methodology used for the current assessment is applicable to chemical substances only and a comprehensive assessment of the suitability of non-chemical alternatives was beyond the resources and time available for its preparation of the current report.

<sup>155</sup> Category IV substances were automatically assigned to class 4.

<sup>156</sup> <http://chm.pops.int/tabid/6176/Default.aspx>.

<sup>157</sup> UNEP/POPS/POPRC.8/INF/28

<sup>158</sup> <http://chm.pops.int/tabid/6176/Default.aspx>.

<sup>159</sup> As indicated 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).

**Table 11 Overview of PFOS alternatives identified for screening and assessment for POPs characteristics**

Substance/Brand name	CAS No.	Applications
Amyl Acetate	628-63-7	Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)
Anisole	100-66-3	Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)
n-Butyl Acetate	123-86-4	Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)
Ethyl lactate	97-64-3	Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)
Methyl-3-methoxypropionate	3852-09-3	Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)
Propylene glycol methyl ether acetate	108-65-6	Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters)
Tri-tert-butyl phenyl phosphate	28777-70-0	Aviation hydraulic fluids
Tris(isobutylphenyl) phosphate	68937-40-6	Aviation hydraulic fluids
Fyrquel 220	55957-10-3	Aviation hydraulic fluids
Pydraul 50E	66594-31-8	Aviation hydraulic fluids
Pydraul 90E	6630-28-3	Aviation hydraulic fluids
Reofos 65	63848-94-2	Flame retardant
Reolube HYD46	107028-44-4	Aviation hydraulic fluids
Skydrol 500B-4	50815-84-4	Aviation hydraulic fluids
Skydrol LD-4	55962-27-1	Aviation hydraulic fluids
Cyclotriphosphazene	291-37-2	Aviation hydraulic fluids
1,2,3-Trichloropropane (TCP)	1330-78-5	Aviation hydraulic fluids
Trixylyl phosphate (TXP)	25155-23-1	Aviation hydraulic fluids
Diphenyl tolyl phosphate	26444-49-5	Aviation hydraulic fluids
Triphenyl phosphate	115-86-6	Aviation hydraulic fluids
Diphenyl isopropylphenyl phosphate	28108-99-8	Aviation hydraulic fluids
P-Tert-butylphenyl diphenyl phosphate	56803-37-3	Aviation hydraulic fluids
Dibutyl phenyl phosphate	2528-36-1	Aviation hydraulic fluids
Nonylphenyl diphenyl phosphate	38638-05-0	Aviation hydraulic fluids
Diphenyl-2-ethylhexyl phosphate	1241-94-7	Aviation hydraulic fluids
Isodecyldiphenylphosphate	29761-21-5	Aviation hydraulic fluids
Tributyl phosphate (TBP, TNBP)	126-73-8	Aviation hydraulic fluids
Isopropylphenyl phosphate	26967-76-0	Aviation hydraulic fluids
o-Tolyl phosphate (TOCP, TOTP)	78-30-8	Aviation hydraulic fluids
Oleylamine, ethoxylated	26635-93-8	Metal plating
Diethylene Glycol Monobutyl Ether / 2-(2-butoxyethoxy)-ethanol	112-34-5	Firefighting foams
Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)	70829-87-7	Firefighting foams ; Chemically driven oil production
Hexylene glycol / 2-methyl-2,4-pentanediol	107-41-5	Firefighting foams
Tris(2-hydroxyethyl)ammonium dodecylsulfate	139-96-8	Firefighting foams
1-propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts	61789-40-0	Firefighting foams

Substance/Brand name	CAS No.	Applications
alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl) C9-11 alkyl ethers, sodium salts	96130-61-9	Firefighting foams
1,2-ethandiol	107-21-1	Firefighting foams
Octylsulfate	142-31-4	Firefighting foams
Decylsulfate	142-87-0	Firefighting foams
Alkylpolyglycoside	68515-73-1	Firefighting foams
1-butoxy-2-propanol / Propylene glycol butyl ether / 3-Butoxy-2-propanol	5131-66-8	Firefighting foams
2-Butoxyethanol	111-76-2	Firefighting foams
Alcohols, C12-16	68855-56-1	Firefighting foams
Acephate	30560-19-1	Insecticides for control of red imported fire ants and termites
Carbaryl	63-25-2	Insecticides for control of red imported fire ants and termites
Cyfluthrin (Pyrethroid)	68359-37-5	Insecticides for control of red imported fire ants and termites
D-Limonene (citrus oil extract)	5989-27-5	Insecticides for control of red imported fire ants and termites
Fenvalerate	51630-58-1	Insecticides for control of red imported fire ants and termites
Metaflumizone	139968-49-3	Insecticides for control of red imported fire ants and termites
Methoprene	40596-69-8	Insecticides for control of red imported fire ants and termites
Permethrin (Pyrethroid)	52645-53-1	Insecticides for control of red imported fire ants and termites

378. In total, 51 'additional' alternatives were identified for assessment (see Table 11 above). To avoid duplication of information, none of the alternatives identified and assessed in the previous report have been assessed in the present study. While some Parties have suggested the reclassification of some of the substances assessed in the previous report, the present study does not reassess previous alternatives.

379. The alternatives to PFOS, its salts and PFOSF assessed in this study, are characterised as 'commercial products' used in the applications listed as specific exemptions (SE) and acceptable purposes (AP) in Annex B to the Convention. The corresponding commercial uses of these alternatives, i.e. the applicable SE or AP, are listed in Table 11. As discussed above, the assessment of alternatives in this study focussed on a select number of sectors, for which information was more readily available. Specifically, these were, Semi-conductors (Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters); Aviation hydraulic fluids and/or flame retardants; Metal plating; Firefighting foams; and Insecticides for control of red imported fire ants and termites.

380. As noted in the previous assessment report, Chemical Abstract Service (CAS) numbers are not always available for the alternative substances/commercial products identified. It is noted above that many of the alternative products known to replace PFOS-containing products in many sectors are known only by their commercial brand name, with limited publicly available information available on their chemical composition. This is an impediment for obtaining information about these alternatives as CAS numbers are essential for retrieving substance-specific information from the majority of databases, and for carrying out modelling. Therefore, due to the time constraints of carrying out this assessment, alternatives with known chemical composition / CAS numbers were prioritised for inclusion.

### 3.3 Methodology for the assessment of POPs characteristics

381. The methodology for the assessment of alternatives to PFOS, its salts and PFOSF, carried out in this report, broadly follows the methodology previously described in Chapters 3 and 4 of the previous alternatives assessment

report.<sup>160</sup> This previous assessment was undertaken by applying and adapting the methodology previously used by the Committee in the assessment of alternatives to endosulfan.<sup>161</sup> An overview of the methodology used is described here.

382. The methodology consists of a two-step screening process. In the first step, the alternatives to PFOS were subject to prioritization to screen for those alternatives that had a potential to be POPs and to identify those that were unlikely to be POP substances. To prioritize the alternatives, bioaccumulation (B) and persistence (P) (i.e., criteria (c) and (b) of Annex D to the Convention) were used. The second step consists of a more detailed assessment of the POPs characteristics of alternatives that had been identified as having a potential to be POPs. Substances that had been identified as unlikely to be POP substances were not further analysed in the second step. In the assessment step, alternatives to PFOS were classified according to their likelihood to meet all the criteria of Annex D.

### 3.3.1. Step 1: Initial screening

383. The initial screening was carried out using, in part, the methodology previously described in UNEP/POPS/POPRC.10/INF/7/Rev.1. Accordingly, the screening of each chemical was made to address bioaccumulation (B) and persistence (P) (i.e., criteria (b) and (c) of Annex D to the Convention). The two criteria were used in combination to reduce the uncertainty in selecting for substances that have a potential to be POPs.

384. Due to the time constraints of carrying out the assessment, the screening step was carried out using the PB-score tool, developed at RIVM<sup>162</sup>. As described previously, this model uses QSAR estimations for screening on persistence and bioaccumulation and generates a score, which reflects the chance that a certain substance is persistent in the environment, and bioaccumulating. It is developed as a first tier in the evaluation of PBT and POP substances. As noted in the previous report, there are a number of potential factors and limitations that may impact the quality and validity of results generated from this screening tool.

385. The overall PB-score varies between 0 and 2. Cut-off values complying with the formal screening criteria in Annex D are  $\geq 0.5$  for the P-score as well as the B-score. Thus, substances with a PB score of  $\geq 1.5$  will have individual P or B-scores of 0.5 or higher and comply with both criteria, whereas substances with a PB-score between 1 and 1.5 might fulfil both criteria or not.

386. In the next step, the collected numerical data were compared to benchmarks/cut off values in order to classify the substances within four categories. Cut off values were selected for the four categories to allow a ranking from a higher likelihood to be a POP (screening category I) to a lower likelihood to be a POP (screening category IV).

387. As described, in UNEP/POPS/POPRC.10/INF/7/Rev.1, the following categories and cut-off values for the screening step are as follows:

#### **Screening category I: Potential persistent organic pollutants**

**Cut-offs:** bioaccumulation: experimental BCF > 5000 and/or experimental log  $K_{ow}$  > 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).

#### **Screening category II: Candidates for further assessment**

**Cut-offs:** bioaccumulation: experimental BCF > 1000 and/or experimental log  $K_{ow}$  > 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). The reason for the selection of a BCF > 1000 is that the Annex D criteria for bioaccumulation includes the consideration of other reasons for concern.

#### **Screening category III: Candidates for further assessment with limited data**

**Cut-offs:** bioaccumulation: no experimental data for BCF and log  $K_{ow}$  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  $K_{ow}$  < 4.0 (for non-fluorinated substances) and BMF/TMF values  $\leq 0.5$  (for fluorinated substances) and/or persistence: half-life

<sup>160</sup> UNEP/POPS/POPRC.10/INF/7/Rev.1

<sup>161</sup> UNEP/POPS/POPRC.8/INF/28.

<sup>162</sup> see Rorije et al. (2011) Identifying potential POP and PBT substances : Development of a new Persistence/Bioaccumulation-score. <https://www.rivm.nl/bibliotheek/rapporten/601356001.html>

(experimental) in water less than 2 month ( 60 days), in soil less than six months (180 days) and sediment less than six months (180 days).

### 3.3.2. Step 2: More detailed assessment of alternatives

388. As described in the previous PFOS alternatives assessment<sup>163</sup> (see Section 3.1), the screened alternatives consequently assigned to one of the four classes based on their likelihood to meet all the criteria in Annex D to the Convention (see Section 3.1).

389. The following approach was used for the assessment of substances in each category:

- (a) Category I and II: an assessment of POPs characteristics and other hazard indicators (toxicity and ecotoxicity) is carried out. A fact sheet of information compiled on the properties selected for assessment when feasible;
- (b) Category III: due to the time constraints of conducting the alternatives assessment, all substances allocated to Category III are automatically **assigned to class 3**, as it is indicated that data is insufficient to complete a detailed assessment;
- (c) Category IV: no further action, substances are **assigned to class 4**.

390. In order to assess selected alternative substances for PFOS and related substances within the given time frame and resources, preference was given to governmental reports, relevant databases and evaluated peer review data. When information was not available from such sources, a search in the primary literature was carried out, where recent sources were consulted. The following sources were used:

- (a) ESIS: <http://esis.jrc.ec.europa.eu/index.php?PGM=cla>
  - (i) C&L (Classification and Labelling, Annex VI to EU CLP Regulation 1272/2008)
  - (ii) Risk Assessment Reports (RAR)
- (b) CLP inventory (for endpoints not covered by ESIS): <http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database>
- (c) EFSA: <http://www.efsa.europa.eu/en/search.htm>
- (d) EU Endocrine Disruption Database:  
[http://ec.europa.eu/environment/chemicals/international\\_conventions/index\\_en.htm](http://ec.europa.eu/environment/chemicals/international_conventions/index_en.htm);
- (e) WHO/EPS: <http://www.who.int/publications/en/>
- (f) EPI SUITE: <http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm>
- (g) IARC: <http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php>
- (h) International limit values (working place): [http://limitvalue.ifa.dguv.de/Webform\\_gw.aspx](http://limitvalue.ifa.dguv.de/Webform_gw.aspx)
- (i) ECETOC: <http://www.ecetoc.org/index.phpECOTOX>
- (j) TOXNET: <http://toxnet.nlm.nih.gov/index.html>
- (k) ECHA information on chemicals: <http://echa.europa.eu/nl/information-on-chemicals>
- (l) Primary literature identified through Scopus: <http://www.scopus.com/>
- (m) MacKay, D. et al. (2006) Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals

391. The following priorities were considered:

- (a) **Substance identity:** CAS no, IUPAC name, molecular weight, chemical structure, chemical group;
- (b) **Physical-chemical properties:** vapour pressure, water solubility, partition coefficient;
  - (i) n-octanol/water (log value), partition coefficient air/water (log value), partition coefficient;
  - (ii) partition coefficient air/octanol (log value), Henry's Law Constant;
- (c) **Bioaccumulation:** experimental BCF and log Kow data (Annex D (c) (i) criterion). For fluorinated substances, data on biomagnification (BMF or TMF). The evidence for assessment was considered reliable when at least two data points were available;

<sup>163</sup> UNEP/POPS/POPRC.10/INF/7/Rev.1

(d) **Persistence:** experimental data when available; modelling data on half-life in water, soil and sediment (Annex D (b) (i) criterion). The evidence for assessment was considered reliable when at least two data points were available;

(e) **Long-range transport:** Gather information on experimental and/or estimated half-life data in air (EpiSuite) (Annex D (d) (ii) criterion);

(f) **Ecotoxicity** (Annex D (e) criterion): GHS (global harmonization system) classification<sup>164</sup> (only European harmonized classifications were considered<sup>165</sup>) on aquatic toxicity, rated as follows:

Classification	Hazard statement	Ecotoxicity level	Acute effect conc. [mg/L]	Chronic effect conc. [mg/L]
Aquatic chronic 1	H410	Severe	1	0,1
Aquatic chronic 2	H411	High	>1-10	> 0,1 - 1
Aquatic chronic 3	H412	Moderate	>10-100	>1-10
Aquatic chronic 4 Aquatic acute 1	H413	Low	>100	>10

(g) Toxicity (Annex D (e) criterion): GHS classification<sup>33</sup> (only harmonized classifications were considered) on toxicity on humans, rated as follows:

Classification	Hazard statement	Toxicity level
Muta 1A/1B Carc. 1A/1B Repro. 1A/1B Carc 2+STOT RE Skin corr	H340 H350 H360	Severe
Muta 2. Carc 2. Repro 2. Skin irrit. Resp. sens. STOT RE1	H341 H351 H361	High
STOT RE 2 Acute tox 1 Acute tox 2		Moderate
Acute tox 3 Acute tox 4		Low

392. Additionally, the following hazards were considered:

- (a) Acute toxicity;
- (b) Mutagenicity;
- (c) Carcinogenicity;
- (d) Toxicity for reproduction;
- (e) Neurotoxicity;
- (f) Immunotoxicity;

<sup>164</sup> [http://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs\\_rev04/English/ST-SG-AC10-30-Rev4e.pdf](http://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev04/English/ST-SG-AC10-30-Rev4e.pdf)

<sup>165</sup> Based on the harmonised classifications specified in Annex VI of Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures.

- (g) Endocrine disruption;
- (h) Mode of action;
- (i) Acceptable exposure levels.

### 3.4 Disclaimer, data limitation and uncertainties

393. It should be noted that, in assessing potential alternatives that are suitable substitutes for persistent organic pollutants (POPs), the criteria in paragraph 1 of Annex D to the Stockholm Convention on POPs should be taken into consideration to ensure that an alternative does not lead to the use of other chemicals that may be a POP. This report provides hazard-based information on potential alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) in a number of applications covered by existing Specific Exemptions or Acceptable Purposes. The results of assessment in this report are based on an analysis on a screening level as to whether or not the identified alternatives to PFOS meets the numerical thresholds in Annex D, but does not analyze monitoring data or other evidence as provided for in Annex D. It should also be noted that the assessment is not equivalent to the work undertaken by the Committee in examining proposals submitted by Parties for listing of chemicals under the Convention in accordance with paragraph 3 of Article 8 of the Convention.

394. Selection of the alternatives is described in section 3.3. This selection was made based on the information submitted by Parties and others and aims to build on the suite of substances assessed in the previous report (UNEP/POPS/POPRC.10/INF/7/Rev.1). A re-assessment of those alternatives previously screened and assessed, with a view to potential reclassification, has not been carried out in this report. The selection of alternative substances to assess is largely dependent on the availability of information of the chemical composition of commercially available products, which is often lacking. The assessment of the alternatives in this report should not be seen as a comprehensive and in-depth assessment of all available information as only a limited number of databases and a limited number of primary sources have been consulted.

395. Parties may use this report when choosing alternatives to PFOS, its salts and PFOSF as an initial source of information. It should be noted that substances which have been identified in this report as not likely to be a POP, may still exhibit hazardous characteristics. As indicated in the General guidance 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 in this report is carried out by Parties within their national framework of authorization before considering such substances as suitable alternatives.

## 3.5 Result of the assessment of POPs characteristics

### 3.5.2 Results of the screening of the alternatives to PFOS

396. Of the 51 alternatives to PFOS identified, 44 were chemical compounds, while seven were commercial products. 42 of the chemical compounds were subject to prioritization, with two substances (alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl) C9-11 alkyl ethers, sodium salts, and sodium p-perfluorous nonenoxybenzene sulfonate (OBS)) used in firefighting foams were not screened due lack of available information. Four substances were selected as screening category I, two substances as screening category II, six substances were screening category III and 31 substances were selected as screening category IV.

397. Additionally, while the following products were selected for screening: Fyrquel 220, Pydraul 50E, Pydraul 90E, Reofos 65, Reolube HYD46, Skydrol 500B-4, Skydrol LD-4; those were not classified in any of the above categories as the information on their chemical constituents was lacking. Those could be classified as a new category V "Substances and/or products that are difficult to classify due to unknown chemical composition".

398. The results of the screening assessment are set out below and the list of alternatives to PFOS with data for the P- and B-score of each substance is reported in the table in Appendix 4 to this report. A brief commentary of initial observations of these results is also provided below. It should be noted that the screening cut-off values described above have not been applied in a strict way in this assessment. For example, permethrin and methoprene had B-scores of 0.48 and 0.43 respectively. The flexible application of the screening cut-offs in this assessment meant that these substances were both taken forward for the detailed analysis, with particular consideration of their relatively high (>0.5) P scores. It has been argued that consideration of persistence is particularly significant in POPs screening as this can provide an indication as to the potential for non-reversible exposure for humans to these chemicals (McLachlan, 2018). McLachlan (2018) also note that bioconcentration in fish and biomagnification, the Annex D criteria primarily used to assess bioaccumulation, are of no relevance in the case of PFOA and PFOS. Furthermore, the authors noted that the reliance on tissue levels in humans or top predators as a substitute for bioaccumulation metrics can be problematic, as chemicals can be rapidly metabolized or excreted and still have adverse effects, therefore bioaccumulation will not necessarily be a requirement for adverse effects of chemicals in remote regions.

Taking these factors into consideration, the flexibility utilised in the interpretation B-values in this assessment is justified.

399. The substance sodium p-perfluorous nonenoxybenzene sulfonate (OBS) did not undergo screening using the RIVM tool due to uncertainties regarding its chemical structure. Upon further analysis, has been designated as screening category I on the basis of manual calculations of  $P=1.00$  and  $B=0.69$ , based on its similarity to other perfluorinated substances. It was considered that both the  $\log K_{ow}$  as well as the potential protein binding of the fluorinated tail contribute to the potential bioconcentration of this substance. If degradation occurs (predicted to be very slow) concerns could also exist regarding the breakdown products. Therefore, it has been taken forward for the more detailed assessment.

**Table 12 Results of the initial screening exercise.**

Screening categories	Substances
<b>Screening category I: potential persistent organic pollutants</b>	<ol style="list-style-type: none"> <li>1. Metaflumizone</li> <li>2. Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)<sup>166</sup></li> <li>3. Tolylyl phosphate (TOCP, TOTP)</li> <li>4. Tricresyl Phosphate (TCP)</li> </ol>
<b>Screening category II: candidates for further assessment</b>	<ol style="list-style-type: none"> <li>1. Methoprene</li> <li>2. Permethrin (Pyrethroid)</li> </ol>
<b>Screening category III: candidates for further assessment with limited data</b>	<ol style="list-style-type: none"> <li>1. Cyfluthrin (Pyrethroid)</li> <li>2. Diphenyl-2-ethylhexyl phosphate</li> <li>3. Diphenyl isopropylphenyl phosphate</li> <li>4. Fenvalerate</li> <li>5. P-Tert-butylphenyl diphenyl phosphate</li> <li>6. Trixylyl phosphate (TXP)</li> </ol>
<b>Screening category IV: not likely to fulfil the criteria on persistence and bioaccumulation in Annex D</b>	<ol style="list-style-type: none"> <li>1. Acephate</li> <li>2. Alcohols, C12-16</li> <li>3. Alkylpolyglycoside</li> <li>4. Amyl Acetate</li> <li>5. Anisole</li> <li>6. 2-Butoxyethanol</li> <li>7. 1-Butoxy-2-propanol / propylene glycol butyl ether / 3-Butoxy-2-propanol</li> <li>8. n-Butyl acetate</li> <li>9. Carbaryl</li> <li>10. Cyclotriphosphazene</li> <li>11. Decylsulfate</li> <li>12. Dibutyl phenyl phosphate</li> <li>13. Diethylene glycol monobutyl ether / 2-(2-butoxyethoxy)-ethanol</li> <li>14. Diphenyl tolylyl phosphate</li> <li>15. D-Limonene (citrus oil extract)</li> <li>16. 1,2-Ethandiol</li> <li>17. Ethyl lactate</li> <li>18. Hexylene glycol / 2-methyl-2,4-pentanediol Methyl-3-methoxypropionate</li> <li>19. Isodecyldiphenylphosphate</li> <li>20. Isopropylphenyl phosphate</li> <li>21. Methyl-3-methoxypropionate</li> <li>22. Nonylphenyl dipenyl phosphate</li> </ol>

<sup>166</sup> Categorisation based on a manual calculation of P and B values, strongly indicating high P (1.00) and B (0.69) characteristics.

	23. Octylsulfate 24. Oleylamine, ethoxylated 25. 1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts 26. Propylene glycol methyl ether acetate 27. Tributyl phosphate (TBP, TNBP) 28. Triphenyl phosphate 29. Tris(2-hydroxyethyl)ammonium dodecylsulfate 30. Tris(isobutylphenyl) phosphate 31. Tri-tert-butyl phenyl phosphate
<b>Screening category V: substances and products that are difficult to classify due to insufficient data (i.e. chemical composition or structure unknown)</b>	1. alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl) C9-11 alkyl ethers 2. Fyrquel 220 3. Pydraul 50E 4. Pydraul 90E 5. Reofos 65 6. Reolube HYD46 7. Skydrol 500B-4 8. Skydrol LD-4

### 3.5.3 Results of the detailed assessment of alternatives to PFOS

400. The results of the more detailed assessment of the six substances identified as Category I and II substances in the initial screening are set out below.

401. Detailed information compiled during the assessment from the sources listed above, is summarised in a fact sheet for each substance in Appendix 5. These tables provide an indication as to whether or not the alternative substance is considered likely to meet the criteria in Annex D to the Convention, but do not analyze monitoring data or other evidence in depth so failure to meet these criteria should not be taken as a determination that the alternative substance is not a POP. An overview of the POPs characteristics of the five substances assessed is provided in the table below.

402. It is noted that none of the chemical substances that underwent the detailed assessment, could be assigned to Class 1 as data was not sufficient enough to reasonably determine if all the Annex D criteria could be met. Three substances, Metaflumizone, Tricresyl Phosphate (TCP) and Tolyphosphate (TOCP, TOTP) were assigned to Class 2 as most of the criteria were potentially met, but data, particularly for LRT, was lacking. There is very little available information on the substance OBS, so no conclusions could be drawn regarding the Annex D criteria. This substance is assigned to Class 3. It is indicated from the assessment that the pesticides Permethrin and Methoprene will not meet all the Annex D criteria so are assigned to Class 4.

**Table 13 Results of the more detailed alternatives assessment**

Substance	Persistence Annex D 1 (b)	Bioaccumulation Annex D 1 (c)	LRT Annex D 1 (d)	Adverse effects: ecotoxicity Annex D 1 (e)	Adverse effects to human health Annex D 1 (e)	Assigned class
Metaflumizone	Yes	Insufficient data	Insufficient data	Yes	Yes	2
Tolyphosphate (TOCP, TOTP)	Yes	Yes	Insufficient data	Yes	Yes	2
Tricresyl Phosphate (TCP)	Yes	Yes	Insufficient data	Yes	Yes	2
Sodium p-perfluorooxypentylbenzene sulfonate (OBS)	Insufficient data	Insufficient data	Insufficient data	Insufficient data	Insufficient data	3

Substance	Persistence Annex D 1 (b)	Bioaccumulation Annex D 1 (c)	LRT Annex D 1 (d)	Adverse effects: ecotoxicity Annex D 1 (e)	Adverse effects to human health Annex D 1 (e)	Assigned class
Methoprene	Insufficient data	Yes	Insufficient data	Yes	No	4
Permethrin	Yes	No	Insufficient data	Yes	Insufficient data	4

### 3.6 Data availability and uncertainties

403. In the current assessment, the data collection and analysis for the identified alternatives was for the most part limited to the sources identified in Section X.X. Where data from these sources was limited, a wider search of available primary literature.

404. As discussed in the previous PFOS alternatives assessment<sup>167</sup> the availability data for alternatives to PFOS, which are in majority industrial chemicals, is relatively low and comparatively much lower than for pesticides. The number of peer-reviewed studies from primary literature that was available as second-line references was also limited for the assessed alternatives to PFOS. The conclusions on some of the alternatives may thus change when a more comprehensive literature search is performed, and/or more data become available. The scarcity of data on alternatives to PFOS has been one of the major limitations for the assessment.

405. The other key limitation for the alternatives assessment, is the lack of publicly available information on the chemical composition of many commercially available products, which have been identified as alternatives to PFOS-containing products, used in many sectors discussed in Section 2. Alternatives to PFOS were not reported for a number of applications listed in part I of Annex B to the Convention. This assessment has therefore only been able to cover a relatively small number of sectors, for which more information was available.

406. As noted in the previous assessment<sup>168</sup>, a comprehensive assessment of PFOS alternatives based on experimental data is preferable to using estimated data on persistence and bioaccumulation generated by modelling tools for all PFOS alternatives – ideally should be based on comprehensive assessment of experimental data. Due to the time constraints of the study, this was not feasible. In addition, one major limitation of this exercise was the scarcity of data in public databases about many of the alternatives.

407. As noted previously, for fluorinated substances, no data on BMF or TMF was available from the sources consulted. It should be noted that the bioaccumulation potential of fluorinated chemicals is overestimated in the current RIVM model which uses Kowwin 1.67. The underlying US-EPA models, such as Kowwin1.68, have been updated for the fluorinated substances recently. This new models generate lower log Kow values than the previous version. As an example, PFOA has received a log Kow of 6.3 in our tool using Kowwin v1.67. If you now run EPISuite you get an estimate of 4.81. With the "old" log Kow the substance has a B-score of 0.87, with the new log Kow being 0.56. The PB score screening is conservative, as it is considered preferable to end up with false positives than with false negatives. Those false positives should be screened out as a result of more in depth assessment based on experimental data whenever available.

### 3.7 Conclusions of the screening assessment on persistent organic pollutants characteristics of alternatives to PFOS

408. Based on the results of the screening assessment the conclusions below are suggested. However, the assessment provides only an indication as to whether or not the alternative substances meet the numerical threshold in Annex D to the Convention and does not analyse monitoring data or other evidence as provided for in Annex D, so failure to meet the thresholds should not be taken as a determination that the alternative substance is not a POP. Furthermore, this work is only a first screening indicating the likelihood and not a definite classification of the substances concerning their POP characteristics.

409. In summary, 51 'additional' alternatives to PFOS to the previous assessment, were analysed following a methodology previously used in the assessment of alternatives to both endosulfan and PFOS. There were no substances identified as being likely to meet all the Annex D criteria. Metaflumizone, Tricresyl Phosphate (TCP) and Toly Phosphate (TOCP, TOTP) were noted as meeting most of the criteria but remained undetermined due to equivocal or insufficient data. Six substances are noted as being difficult for classification due to insufficient data. A

<sup>167</sup> UNEP/POPS/POPRC.10/INF/7/Rev.1

<sup>168</sup> UNEP/POPS/POPRC.10/INF/7/Rev.1.

further 33 substances were classified as unlikely to be POPs. Additionally, seven alternative commercial products were unable to undergo a full assessment due to a lack of information on their chemical composition.

***Class 1: Substances likely all Annex D criteria***

<i>0 substances</i>	
CAS No	Substance
None	none

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

<i>3 substances</i>	
CAS No	Substance
139968-49-3	Metaflumizone
78-30-8	o-Tolyl phosphate (TOCP, TOTP)
1330-78-5	Tricresyl Phosphate (TCP)

***Class 3: Substances that are difficult for classification due to insufficient data***

<i>7 substances</i>	
CAS No	Substance
70829-87-7	Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)
1241-94-7	Diphenyl-2-ethylhexyl phosphate
28108-99-8	Diphenyl isopropylphenyl phosphate
51630-58-1	Fenvalerate
56803-37-3	P-Tert-butylphenyl diphenyl phosphate
25155-23-1	Trixylyl phosphate (TXP)
68359-37-5	Cyfluthrin (Pyrethroid)

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

It should be noted that the following substances, which are not likely to be a POP, may exhibit hazardous characteristics (e.g. mutagenicity, carcinogenicity, reproductive and developmental toxicity, endocrine disruption, immune suppression or neurotoxicity) that should be assessed by Parties before considering such substances as a suitable alternative.

<i>33 substances</i>	
CAS No	Substance
30560-19-1	Acephate
68855-56-1	Alcohols, C12-16
68515-73-1	Alkylpolyglycoside
628-63-7	Amyl Acetate
100-66-3	Anisole
111-76-2	2-Butoxyethanol
123-86-4	n-Butyl acetate
5131-66-8	1-Butoxy-2-propanol / propylene glycol butyl ether / 3-Butoxy-2-propanol
63-25-2	Carbaryl
291-37-2	Cycltriphosphazene

142-87-0	Decylsulfate
2528-36-1	Dibutyl phenyl phosphate
112-34-5	Diethylene glycol monobutyl ether / 2-(2-butoxyethoxy)-ethanol
26444-49-5	Diphenyl tolyl phosphate
5989-27-5	D-Limonene (citrus oil extract)
107-21-1	1,2-Ethandiol
97-64-3	Ethyl lactate
107-41-5	Hexylene glycol / 2-methyl-2,4-pentanediol
29761-21-5	Isodecyldiphenylphosphate
26967-76-0	Isopropylphenyl phosphate
40596-69-8	Methoprene
3852-09-3	Methyl-3-methoxypropionate
38638-05-0	Nonylphenyl dipenyl phosphate
142-31-4	Octylsulfate
26635-93-8	Oleylamine, ethoxylated
52645-53-1	Permethrin
61789-40-0	1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts
108-65-6	Propylene glycol methyl ether acetate
126-73-8	Tributyl phosphate (TBP, TNBP)
115-86-6	Triphenyl phosphate
139-96-8	Tris(2-hydroxyethyl)ammonium dodecylsulfate
68937-40-6	Tris(isobutylphenyl) phosphate
28777-70-0	Tri-tert-butyl phenyl phosphate

*Products, for which an assessment of POPs criteria could not be carried out due to insufficient data on their chemical composition or structure.*

<i>8 products</i>	
<b>CAS No</b>	<b>Substance</b>
96130-61-9	alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl) C9-11 alkyl ethers
55957-10-3	Fyrquel 220,
66594-31-8	Pydraul 50E,
6630-28-3	Pydraul 90E,
63848-94-2	Reofos 65,
107028-44-4	Reolube HYD46,
50815-84-4	Skydrol 500B-4,
55962-27-1	Skydrol LD-4

## 4 Conclusions and recommendations

410. An overall summary of the availability, suitability and implementation of the identified alternatives to PFOS and related compounds, the identified information gaps and limitations, and an assessment for the need to maintain an acceptable purpose/specific exemption for these uses is provided in the table below.

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
Photo imaging	AP	Chemical: Commercial products available but trade names and chemical formulations not identified; level of availability and accessibility is unclear.  Non-chemical: rapid shift towards digital technology for photo-imaging.	Some chemical alternatives are technically feasible, but development is associated with high R&D costs.  Silicone products and siloxane compounds, are in practice not usable in practice.  Digital imaging (e.g. in medical applications) is considered the most effective and viable alternative.	I&P Europe Imaging & Printing Association forecast a total phase out by the end of 2019.  Parties report rapidly declining volumes of PFOS use in this sector.  Indicated there is a rapid switch to digital imaging in medical applications, including in developing countries.	<ul style="list-style-type: none"> <li>No specific information has been provided for chemical alternatives in terms of their availability, accessibility, technical and economic feasibility, environmental and health effects;</li> <li>The trade names and chemical composition of alternatives in this sector are not available;</li> <li>There are considerable data gaps relating to the technical feasibility of siloxane compounds used on the market for photographic application;</li> <li>There are information gaps around the levels of PFOS still used globally for this application.</li> </ul>	No

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
Photo-resist and anti-reflective coatings for semi-conductors; etching agent for compound semi-conductors and ceramic filters	AP	Commercially available products for photo-resist, ARCs and etching agent, and suppliers identified.  Dry etching (including plasma etching) are commercially available in place of wet etching processes, suppliers identified.	Industry indicate potential difficulties in developing chemical alternative to PFOS  Not possible to definitively determine if it is feasible to replace PFOS and related compounds technically, due to a lack of information about the alternatives.  The reported successful phase out by industry would suggest technical challenges have been addressed and technically and economically viable alternatives have been developed.	Semiconductor industry globally has successfully completed the phase-out of PFOS.  Rapid decline in PFOS use in this sector is reported by Parties (e.g. EU) and companies (e.g. IBM).  Attributed more strongly to new photolithography technologies, use of less photo-resist per wafer, and the new photo-resist formulations containing lower concentrations of PFOS.	<ul style="list-style-type: none"> <li>Information on the type and chemical composition of alternatives is lacking (often based on confidential business information).</li> <li>Industry claims that they need more time to develop a full range of qualitatively comparable alternatives.</li> </ul>	No
Aviation hydraulic fluids	AP	Very limited knowledge of alternative substances and technology is available.  Commercially available products, for example containing phosphate esters exist and are on the market through a range of different products; trade names known.	Not possible to make a detailed assessment of the technical or economic feasibility of alternatives due to the very limited information available, largely due to confidentiality of trade secret information.	EU and Norway withdrew their notification for acceptable purposes for this use in 2017 and Canada note PFOS use in aviation fluids is prohibited.  More detailed information on the implementation of PFOS alternatives has not been made available.	<ul style="list-style-type: none"> <li>Specific chemical composition of different aviation hydraulic fluids is unknown.</li> <li>Lack of data available to assess technical and economic feasibility, environmental and health impacts etc</li> <li>Lack of information on the volumes of PFOS still in use for this sector.</li> </ul>	No

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
Metal-plating	AP* / SE**	<p>Wide range of short-chain fluorinated (e.g. 6:2 FTS) and fluorine-free alternatives are commercially available; chemical composition known, and trade names identified in many cases. Fluorine-free are still the subject of R&amp;D activity and are less readily available.</p> <p>A number of process-based approaches to replace PFOS are also identified and are commercially available e.g. High Velocity Oxygen Fuel (HVOF) process.</p> <p>Cr(III) plating is available as an alternative to Cr(VI) plating for some decorative plating applications.</p>	<p>PFOS-free alternatives are considered to be less stable and durable in the chrome bath than PFOS due several limitations, including the potential for degradation to hazardous products in the environment.</p> <p>Use of identified alternatives in a closed loop process may be more problematic due to potential issues with preventing release to the environment.</p> <p>Overall, the use of fluorine-free alternative substances is not considered economically viable for all applications and should be considered on a case-by-case basis.</p>	<p>Use of chromium (III) instead of chromium (VI) for certain decorative chrome plating processes has made PFOS use in decorative plating obsolete.</p> <p>A continuous need for PFOS use for hard metal plating is indicated by some Parties, while others have indicated the use of PFOS is either declining or has been completely phased out, indicating the viability and feasibility of alternatives.</p>	<ul style="list-style-type: none"> <li>Lack of harmonised definition of 'closed loop' process.</li> <li>Information is lacking regarding the processes suitable for use as alternatives, as well as processes where they cannot be used and why</li> <li>Require a more detailed understanding of the degradation products of potential alternatives to fully establish the environmental performance of different alternatives.</li> <li>Knowledge gaps concerning new novel plating practices, including details of the processes themselves, chemicals used, best practices and levels of market acceptance.</li> </ul>	<p>No</p> <p>Conversion from AP to SE*</p>

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
Certain medical devices	AP	<p>Very little information on the availability of potential alternatives in this sector.</p> <p>PFBS may be used in as a dispersant of contrast agents in ETFE layers for radio-opaque catheters, but no information of specific suppliers or product names available.</p> <p>No information available on the specific composition of alternatives.</p>	<p>Very little information on the technical feasibility or the economic viability of potential alternatives in this sector.</p> <p>Considered to be technically possible to produce PFOS-free CCD filters for use in new equipment but no further information provided.</p> <p>Use of chlorodifluoromethane in ETFE synthesis is problematic due to environmental implications and requirement to phase this substance out.</p>	<p>Only three Parties currently maintain notifications for use of PFOS for this acceptable purpose (China, Japan and Vietnam), suggesting that PFOS-free medical devices are implemented in most other parts of the world.</p> <p>In Japan, PFOS was banned to manufacture and use except for the use of research and development in April 2018.</p> <p>The status of phasing out PFOS use for this acceptable purpose in China and Vietnam is unclear.</p>	<ul style="list-style-type: none"> <li>• Current levels of use/continued need for PFOS in Japan, China, Vietnam and development of alternatives is unclear.</li> <li>• No recent information has been provided to update the status of proposed phase-out of PFOS in Japan.</li> <li>• The steps in place to control the potential release chlorodifluoromethane in the production of ETFE are unclear.</li> <li>• No information available for alternatives to PFOS for use in radio-opaque ETFE or certain in-vitro diagnostic devices.</li> </ul>	No

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
Fire-fighting foam	AP	<p>The industry standard for fire-fighting foams is rapidly switching from C<sub>8</sub> fluorinated compounds towards the short-chained PFAS and fluorinated telomers.</p> <p>Large number of alternative fluorinated and fluorine-free substances are available on the commercial market, with trade names and chemical composition known in some cases. Many products available for which trade names are known but chemical formulation is not – due to trade secrets.</p> <p>Alternative processes/practices have also been developed to minimise the release of PFOS from certain applications e.g. training operations.</p>	<p>Alternative foam formulations, both fluorinated and fluorine-free are shown to be technically and economically viable for a number of applications.</p> <p>PFOS-free alternatives have been shown to meet required fire safety standards, however there is some variability between test studies and some discrepancy noted in the relative performance reported for fluorinated and fluorine-free foams.</p> <p>Alternative foams (based both on fluorinated and fluorine-free chemistry) should not be considered direct ‘drop in’ replacements for all required uses. The compliance with fire safety standards and the compatibility with existing application methods will need to be considered on a case-by-case basis or different specific applications.</p>	<p>The use of non-PFOS containing foams now widespread across Europe, North America and Australia.</p> <p>Available information from Parties and industry indicates use of PFOS in this sector is declining rapidly.</p> <p>Industry indicate that most manufacturers have transitioned to only short-chain (C<sub>6</sub>) fluorosurfactant foams fluorine-free foams, and these meet the required standards.</p>	<ul style="list-style-type: none"> <li>• More information needed on the capabilities and limitations of non-fluorinated alternatives; continued R&amp;D effort required to improve the performance and capability.</li> <li>• Lack of available information in the composition of commercial fire-fighting foams.</li> <li>• Assessment and full screening of the toxicological properties of newly identified alternatives against POPs criteria, where data is available.</li> </ul>	<p>No</p> <p>Conversion from AP to SE</p>

<p>Insect baits for control of leaf-cutting ants</p>	<p>AP</p>	<p>Wide range of commercially available alternatives (pesticides) on the market; techniques for application (e.g. dry powder formulation) have been developed.</p> <p>Non-chemical (mechanical, cultural, and biological) control methods have been developed but are not fully commercialised or available in all locations.</p>	<p>Sulfluramid is considered to be the only active ingredient registered for the control of leaf-cutting ants, efficient for all species in all settings, that fulfils all of the technical criteria.</p> <p>BAT/BEP guidance indicates in general, chemical control with toxic baits containing sulfluramid seems often more practical, economical and operational to control the pests.</p> <p>BAT/BEP guidance states that “alternative technologies are only effective and efficient in specific situations”; notes there are some specific applications for which alternative substances/application methods are considered best practice, but limitations mean there is no single approach that can replicate the technical efficiency of sulfluramid.</p> <p>A number of promising biological and physical control methods are outlined. The currently level of implementation of these techniques is unknown. It is not currently clear whether the technical effectiveness in terms of ant control, can be appropriately replicated using these techniques and further research is required to demonstrate their operational feasibility.</p>	<p>The data provided by Brazil on levels of production, use and export of sulfluramid suggest there has not been a significant switch to any alternative substances or techniques for this acceptable purpose.</p> <p>Shown to meet required fire safety standards, however there is some variability between test studies and some discrepancy noted in the relative performance reported for fluorinated and fluorine-free foams.</p> <p>Alternative foams (based both on fluorinated and fluorine-free chemistry) should be considered direct ‘drop in’ replacements. The compliance with fire safety standards and the compatibility with existing application methods will need to be considered on a case-by-case basis or different specific applications.</p>	<ul style="list-style-type: none"> <li>• Further scientific studies and research should be undertaken to further reduce and eliminate the use of sulfluramide in the future.</li> <li>• In particular – demonstration of non-chemical measures – biological control measures in field tests to develop and demonstrate feasibility as a widespread control measure.</li> <li>• Data on conversion rate of sulfluramid to PFOS under natural conditions</li> </ul>	<p>Yes</p>
<p>Photo masks</p>	<p>SE</p>	<p>Information on alternatives is available but chemical identify, properties, and trade names and producers were not identified</p>	<p>According to industry information this use has been eliminated.</p>	<p>Industry has largely phased out the use of PFOS from this use, with China the only party maintaining a notification for this specific exemption.</p>	<ul style="list-style-type: none"> <li>• Very little information on the specific identity, technical or economic feasibility or implementation of alternatives, either chemical or non-chemical (process-based).</li> <li>• No data on continued level of use or level of need for this use in</li> </ul>	<p>No</p>

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
					China, or estimated timescale for a phase-out.	
Electric and electronic parts for some colour printers and colour copy machines	SE	Alternatives are available  Specific identities of replacements or substitutes for PFOS, PFOS-related chemicals and mixtures are not publicly available due to trade secrets restrictions.	No information available  PFOS-related chemicals are no longer used on colour printers and colour copy machines.	China is the only Party with a registration for this specific exemption.  Indicates that PFOS for these uses has been phased out everywhere else in favour of viable alternatives	(a) There is a lack of information available on the chemical identify and properties, trade names, producers, technical feasibility or environmental impacts of PFOS alternatives in this sector.	No
Insecticides for control of red imported fire ants and termites	SE	Alternative substances and (non-chemical) technologies to sulfluramid are commercially available on the market and have been implemented globally.  Biological controls have also been developed but are not fully developed commercially.	BAT/BEP guidance states that 'alternative substances to sulfluramid should be used to control RIFA effectively'	China is the only Party maintaining a registration for a specific exemption fort this use, with manufacture and use ceasing for this application in USA and Europe.  This suggests that viable alternatives are readily available and have been implemented everywhere else in the world	<ul style="list-style-type: none"> <li>Information on levels of use and need for continued use in China is lacking</li> <li>A number of chemical alternatives listed in Table 10 have not been previously screened for POPs criteria in previous studies;</li> <li>Limited information is available on the effectiveness of chemical methods (i.e. biological controls) and consistency of these methods.</li> </ul>	No

Measure	AP/SE	Availability	Suitability	Implementation	Data gaps/ limitations	Specific exemption/ acceptable purpose should be retained?
		<i>Commercial availability on the market; geographic, legal or other limiting factors.</i>	<i>Technically feasibility, economic viability, cost-effectiveness</i>	<i>Trends in use of PFOS and related compounds, extent to which alternatives as already used.</i>	<i>Key areas where information is lacking</i>	<i>Yes / No / Insufficient information</i>
Chemically driven oil production	SE	Information on chemical identity/properties and trade names/producers is available but quite limited.  Chemical alternatives to PFOS have been identified and it is indicated these are readily available, but limited information available on trade names/suppliers.	BAP/BEP guidance states that 'non-PFOS-related compounds should be used for this application'.  The BAP/BEP guidance document also notes that 'oil and gas production were reportedly carried out without the use of PFOS in other countries, including developing countries, thus indicating the existence of alternative processes that did not require PFOS'	Use of PFOS-related compounds in this sector is only reported in China, with indication it has been phased out in favour of alternatives everywhere else.  Levels of PFOS still used, and the necessity of its continued use in China are unclear.	<ul style="list-style-type: none"> <li>Available information on the relative availability, technical and economic feasibility, environmental viability and implementation of identified alternatives is lacking;</li> <li>Very few products on the market have been identified</li> </ul>	No
Carpets, leather and apparel, textiles and upholstery, paper and packaging, coatings and coating additives, rubber and plastics	SE***	Range of commercial products are widely available on the market and suppliers are identified for these uses, with some knowledge of the substances involved but limited understanding of precise chemical formulations.  Includes both fluorinated and non-fluorinated products.	Alternatives proven to be technically feasible and economically viable in most cases and approved for use by relevant authorities.	No existing Parties registered for specific exemptions for production or use in these sectors. It is indicated that alternatives to PFOS in most uses are widely available and technically viable and have been implemented globally.	<ul style="list-style-type: none"> <li>Carpets and textiles – information required on alternatives used that provide dirt and stain replant properties as it is indicated that the required functionality is not currently provided</li> </ul>	Specific exemption already expired.  No further registrations should be accepted.

\*Hard metal plating (closed loop process only) ; \*\* Hard metal and decorative plating ; \*\*\* SE has expired

## 5 References

### Information input from Parties and others:

- Brazil (2018) Information submitted, February 2018 (see Appendix 1)
- Canada (2018) Information submitted, February 2018 (see Appendix 1)
- EU (2018) Information submitted, February 2018 (see Appendix 1)
- FluoroCouncil (2018) Information submitted, February 2018 (see Appendix 1)
- Germany (2018) Information submitted, February 2018 (see Appendix 1)
- I&P Europe, (2018) Information submitted, February 2018 (see Appendix 1)
- IPEN (2018) Information submitted, February 2018 (see Appendix 1)
- Netherlands (2018) Information submitted, February 2018 (see Appendix 1)
- Poland (2018) Information submitted, February 2018 (see Appendix 1)
- SIA (2018) Information submitted, February 2018 (see Appendix 1)
- ZVO(2018) Information submitted, February 2018 (see Appendix 1)

### POPs Review Committee and related documents:

- Decision 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.
- UNEP/POPS/POPRC.10/INF/7/Rev.1: Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride.
- UNEP/POPS/POPRC.10/INF/8/Rev.1: Factsheets on alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride.
- UNEP/POPS/COP.7/INF/11: Report for the evaluation of information on perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride.
- Decision POPRC-8/8: Perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals in open applications.
- 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.
- UNEP/POPS/POPRC.12/INF/15/Rev.1: Consolidated guidance on alternatives to PFOS and its related chemicals.
- 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 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 (2017).
- UNEP/POPS/POPRC.13/7/Add.2: Risk management evaluation on pentadecafluorooctanoic acid (CAS No: 335-67-1, PFOA, perfluorooctanoic acid), its salts and PFOA-related compounds.
- UNEP/POPS/POPRC.8/INF/12: Report on the assessment of chemical alternatives to endosulfan and DDT.

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## Appendix 1: Overview of information provided by Parties and observers

Submitter	Title	Date
<b>Parties</b>		
Brazil	Form	9 Feb 2018
Canada	Form	15 Feb 2018
Canada	Chu et al. 2018	15 Feb 2018
Canada	D'Agostino and Mabury 2018	15 Feb 2018
Canada	Gobelius et al. 2017	15 Feb 2018
Canada	Hermann et al. 2018	15 Feb 2018
Canada	Letcher et al. 2018	15 Feb 2018
Canada	Government of Canada, 2013. Second Report on Human Biomonitoring of Environmental Chemicals in Canada: Results of the Canadian Health Measures Survey Cycle 2 (2009-2011) <sup>169</sup> .	15 Feb 2018
European Union	Assessment of the continued need for PFOS, Salts of PFOS and PFOS-F	16 Feb 2018
Germany	Form	16 Feb 2018
Japan	Form	14 Feb 2018
Poland	Form	16 Feb 2018
United Kingdom	Form	15 Feb 2018
<b>Observers</b>		
Leaf-Cutting Ant Baits Industries Association (ABRAISCA)	Form	15 Feb 2018
Fire Fighting Foam Coalition	Form	15 Feb 2018
FluoroCouncil	Form	14 Feb 2018
Galvano Röhrig GmbH	Form	13 Feb 2018
I&P Europe	Information	15 Feb 2018
International POPs Elimination Network (IPEN)	Information	22 Feb 2018
Pesticide Action Network (PAN)	Form	15 Feb 2018
PAN	Communication	15 Feb 2018
PAN	Photo of atratex label	15 Feb 2018
PAN	Photo of atratex purchased in Curitiba	15 Feb 2018
PAN	Photo of store supplying atratex	15 Feb 2018
Semiconductor Industry Association	Information	15 Feb 2018
Zentralverband Oberflächentechnik (ZVO)	Form	15 Feb 2018

<sup>169</sup> <https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/environmental-contaminants/second-report-human-biomonitoring-environmental-chemicals-canada-health-canada-2013.html>

## Appendix 2: Overview of results from the alternatives assessment in UNEP/POPS/POPRC.10/INF/7/Rev.1

Substance/Brand name	CAS No	Type	Functionality	Applications
<b>Class 1: Substances that the committee considered met all Annex D criteria</b>				
Octamethyl cyclotetrasiloxane (D4)	556-67-2	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
<b>Class 2: Substances that the committee considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data</b>				
Chlorpyrifos	2921-88-2	Pesticides		
<b>Class 3: Substances that are difficult for classification due to insufficient data</b>				
Perfluorobutane sulfonate potassium salt (PFBS K)	29420-49-3	Fluorinated substance	Fluorosurfactant	Coating and coating agents, carpets, leather and apparel, textiles and upholstery, paper and packaging, rubber and plastics.
Perfluorohexanesulfonate potassium salt (PFHxS K)	3871-99-6	Fluorinated substance	Fluorosurfactant	Carpets, leather and apparel, textiles and upholstery
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol* (6:2 FTOH) <sup>170</sup>	647-42-7	Fluorinated substance	Raw material for surfactant and surface protection products	Carpets, leather and apparel, textiles and upholstery
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulfonate (6:2 FTS)	27619-97-2	Fluorinated substance	Fluorosurfactant	Metal plating
Tris(octafluoropentyl) phosphate	355-86-2	Fluorinated substance	Fluorosurfactant	Paper and packaging
Tris(heptafluorobutyl) phosphate	563-09-7	Fluorinated substance	Fluorosurfactant	Paper and packaging
Sodium bis(perfluorohexyl) phosphonate	40143-77-9	Fluorinated substance	Fluorosurfactant	Paper and packaging
Carboxymethyl dimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl] amino]propylammonium hydroxide <sup>171</sup>	34455-29-3	Fluorinated substance	Fluorosurfactant	Fire-fighting foams
Tris(trifluoroethyl) phosphate	358-63-4	Fluorinated substance	Fluorosurfactant	Paper and packaging
Methyl nonafluorobutyl ether	163702-07-6	Fluorinated substance	Fluorosurfactant	Coating and coating additives
Methyl nonafluoro isobutyl ether <sup>172</sup>	163702-08-7	Fluorinated substance	Fluorosurfactant	Coating and coating additives
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-	59587-38-1	Fluorinated substance	Fluorosurfactant	Metal plating

<sup>170</sup> A NICNAS (2015) assessment considered the environmental risks associated with the industrial uses of nine per- and poly-fluorinated organic chemicals which are indirect precursors to short-chain perfluorocarboxylic acids (PFCAs). Insufficient data are presented in the assessment to categorise the parent chemicals in this group according to domestic environmental hazard thresholds or the aquatic hazards of chemicals in this group according to the third edition of the United Nations' Globally Harmonised System of Classification and Labelling of Chemicals (GHS). Available data indicate that chemicals in this group have the potential to degrade to PFHxA, PFPeA and PFBA. Therefore, the principal risk posed by the chemicals in this group is assumed to result from cumulative releases of these short-chain perfluorocarboxylic acid degradation products. The specific uses of these substances was not specified in the assessment.

<sup>171</sup> See above

<sup>172</sup> See above

Substance/Brand name	CAS No	Type	Functionality	Applications
sulphonate potassium salt (6:2 FTS K)				
1H,1H,2H,2H-Perfluorohexanol or 3,3,4,4,5,5,6,6,6-nonafluorobutyl ethanol* (4:2 FTOH)	2043-47-2	Fluorinated substance	Raw material for surfactant and surface protection products	Carpets, leather and apparel, textiles and upholstery
2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate (F-53B)		Fluorinated substance	Fluorosurfactant	Metal plating
1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate (F-53)		Fluorinated substance	Fluorosurfactant	Metal plating
Perfluorohexane ethyl sulfonate		Fluorinated substance	Fluorosurfactant	Fire-fighting foams
Dodecafluoro-2-methylpentan-3-one	756-13-8	Fluorinated substance	Fluorosurfactant	Fire-fighting foams
Perfluorohexyl phosphonic acid (PFHxPA)	40143-76-8	Fluorinated substance	Fluorosurfactant	Paper and packaging
1-chloro-perfluorohexyl phosphonic acid		Fluorinated substance	Fluorosurfactant	Paper and packaging
2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester* (6:2 FMA)	2144-53-8	Fluorinated substance	Raw material for surfactant and surface protection products	Carpets, leather and apparel, textiles and upholstery
Decamethyl cyclopentasiloxane (D5) <sup>173*</sup>	541-02-6	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
Di-2-ethylhexyl sulfosuccinate, sodium salt	577-11-7	Non-fluorinated substance	Waxes and resins	Carpets, leather and apparel, textiles and upholstery
Stearamidomethyl pyridine chloride	4261-72-7	Non-fluorinated substance	Waxes and resins	Carpets, leather and apparel, textiles and upholstery
(Hydroxyl) Terminated polydimethylsiloxane	67674-67-3	Non-fluorinated substance	Non-ionic surfactant	Coating and coating additives
Polyfox®		Commercial brand	Polymer coating	Coating and coating additives
Emulphor® FAS		Commercial brand	Polymer coating	Coating and coating additives Metal plating
Enthone®		Commercial brand	Polymer coating	Coating and coating additives Metal plating
Zonyl® <sup>174</sup>		Commercial brand	Polymer coating	Coating and coating additives Metal plating
Capstone®		Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Nuva®		Commercial brand	Polymer coating	Coating and coating additives carpets, leather and apparel,

<sup>173</sup> There is ongoing work through which new information is becoming available to further support the assessment of these substances.

<sup>174</sup> According to FluoroCouncil, production of Zonyl® was discontinued in 2014.

Substance/Brand name	CAS No	Type	Functionality	Applications
				textiles and upholstery, and metal plating
Unidyne®		Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Rucoguard®		Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Oleophobol®		Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Asahiguard®		Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Solvera®		Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
<b>Class 4: Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e)</b>				
Dodecamethyl cyclohexasiloxane (D6)*	540-97-6	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers <sup>175</sup>	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
Hexamethyl disiloxane (MM or HMDS)*	107-46-0	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers <sup>176</sup>	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
Octamethyl trisiloxane (MDM)*	107-51-7	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers.	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
Decamethyl tetrasiloxane (MD2M)*	141-62-8	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers. <sup>177</sup>	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
Dodecamethyl pentasiloxane (MD3M)*	141-63-9	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers	Carpets, leather and apparel, textiles and upholstery, coating and coating additives
1-Isopropyl-2-phenylbenzene	25640-78-2	Non-fluorinated substance	Waxes and resins	Coating and coating additives
Diisopropyl-naftalene (DIPN)	38640-62-9	Non-fluorinated substance	Waxes and resins	Coating and coating additives
Triisopropyl-naftalene /TIPN)	35860-37-8	Non-fluorinated substance	Waxes and resins	Coating and coating additives
Diisopropyl-1,1'-biphenyl	69009-90-1	Non-fluorinated substance	Waxes and resins	Coating and coating additives
Cypermethrin	52315-07-8	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites
Deltamethrin	52918-63-5	Pesticide	Pesticide	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

<sup>175</sup> 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>.

<sup>176</sup> <http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f>.

<sup>177</sup> <http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f>.

Substance/Brand name	CAS No	Type	Functionality	Applications
Pyriproxyfen	95737-68-1	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites
Imidacloprid	138261-41-3, 105827-78-9	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites
Fipronil	120068-37-3	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta spp</i> and <i>Acromyrmex spp</i>
Fenitrothion	122-14-5	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta spp</i> and <i>Acromyrmex spp</i>
Abamectin	71751-41-2	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites
Hydramethylnon	67485-29-4	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites. Insect bait for control of leaf-cutting ants from <i>Atta spp</i> and <i>Acromyrmex spp</i>
<b>Not classified; Not prioritised*</b>				
Perfluorohexanoic acid (PFHxA) <sup>178</sup>	307-24-4	N/A	N/A	N/A
Perfluorohexanoic acid sodium salt (PFHxA Na)	2923-26-4	N/A	N/A	N/A
Perfluoro butanoic acid (PFBA)	375-22-4	N/A	N/A	N/A
Perfluoro heptanoic acid (Phal)	375-85-9	N/A	N/A	N/A

\* Substances not classified/not prioritised as they are degradation products

<sup>178</sup> A NICNAS (2018c) assessment of homologous short-chain perfluorocarboxylic acids and their direct precursors, indicated that PFHxA to be highly persistent and mobile and, as a result, have the potential to become globally distributed. Nevertheless, currently available data indicate that these substances are not expected to be highly bioaccumulative or toxic to aquatic organisms. The chemicals in this group are not PBT substances according to domestic environmental hazard criteria.

## Appendix 3: Excerpt of the annex to decision POPRC-10/4

### Summary of the report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride

#### Introduction

1. The present annex is a summary of a report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF)<sup>179</sup> conducted by the Persistent Organic Pollutants Review Committee in accordance with decisions SC-6/4 and POPRC-9/5.
2. 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.<sup>180</sup> 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.
3. Information on alternatives to PFOS, its salts and PFOSF was provided by Parties and observers<sup>181</sup> using a format developed by the Committee.<sup>182</sup> 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 chemicals<sup>183</sup> 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.<sup>184</sup> 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.<sup>185</sup>
4. 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

5. The methodology used for the assessment consists of a two-step screening process, as mandated. 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.
6. 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

<sup>179</sup> UNEP/POPS/POPRC.10/INF/7/Rev.1.

<sup>180</sup> UNEP/POPS/POPRC.8/INF/28.

<sup>181</sup> The information, submitted by 11 Parties and three others, is available on the website of the Stockholm Convention at: <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/tabid/3565/Default.aspx>.

<sup>182</sup> UNEP/POPS/POPRC.9/INF/10/Rev.1.

<sup>183</sup> UNEP/POPS/POPRC.9/INF/11/Rev.1.

<sup>184</sup> UNEP/POPS/POPRC.8/INF/17/Rev.1.

<sup>185</sup> 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), [http://www.oecd.org/env/ehs/risk-management/PFC\\_FINAL-Web.pdf](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>.

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.

7. 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 K<sub>ow</sub> > 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 K<sub>ow</sub> > 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 K<sub>ow</sub> 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 K<sub>ow</sub> < 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).

8. 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 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).

9. 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.

10. 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).

11. 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**

<b>Non-fluorinated alternatives (one substance)</b>	
<b>CAS No.</b>	<b>Substance</b>
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**

<b>Pesticides (one substance)</b>	
<b>CAS No.</b>	<b>Substance</b>
2921-88-2	Chlorpyrifos

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

<b>Fluorinated alternatives (20 substances)</b>	
<b>CAS No.</b>	<b>Substance</b>
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) phosphonate
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*
<b>Non-fluorinated alternatives (four substances)</b>	
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
<b>Commercial brands (11 brands)</b>	
	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)**

<b>Non-fluorinated alternatives</b> (nine substances)	
<b>CAS No.</b>	<b>Substance</b>
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
<b>Pesticides</b> (eight substances)	
<b>CAS No.</b>	<b>Substance</b>
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.

12. 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 PFOSF 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.

13. 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 PFOSF.

## **B. Information gaps**

14. The methodology used for the assessment of alternatives to endosulfan, 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 PFOSF 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 PFOSF, as evidenced by the large number of chemicals that the Committee could not assess because of a lack of data.

15. The scarcity of experimental data about alternatives to PFOS, its salts and PFOSF 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.

16. The identification of alternatives to PFOS, its salts and PFOSF in the report is based largely on information provided by Parties and observers. Alternatives to PFOS, its salts and PFOSF 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 PFOSF were not reported for some applications. 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.

17. 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 (UNEP/POPS/POPRC.5/10/Add.1). 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 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.

18. 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, firefighting 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. Where possible, the functionality and application of alternative substances have been indicated in the table in annex 1 to the full report.

19. 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.

## Appendix 4 : Output of screening results for 'additional' PFOS alternatives carried out in the current assessment

Name	CAS No.	P-Score	B-Score <sup>186</sup>	PB-Score	PB category
Acephate	30560-19-1	0.0893	0.00849	0.10	-
Alcohols, C12-16	68855-56-1	0.0708	0.44812	0.52	B
Alkylpolyglycoside	68515-73-1	0.0113	0.00095	0.01	-
Alpha-sulfo-omega-hydroxypoly(oxy-1,2-ethanediyl) C9-11 alkyl ethers, sodium salts	96130-61-9	N/A	N/A	N/A	-
Amyl acetate	628-63-7	0.0153	0.0113	0.03	-
Anisole	100-66-3	0.04	0.02	0.06	-
2-Butoxyethanol	111-76-2	0.0106	0.00481	0.02	-
1-Butoxy-2-propanol / propylene glycol butyl ether / 3-Butoxy-2-propanol	5131-66-8	0.0125	0.01948	0.03	-
n-Butyl acetate	123-86-4	0.01	0.01	0.02	-
Carbaryl	63-25-2	0.147	0.10433	0.25	-
Cyclotriphosphazene	291-37-2	0.01	0.22	0.24	-
Cyfluthrin (Pyrethroid)	68359-37-5	0.9836	0.19397	1.18	vP
Decylsulfate	142-87-0	0.0656	0.02381	0.09	-
Dibutyl phenyl phosphate	2528-36-1	0.04	0.22	0.26	-
Diethylene glycol monobutyl ether / 2-(2-butoxyethoxy)-ethanol	112-34-5	0.02	0.02	0.03	-
Diphenyl-2-ethylhexyl phosphate	1241-94-7	0.29	0.33	0.62	B
Diphenyl isopropylphenyl phosphate	28108-99-8	0.82	0.33	1.15	vPB
Diphenyl tolyl phosphate	26444-49-5	0.40	0.02	0.42	P
D-Limonene (citrus oil extract)	5989-27-5	0.0547	0.22434	0.28	-
1,2-Ethandiol	107-21-1	0.0131	0.00149	0.01	-
Ethyl lactate	97-64-3	0.02	0.00	0.02	-
Fenvalerate	51630-58-1	0.9481	0.14672	1.09	vP
Hexylene glycol / 2-methyl-2,4-pentanediol	107-41-5	0.06	0.01	0.06	-
Isodecyldiphenylphosphate	29761-21-5	0.86	0.18	1.03	vP
Isopropylphenyl phosphate	26967-76-0	0.95	0.29	1.24	vP
Metaflumizone	139968-49-3	0.99	0.54	1.53	vPvB
Methoprene	40596-69-8	0.6575	0.43153	1.09	vPB
Methyl-3-methoxypropionate	3852-09-3	0.02	0.00	0.02	-
Nonylphenyl dipenyl phosphate	38638-05-0	0.83	0.23	1.06	vP
Octylsulfate	142-31-4	0.0477	0.00535	0.05	-
Oleylamine, ethoxylated	26635-93-8	0.33	0.23	0.56	P
Permethrin (Pyrethroid)	52645-53-1	0.9636	0.48228	1.45	vPB
1-Propanaminium, 3-amino-N-(carboxymethyl)-N,N-dimethyl-,N-coco acyl derivs.,hydroxides, inner salts	61789-40-0	0.0341	0.00434	0.04	-
Propylene glycol methyl ether acetate	108-65-6	0.03	0.00	0.03	-

<sup>186</sup> 0.5 represents BCF = 5000 and 0.33 represents BCF = 2000.

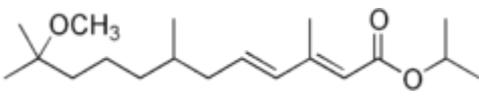
Name	CAS No.	P-Score	B-Score <sup>186</sup>	PB-Score	PB category
Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)	70829-87-7	1.00*	0.69*	N/A	
P-Tert-butylphenyl diphenyl phosphate	56803-37-3	0.90	0.33	1.23	vPB
o-Tolyl phosphate (TOCP, TOTP)	78-30-8	0.90	0.76	1.66	vPvB
Tributyl phosphate (TBP, TNBP)	126-73-8	0.01	0.22	0.24	-
Tricresyl phosphate (TCP)	1330-78-5	0.90	0.76	1.66	vPvB
Triphenyl phosphate	115-86-6	0.26	0.20	0.46	-
Tris(2-hydroxyethyl)ammonium dodecylsulfate	139-96-8	0.0363	0.00286	0.04	-
Tris(isobutylphenyl) phosphate	68937-40-6	0.98	0.04	1.03	vP
Tri-tert-butyl phenyl phosphate	28777-70-0	0.98	0.04	1.03	vP
Trixylyl phosphate (TXP)	25155-23-1	0.96	0.37	1.33	vPB

\* Based on manual calculations

## Appendix 5: PFOS alternatives detailed assessment results

### Methoprene

**Overall conclusion: Class 4: Substance not likely to meet all Annex D criteria (b), (c), (d) and (e)**

Summary		
<b>Bioaccumulation</b>		
A calculated BCF value of ~2000, and $K_{ow} > 5$ suggest a potential for bioaccumulation. Methoprene could potentially meet the Annex D (c) (i) criterion for bioaccumulation potential. However, more data would be required to determine if the criteria (BCF=5000) is met in the environment.		
<b>Persistence</b>		
This substance is, according to ECHA Annex III inventory, suspected persistent in the environment. Relatively short (<3 month) half-lives have been estimated in soil and water, with a lack of information available for sediments. Overall, there is not sufficient evidence to indicate if Annex D 1 (b) (i) could be met.		
<b>Long-range transport (LRT)</b>		
A short (<5 hour) estimate half-life in air for the reaction of metaflumizone with OH radicals, suggests the Annex D 1 (d) (iii) criteria is not likely to be met, but there are no monitoring/sampling data available to fully assess the LRT potential of this compound.		
<b>Ecotoxicity</b>		
Notified classification and labelling according to CLP criteria designates this substance as toxic to aquatic life. This substance is highly toxic to freshwater invertebrates, so is therefore considered likely to fulfil the Annex D 1 (e) criteria for ecotoxicity.		
<b>Toxicity to human health</b>		
WHO has classified methoprene as —unlikely to present acute hazard in normal use, and JMPR concluded that methoprene was unlikely to pose a carcinogenic risk to humans. The Annex D 1 (e) criteria for human health toxicity is therefore not likely to be met.		
General Information		
CAS Name	Methoprene	
CAS Number	40596-69-8	
Chemical name	Methoprene	
IUPAC Name	1-methylethyl (E,E)-11-methoxy-3,7,11-trimethyl-2,4-dodecadienoate	
Structure		
Molecular formula	$C_{19}H_{34}O_3$	
Molecular weight	310.48 g/mol	
Functionality & occurrence	Pesticide for the treatment of RIFAs and termites	
Physico-chemical properties		
Property	Value	References
Vapour Pressure	$3.15 \times 10^{-6}$ kPa at 20 °C [1]; $2.4 \times 10^{-5}$ mm Hg at 25 °C [2]	[1], [2]
Water solubility	1.39 mg/L at 20 °C  Calculation according to EPISUITE performed with the module WSKOW- v1.41: 0.214 mg/L (25°C)	[1]

<i>Partition coefficient n-octanol/water (Log K<sub>ow</sub>)</i>	Experimental: 1.50 [1]  6.34 (calculation according to EPISUITE performed with the module KOWWIN, v1.68)	[1]
<i>Partition coefficient air/octanol (Log K<sub>oa</sub>)</i>		
<i>Partition coefficient air/water Partition coefficient (Log K<sub>aw</sub>)</i>	Calculated using EPISUITE KOAWIN v 1.10 (25oc):  9.050	
<i>Henry's law constant</i>	Experimental value  6.89x10 <sup>-6</sup> atm·m <sup>3</sup> /mole at 25°C  Calculated using EPISUITE HENRYWIN v 3.2  5.71 x 10 <sup>-5</sup> atm m <sup>3</sup> /mole (Bond Method)  2.13 x 10 <sup>-6</sup> atm m <sup>3</sup> /mole (Group Method)	
<b>Bioaccumulation</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>BCF</i>	Suspected bioaccumulative: EpiSuite data included in the Toolbox contain at least one experimental log K <sub>ow</sub> value equal to or higher than 4.5 [3].  An estimated BCF of 2000 (estimated from K <sub>ow</sub> value of 5.5) - suggests the potential for bioconcentration in aquatic organisms is very high.  Calculation using EPISUITE BCFBAF model (using K <sub>ow</sub> = 5.5): BCF = 1977.	[3]
<i>BMF/TMF data</i>	n/a	
<b>Persistence</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Environmental fate	Suspected persistent in the environment: The Danish QSAR database contains information indicating that the substance is predicted as non-readily biodegradable [1].  Extensive studies have shown that methoprene breaks down rapidly in the environment (USEPA, 2001). It undergoes demethylation, hydrolysis and oxidative cleavage in microbes, insects and plants and is rapidly metabolized in fish, birds and mammals (Glare & O'Callaghan, 1999) [5].  In water, it would be expected to adsorb to suspended solids. It is fairly rapidly biodegraded in both soil and water and rapidly degraded when exposed to sunlight (WHO/FAO, 1996) [1].  Methoprene degrades rapidly in sunlight, both in water and on inert surfaces. The pesticide also is metabolized rapidly in soil and does not leach. Thus, it should not persist in soil or contaminate ground water [6].	[1],[3],[5],[6]
Water : half/life	The half- life of this material is less than two days in the field.  Methoprene is rapidly degraded in both sterile and nonsterile pond water exposed to sunlight (>80% of applied methoprene is degraded within 13 days). Degradation is somewhat less rapid under sterile conditions than under nonsterile conditions indicating	[2]

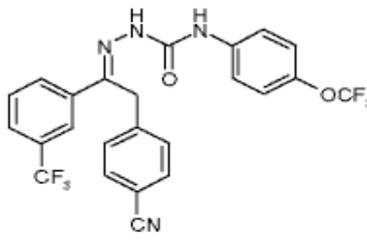
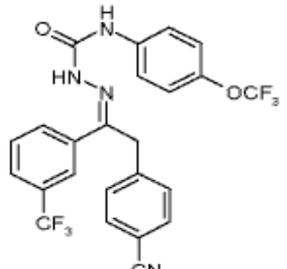
	<p>that, although photolysis may be the main degradation route, microbial metabolism contributes to methoprene degradation.</p> <p>Estimated volatilization half-lives for a model river and model lake are 32 hours and 15 days, respectively. The estimated volatilization half-life from a model pond is 278 days if adsorption is considered.</p> <p>Degradation proceeds more rapidly at 20 °C than at 4.5 °C, with associated half-lives of 10-35 days and &gt;35 days, respectively.</p> <p>Modelled half-life in water due to volatilisation (using EPISUITE) (based on based upon a Henry's Law constant of <math>6.89 \times 10^{-6}</math> atm-cu m/mole):</p> <p>6.314 days (river water) 75.03 days (lake water)</p>													
Water : other data	<p>Methoprene degrades rapidly in water.</p> <p>Methoprene degrades rapidly in sunlight, both in water and on inert surfaces.</p>	[2]												
Soil : half/life	The biodegradation half-life of methoprene was approximately 10 days at a surface treatment rate of 1 kg/ha in sandy and silty loam soils.	[2]												
Soil : other data	Methoprene is not persistent in soils. The breakdown, or degradation, of methoprene was rapid in experimental soil tests. In soil, microbial degradation is rapid and appears to be the major route of its disappearance from soil.	[4]												
Sediment : half/life	No data available													
Sediment : other data	No data available													
<b>Long-range transport</b>														
<i>Property</i>	<i>Value</i>	<i>References</i>												
Half-life : air (exp)	<p>Vapor-phase methoprene will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals and ozone; the half-lives for these reactions in air are estimated to be 4.6 hours and 48 minutes, respectively (derived using a structure estimation method).</p> <p>Methoprene contains chromophores that absorb at wavelengths &gt;290 nm and, therefore, may be susceptible to direct photolysis by sunlight.</p>	[2]												
Half-life : air (estimated) - EpiSuite	When applying the US Environmental Protection Agency (EPA) modelling program AOPWIN (v1.9), a half-life of about 1.547 hours can be calculated, using a rate constant for the hydrogen abstraction ( $K_{OH}$ ) of $82.95 \times 10^{-12}$ cm <sup>3</sup> /s per molecule and a hydroxyl radical concentration of $1.5 \times 10^6$ molecules/cm <sup>3</sup> .													
LRAT, other data	According to a model of gas/particle partitioning of semi volatile organic compounds in the atmosphere, methoprene, based in its vapour pressure, is expected to exist solely as a vapor in the ambient atmosphere.	[2]												
<b>Toxicity</b>														
<i>Property</i>	<i>Value</i>	<i>References</i>												
Ecotoxicity hazard assessment	<p>Notified classification and labelling according to CLP criteria:</p> <p>Classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008</p> <table border="1"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>Aquatic Chronic</td> <td>2</td> <td>H411</td> <td>HIGH</td> </tr> <tr> <td>Acute Aquatic</td> <td>2</td> <td>H401</td> <td></td> </tr> </tbody> </table>	Classification	Category	Code	Indicative Toxicity level	Aquatic Chronic	2	H411	HIGH	Acute Aquatic	2	H401		[3], [6], [7], [8]
Classification	Category	Code	Indicative Toxicity level											
Aquatic Chronic	2	H411	HIGH											
Acute Aquatic	2	H401												

	<p>Suspected hazardous to the aquatic environment [3].</p> <p>Methoprene is highly acutely toxic to estuarine invertebrates [6].</p> <p>Methoprene is very highly toxic to freshwater invertebrates, as seen in studies with crayfish and <i>Daphnia magna</i>. The pesticide also can be very highly acutely toxic to estuarine and marine invertebrates, as seen in studies with grass shrimp and mud-crabs [6] The pesticide also can be very highly acutely toxic to estuarine and marine invertebrates, as seen in studies with grass shrimp and mud-crabs.</p> <p>Methoprene has been shown to be practically non-toxic to terrestrial species [8].</p>																	
Human health hazard assessment	<p>Notified classification and labelling according to CLP criteria:</p> <p>Classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008.</p> <table border="1"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>Skin Irrit.</td> <td>2</td> <td>H315</td> <td>HIGH</td> </tr> <tr> <td>Eye Irrit</td> <td>2</td> <td>H319</td> <td>N/A</td> </tr> <tr> <td>STOT SE</td> <td>3</td> <td>H335</td> <td>N/A</td> </tr> </tbody> </table> <p>HUMAN EXPOSURE AND TOXICITY: There are no data available [2].</p> <p>The studies available to EPA indicate that the biochemical insect growth regulator methoprene is of low toxicity and poses very little hazard to people and most other nontarget species [6].</p>	Classification	Category	Code	Indicative Toxicity level	Skin Irrit.	2	H315	HIGH	Eye Irrit	2	H319	N/A	STOT SE	3	H335	N/A	[2], [6], [7]
Classification	Category	Code	Indicative Toxicity level															
Skin Irrit.	2	H315	HIGH															
Eye Irrit	2	H319	N/A															
STOT SE	3	H335	N/A															
Additional health hazards:																		
(a) Acute toxicity	<p>No toxicological reference values established in EU [8]</p> <p>WHO has classified methoprene as —unlikely to present acute hazard in normal use [9]</p> <p>LD50 in animals has been greater than 3 g/kg [2]</p> <p>No definitive conclusion can be drawn about the genotoxic potential [9]</p>	[2] [8], [9]																
(b) Mutagenicity	<p>No mutagenic effects on rats at 2000 mg/kg</p> <p>Methoprene induces a weak mutagenic effect in the <i>Drosophila</i> wing spot test.</p>	[2]																
(c) Carcinogenetic	<p>JMPR concluded that methoprene was unlikely to pose a carcinogenic risk to humans [5]</p> <p>NOELs for carcinogenicity in rats or mice, if any, are higher than the highest dose levels tested in these species [4]</p>	[4], [5]																
(d) Toxicity for reproduction	<p>No reproductive adverse effects in 3-generation reproduction studies on rats at 2500 /ppm in the/ diet.</p> <p>NEGATIVE for teratogenic effects in rats, hamsters, rabbits, rats, sheep, and swine.</p>	[2]																
(e) Neurotoxicity	<p>Methoprene applied at a concentration of 0.2 ppm did not significantly affect the locomotor activities of mosquitofish or goldfish. This application rate is ten times the suggested rates [2]</p>	[2]																

(f) Immunotoxicity	No data available	
(g) Endocrine disruption	No data available	
(h) Mode of action	No data available	
(i) Acceptable exposure levels	<p>NOAEL of 500 mg/kg diet, equivalent to 8.6 mg/kg body weight per day. The low solubility and the high log octanol–water partition coefficient of methoprene indicate that it is unlikely to remain in solution at the maximum recommended applied dose, and the actual levels of exposure are likely to be much lower than those calculated. Exposure from food is considered to be low [10]</p> <p>Exposure guidelines:  NOEL: 250 ppm for systemic toxicity, based on an 18-month oncogenicity study.  MPI: 0.3750 mg/day for a 60 kg person. [100]</p>	[10]
<b>Other relevant information</b>		<i>References</i>
None		
<b>References</b>		
[1]	WHO/FAO (1996) Methoprene. Geneva, World Health Organization and Food and Agriculture Organization of the United Nations (WHO/FAO Datasheets on Pesticides No. 47; VBC/DS/84.47; <a href="http://www.inchem.org/documents/pds/pds/pest47_e.htm">http://www.inchem.org/documents/pds/pds/pest47_e.htm</a> ).	
[2]	U.S National Library of Medicine, Toxicology Data Network (TOXNET) Hazardous Substances Data Bank (HSDB); <a href="https://toxnet.nlm.nih.gov/">https://toxnet.nlm.nih.gov/</a>	
[3]	ECHA, REACH Annex III inventory: <a href="https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.049.977">https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.049.977</a>	
[4]	Extension Toxicology Network (ECOTOXNET): <a href="http://pmep.cce.cornell.edu/profiles/extoxnet/haloxfop-methylparathion/methoprene-ext.html#16">http://pmep.cce.cornell.edu/profiles/extoxnet/haloxfop-methylparathion/methoprene-ext.html#16</a>	
[5]	WHO (2008) Methoprene in Drinking-water: Use for Vector Control in Drinking-water Sources and Containers Background document for development of WHO Guidelines for Drinking-water Quality	
[6]	United States Environmental Protection Agency (1991), R.E.D Factsheet. <a href="https://archive.epa.gov/pesticides/reregistration/web/pdf/0030fact.pdf">https://archive.epa.gov/pesticides/reregistration/web/pdf/0030fact.pdf</a>	
[7]	ECHA, Summary of Classification and Labelling criteria : <a href="https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/108719">https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/108719</a>	
[8]	European Food Safety Authority (2017) Scientific support for preparing an EU position in the 49th Session of the Codex Committee on Pesticide Residues (CCPR), <a href="https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2017.4929">https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2017.4929</a>	
[9]	WHO (1999) Recommended classification of pesticides by hazard and guidelines to classification 1998–1999. Geneva, World Health Organization, International Programme on Chemical Safety	
[10]	WHO Chemical Factsheet : Methoprene ( <a href="http://www.who.int/water_sanitation_health/water-quality/guidelines/chemicals/methoprene-fs-new.pdf?ua=1">http://www.who.int/water_sanitation_health/water-quality/guidelines/chemicals/methoprene-fs-new.pdf?ua=1</a> )	

## Metaflumizone

**Overall conclusion: Class 3: Substances that are difficult for classification due to insufficient data;**

Summary	
<p><b>Bioaccumulation</b></p> <p>Steady state whole fish BCF values exceed 1,000 following normalisation to a 5% lipid content, suggesting bioaccumulation could occur in the environment. Log <math>K_{ow}</math> value of this substance is indicated to be &lt;5. This substance could potentially meet the Annex D (c) (i) criterion for bioaccumulation. But further evidence would be required to determine this.</p>	
<p><b>Persistence</b></p> <p>This substance is suspected to be persistent in the environment due to relatively low biodegradability. Relatively short (&lt;3 month) half-lives are reported under most conditions, however under certain conditions (e.g. aerobic dry soils, absence of light in sediments) this substance has long (&gt;6 month) half-life, suggesting Annex D 1 (b) (i) could be met in some conditions.</p>	
<p><b>Long-range transport (LRT)</b></p> <p>A short (&lt;6 hour) estimate half-life in air for the reaction of metaflumizone with OH radicals, suggests the Annex D 1 (d) (iii) criteria is not likely to be met, but there are no monitoring/sampling data available to fully assess the LRT potential of this compound.</p>	
<p><b>Ecotoxicity</b></p> <p>Notified classification and labelling according to CLP criteria designates this substance as ‘very toxic to aquatic life with long lasting effects. This substance is therefore considered likely to fulfil the Annex D 1 (e) criteria for ecotoxicity.</p>	
<p><b>Toxicity to human health</b></p> <p>While the ECHA REACH Annex III Inventory designates this substance as a ‘suspected carcinogen’, experimental studies have not identified significant toxic effects associated with exposure to this substance. The Annex D 1 (e) criteria for human health toxicity could be met, but a more comprehensive assessment will be required to establish this.</p>	
General Information	
CAS Name	Hydrazinecarboxamide, 2-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]-N-[4-(trifluoromethoxy)phenyl]-
CAS Number	139968-49-3
Chemical name	Metaflumizone
IUPAC Name	(EZ)-2'-[2-(4-cyanophenyl)-1-( $\alpha,\alpha,\alpha$ -trifluoro-m-tolyl)ethylidene]-[4-(trifluoromethoxy)phenyl]carbanilohydrazide
Structure	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p><b>BAS 320 I (E-isomer)</b></p> </div> <div style="text-align: center;">  <p><b>BAS 320 I (Z-isomer)</b></p> </div> </div>
Molecular formula	C <sub>24</sub> H <sub>16</sub> F <sub>6</sub> N <sub>4</sub> O <sub>2</sub>
Molecular weight	506.4 g/mol

Functionality & occurrence	Pesticide for treatment of RIFAs and termites	
<b>Physico-chemical properties</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>Vapour Pressure</i>	<u>Experimental data:</u>  Mixture of E/Z (unspecified ratio) <sup>187</sup> : 1.24 x 10 <sup>-8</sup> Pa at 20 °C 3.41 x 10 <sup>-8</sup> Pa at 25 °C  E isomer: 7.94 x 10 <sup>-10</sup> Pa at 20 °C 2.46 x 10 <sup>-9</sup> Pa at 25 °C  Z isomer: 2.42 x 10 <sup>-7</sup> Pa at 20 °C 5.82 x 10 <sup>-7</sup> Pa at 25 °C	[1]
<i>Water solubility</i>	<u>Experimental data</u> EEC method A6 1.4.1 (column elution method) : Mixture of E/Z (92.2:7.8): pH 5 – 1.35 µg/l pH 7 – 1.81 µg/l pH 9 – 1.73 µg/l Deionized water – 1.79 µg/l  E isomer: 1.43 µg/l Z isomer: 2.03 µg/l Determined in deionized water at 20 °C (pH 8.1 – 8.7)	[1]
<i>Partition coefficient n-octanol/water (Log K<sub>OW</sub>)</i>	<u>Experimental data:</u>  Z isomer: 4.4 at pH 5, 30°C E isomer: 5.1 at pH 5, 30°C  Z isomer: 4.2 at pH 7, 20°C E isomer: 4.9 at pH 7, 20°C  Z isomer: 3.8 at pH 3, 20°C E isomer: 4.4 at pH 3, 20°C	[1]
<i>Partition coefficient air/octanol (Log K<sub>OA</sub>)</i>	No data available	
<i>Partition coefficient air/water Partition coefficient (Log K<sub>AW</sub>)</i>	No data available	
<i>Henry's law constant</i>	Calculated (using water solubility data generated at 20°C): E isomer 7.8 x 10 <sup>-4</sup> Pa m <sup>3</sup> mol <sup>-1</sup> Z isomer 0.11 x 10 <sup>-4</sup> Pa m <sup>3</sup> mol <sup>-1</sup> .	[1]
<b>Bioaccumulation</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>BCF</i>	Experimental aquatic BCF test in fish to OECD Guideline 305, GLP:  Kinetic whole fish BCFk: <b>5,769</b> and <b>4,099</b> L/kg (based on Total Radioactive Residues, normalised for 5% lipid content - (a flow-through system with Bluegill Sunfish ( <i>Lepomis macrochirus</i> ))	[1]

<sup>187</sup> <https://echa.europa.eu/documents/10162/be360a1e-74d5-5df0-b310-39c0c6e1a364>

	Steady state whole fish BCF: <b>1,667</b> to <b>1,705</b> l/kg wet weight (normalised for 5% lipid content - a flow-through system with Common Carp ( <i>Cyprinus carpio</i> )).	
<i>BMF/TMF data</i>	The kinetic biomagnification factor (BMF) was <b>0.326</b> . Accounting for the fish growth rate the growth corrected BMF was <b>0.554</b> .	[1]
<b>Persistence</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Environmental fate	Suspected persistent in the environment: The Danish QSAR database contains information indicating that the substance is predicted as non-readily biodegradable	[2]
Water : half/life	Experimental data:  Aquatic hydrolysis: Half-life at pH 4 = <b>5.37-18.4 days</b> (12 °C) ; <b>5.37 to 5.95 days</b> (25 °C)  Half-life at pH 5 = <b>77.2-88.8 days</b> (12 °C) ; <b>27.2 to 27.5 days</b> (25 °C)  Aquatic photolysis: Half-life = 2.4 – 6.3 days	[1], [3]
Water : other data	Metaflumizone is considered hydrolytically stable at pH 7 and 9. Under acidic conditions metaflumizone undergoes hydrolysis. Metaflumizone is susceptible to photodegradation under suitable conditions. The actual degree of photodegradation in the aquatic environment depends on local conditions and seasons.	[1]
Soil : half/life	Experimental data:  Measured value (field test) : Soil half-life = 13.7 days  Medium to very high persistence single first order (SFO) laboratory soil half-life = <b>65-376 days</b> (20°C, pF2 soil moisture, dark)  Degradation of metaflumizone in two sandy loam soils was enhanced in the presence of light, SFO soil half-life ranged from <b>19.1 to 24.1 days</b> at 22°C under continuous irradiation.  Degradation of metaflumizone in soil followed the first order reaction kinetics and its half-life values varied from ~20 to 150 days.  Under anaerobic condition, degradation of metaflumizone was faster ( $t_{1/2}$ = <b>33.4 days</b> ) compared to aerobic condition ( $t_{1/2}$ = <b>50.1 days</b> ) and dry soil ( $t_{1/2}$ = <b>150.4 days</b> ).[5]	[1], [3], [4], [5]
Soil : other data	n/a	
Sediment : half/life	Experimental data:  Water/sediment simulation. In an aerobic water-sediment study performed in the dark, metaflumizone was observed to dissipate from the water column to sediment in two systems.  Half-life = 322 – 581 days (total system, dark) Half-life = 6.32 days (total system, irradiated)	[1]
Sediment : other data	No data available	
<b>Long-range transport</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Half-life : air (experimental)	No data available	
Half-life : air (estimated) - EpiSuite	Calculated rate constant for the reaction of metaflumizone with OH radicals: $k = 39.55 \times 10^{-12} \text{ cm}^3 \times \text{molecule}^{-1} \times \text{s}^{-1}$	[6]

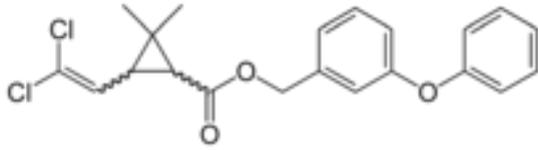
	Calculated atmospheric degradation half-life of metaflumizone (based on rate constant above) : $t_{1/2} = 0.25$ days (= 6 hours) [6]													
LRAT, other data	No monitoring or sampling data available													
<b>Toxicity</b>														
<i>Property</i>	<i>Value</i>	<i>References</i>												
Ecotoxicity hazard assessment	<p>Notified classification and labelling according to CLP criteria – Classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008:</p> <table border="1"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>Aquatic Chronic</td> <td>1</td> <td>(H410) Very toxic to aquatic life with long lasting effects</td> <td>SEVERE</td> </tr> <tr> <td>Aquatic Acute</td> <td>1</td> <td>(H400) Very toxic to aquatic life</td> <td>LOW</td> </tr> </tbody> </table> <p><u>Aquatic Acute Toxicity</u> Aquatic acute toxicity data on metaflumizone are available for fish, invertebrates, algae and aquatic plants. No acute/short-term L(E)C<sub>50</sub> endpoints were observed for fish, invertebrates or algae/aquatic plants up to the quoted limit of water solubility using metaflumizone (0.00181 mg/L at 20°C and pH 7).</p> <p><u>Aquatic Chronic Toxicity</u> Chronic toxicity data on metaflumizone are available for fish, invertebrates, algae and aquatic plants using standard test species. In each case, the NOEC or EC<sub>10</sub> was equal to or greater than the highest tested concentration. This is interpreted as no chronic effects up to the limit of water solubility for the purpose of classification.</p> <p><u>Soil toxicity</u> Low risk to soil organisms is expected.</p>	Classification	Category	Code	Indicative Toxicity level	Aquatic Chronic	1	(H410) Very toxic to aquatic life with long lasting effects	SEVERE	Aquatic Acute	1	(H400) Very toxic to aquatic life	LOW	[1], [7]
Classification	Category	Code	Indicative Toxicity level											
Aquatic Chronic	1	(H410) Very toxic to aquatic life with long lasting effects	SEVERE											
Aquatic Acute	1	(H400) Very toxic to aquatic life	LOW											
Human health hazard assessment	<p>Notified classification and labelling according to CLP criteria - Classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008:</p> <table border="1"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>STOT RE 2</td> <td>(H373)</td> <td>Causes damage to organs through prolonged or repeated exposure</td> <td>MODERATE</td> </tr> </tbody> </table>	Classification	Category	Code	Indicative Toxicity level	STOT RE 2	(H373)	Causes damage to organs through prolonged or repeated exposure	MODERATE	[7]				
Classification	Category	Code	Indicative Toxicity level											
STOT RE 2	(H373)	Causes damage to organs through prolonged or repeated exposure	MODERATE											
Additional health hazards:	No additional data													
(a) Acute toxicity	<p>Overall, metaflumizone should not be classified for Aquatic Acute classification.</p> <p><u>Experimental data – human studies:</u> There are no human data available</p> <p><u>Experimental data – animal studies:</u></p>	[1], [5], [8]												

	<p>Metaflumizone was found to be of low toxicity by the oral, inhalation and dermal routes following a single exposure in rats and mice, with LD50 &gt; 5000 mg/kg bw for oral and dermal routes and LC50 &gt; 5.3 mg/L following inhalation exposure.</p> <p>Acute oral toxicity – Rat, LD50, &gt;5000 mg/kg bw</p> <ul style="list-style-type: none"> <li>• Acute dermal toxicity – Rat, LD50, &gt;5000 mg/kg bw</li> <li>• Acute inhalation toxicity – Rat, LD50, &gt; 5.3 mg/L</li> </ul> <p>Metaflumizone demonstrates low toxicological potential following chronic oral exposure to rats, mice, and dogs. Overall, the lowest no observed adverse effect level (NOAEL) is 12 mg/(kg day) from the 1-year chronic dog study.</p> <p>It was deemed not necessary to establish an acute reference dose (ARfD) for metaflumizone in view of its low acute toxicity and the absence of developmental toxicity and any other toxicological effects that would be likely to be elicited by a single dose.</p>	
(b) Mutagenicity	<p>The potential mutagenicity of metaflumizone has been well investigated in experimental studies.</p> <p>In vitro, negative results were obtained with and without S9 in bacterial and mammalian cell gene mutation tests. Similarly, no increases in chromosome aberrations were seen in CHO V79 cells with S9, but a reproducible dose-related increase was seen in the absence of any exogenous metabolic activation system.</p> <p>In vivo, well conducted tests for micronuclei in the bone marrow of mice and UDS in rat liver cells both gave negative results. Overall, it can be concluded that metaflumizone lacks mutagenic potential. As metaflumizone lacks mutagenic potential, no classification is required for this endpoint.</p>	[1],[8]
(c) Carcinogenicity	<p>According to the ECHA REACH Annex III Inventory: ‘Suspected carcinogen: The Toolbox profiler Carcinogenicity (genotox and nongenotox) alerts by ISS gives an alert for carcinogenicity’ [2]</p> <p>No evidence for carcinogenicity found in experimental studies in rats or mice</p> <p>There were no neoplastic findings attributable to treatment with metaflumizone in a 24-month rat study or an 18-month mouse carcinogenicity study. Therefore, classification with carcinogenicity is not required.</p> <p>No information on the carcinogenicity of metaflumizone in humans is available.</p>	[1], [2], [8]
(d) Toxicity for reproduction	<p>In a two generation study in rats, metaflumizone was shown to cause a reduced fertility index in top dose-treated males and females of the F0 generation. This was observed in the presence of maternal toxicity (reduced bodyweight gain and poor general health). There were no effects on reproductive organs in this study. Therefore, it is not proposed to classify metaflumizone for effects on fertility.</p> <p>Reduced male and female fertility in the presence of severe systemic toxicity (lowest relevant reproductive NOAEL 50 mg/kg bw per day for effects on fertility (two-generation study in rats).</p> <p>No developmental toxic effects at maternally toxic dose in rats; decreased fetal weights, incomplete ossification of sternbrae at maternally toxic dose in rabbits (Lowest relevant developmental NOAEL 100 mg/kg bw per day (rabbits).</p>	[1],[8]

(e) Neurotoxicity	<p>In the acute neurotoxicity study, metaflumizone was administered to Wistar rats (10/sex/group) by oral gavage at doses of 0, 125, 500 and 2000 mg/kg bw. There were no signs of general toxicity or neurotoxicity observed.</p> <p>In the sub-chronic neurotoxicity study, metaflumizone was administered to Wistar rats (10/sex/group) by oral gavage at doses of 0, 1, 12, 36 or 150 mg/kg bw/day and to males (n = 10) at 300 mg/kg bw/day for 90 days. Clinical signs of toxicity and reductions in bodyweight, bodyweight gain and food consumption were noted in males at 300 mg/kg bw/day and males and females at 150 mg/kg bw/day. No clinical or neuropathological signs of neurotoxicity were noted.</p> <p><u>Acute neurotoxicity</u></p> <p>No evidence of neurotoxicity - NOAEL: 2000 mg/kg bw (highest dose tested).</p> <p><u>Sub chronic neurotoxicity</u></p> <p>No evidence of neurotoxicity; NOAEL: 300/150 mg/kg bw per day (highest dose tested; 90-day study in rats).</p>	[1],[8]
(f) Immunotoxicity	In an immunotoxicity study carried out to GLP, Wistar rats (10 females/dose) were administered metaflumizone at dose levels of 0, 15, 40 or 75 mg/kg bw/day for 28 days (DAR: B.6.8.2). Clinical signs of reduced body weight were observed at doses of 40 mg/kg and above. Metaflumizone was not immunotoxic in female Wistar rats.	[1],[8]
(g) Endocrine disruption	No data available	
(h) Mode of action	No data available	
(i) Acceptable exposure levels	<p>Estimate of acceptable daily intake for humans : 0.01 mg/kg bw</p> <p>The Acute Reference Dose (ARfD) is 0.13 mg/kg bw</p> <p>Acceptable Operator Exposure Level (AOEL) is 0.01 mg/kg bw per day</p>	[3], [8]
<b>Other relevant information</b>		<i>References</i>
None		
<b>References</b>		
[1]	Proposal for Harmonised Classification and Labelling, Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2, Metaflumizone. See <a href="https://echa.europa.eu/documents/10162/be360a1e-74d5-5df0-b310-39c0c6e1a364">https://echa.europa.eu/documents/10162/be360a1e-74d5-5df0-b310-39c0c6e1a364</a> (and references therein)	
[2]	ECHA REACH Annex III Inventory: <a href="https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.107.480">https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.107.480</a>	
[3]	European Food Safety Authority (EFSA), Conclusion on the peer review of the pesticide risk assessment of the active substance metaflumizone. <a href="https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2013.3373">https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2013.3373</a>	
[4]	Li et al. (2012) Degradation of metaflumizone in rice, water and soil under field conditions. <i>Ecotoxicol Environ Saf.</i> 2012, Dec; 86:73-8. <a href="https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~ej4HxS:1">https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~ej4HxS:1</a>	
[5]	Hempel, K. et al. (2007) Toxicological properties of metaflumizone. <i>Veterinary Parasitology</i> , Volume 150, Issue 3:15, Pages 190-195.	
[6]	FAO fact sheet. Available at: <a href="http://www.fao.org/fileadmin/templates/agphome/documents/Pests/Pesticides/JMPR/Evaluation09/Metaflumizone.pdf">http://www.fao.org/fileadmin/templates/agphome/documents/Pests/Pesticides/JMPR/Evaluation09/Metaflumizone.pdf</a>	
[7]	ECHA, Summary of Classification and Labelling, Harmonised classification - Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation), <a href="https://echa.europa.eu/da/information-on-chemicals/cl-inventory-database/-/discli/details/6232">https://echa.europa.eu/da/information-on-chemicals/cl-inventory-database/-/discli/details/6232</a>	
[8]	Joint FAO/WHO meeting on pesticide residues (2011): <a href="http://apps.who.int/iris/bitstream/handle/10665/44522/9789241665254_eng.pdf?sequence=1&amp;isAllowed=y">http://apps.who.int/iris/bitstream/handle/10665/44522/9789241665254_eng.pdf?sequence=1&amp;isAllowed=y</a>	

## Permethrin

**Overall conclusion: Class 4: Substance not likely to meet all Annex D criteria (b), (c), (d) and (e)**

Summary		
<b>Bioaccumulation</b>		
<p>The physico-chemical properties of permethrin (<math>K_{ow}</math> of up to <math>&gt;7</math>) suggest this substance may tend to bioaccumulate to a significant degree. However, measured BCF factors for permethrin of <math>&lt;1000</math> indicate that in the environment, so it is unlikely this substance will meet the Annex D (c) (i) criterion for bioaccumulation potential.</p>		
<b>Persistence</b>		
<p>This substance is potentially persistent in the environment due to relatively low biodegradability. Half-lives in soil are indicated to be up to <math>&gt;200</math> days under anaerobic conditions, suggesting that under certain environmental conditions, the Annex D 1 (b) (i) could be met.</p>		
<b>Long-range transport (LRT)</b>		
<p>A short (<math>&lt;6</math> hour) estimate half-life in air for the reaction of permethrin with OH radicals, suggests the Annex D 1 (d) (iii) criteria is not likely to be met, but there are no monitoring/sampling data available to confirm the LRT potential of this compound.</p>		
<b>Ecotoxicity</b>		
<p>Permethrin is noted as being extremely toxic to fish and aquatic life in general. Notified classification and labelling according to CLP criteria designates this substance as 'very toxic to aquatic life with long lasting effects'. This substance is therefore considered likely to fulfil the Annex D 1 (e) criteria for ecotoxicity.</p>		
<b>Toxicity to human health</b>		
<p>It is considered that permethrin is relatively non-toxic to mammals and acute toxic effects of permethrin vary in with the route of exposure. While permethrin is noted in the ECHA REACH Annex III Inventory as a suspected mutagen, data on carcinogenic and other toxicological effects are lacking. The Annex D 1 (e) criteria for human health toxicity could be met, but a more comprehensive assessment will be required to establish this.</p>		
General Information		
CAS Name	3-(2,2-Dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (3-phenoxyphenyl)methyl ester	
CAS Number	52645-53-1	
Chemical name	Permethrin	
IUPAC Name	m-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate	
Structure		
Molecular formula	$C_{21}H_{20}Cl_2O_3$	
Molecular weight	391.288 g/mol	
Functionality & occurrence	Insecticides for control of red imported fire ants and termites	
Physico-chemical properties		
<i>Property</i>	<i>Value</i>	<i>References</i>
Vapour Pressure	$1.3 - 45 (x 10^{-6})$ Pa at $25^{\circ}C$ (range of experimental values) [1]	[1]

	Modelled, EpiSuite MPBPVP : 8.26 x 10 <sup>-7</sup> mmHg (25°C)	
<i>Water solubility</i>	Experimental data:  0.006 - 0.2 mg/L; - nearly insoluble in water (20-30°C) [1]  Calculation according to EPISUITE performed with the module WSKOW- v1.41: 0.009747 mg/L (25°C)	[1]
<i>Partition coefficient n-octanol/water (Log K<sub>OW</sub>)</i>	2.88 – 6.5 (range of experimental values) [1]  6.1 [2]  7.43 (calculation according to EPISUITE performed with the module KOWWIN, v1.68)	[1], [2]
<i>Partition coefficient air/octanol (Log K<sub>OA</sub>)</i>	10.617 (calculated using EPISUITE KOAWIN v1.10)	
<i>Partition coefficient air/water Partition coefficient (Log K<sub>AW</sub>)</i>	No data available	
<i>Henry's law constant</i>	Experimental: 2.5 – 8670 (x 10 <sup>-5</sup> ) Pa·m <sup>3</sup> /mol at 25°C (range of experimental values) [1]  Calculated using EPISUITE HENRYWIN v 3.2 :  1.87 x 10 <sup>-6</sup> atm m <sup>3</sup> /mole (Bond Method)	[1]
<b>Bioaccumulation</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>BCF</i>	Not considered to be bioaccumulative [4]  BCF value of 570 is quoted in [2]  BCF values for rainbow trout and sheepshead minnow of approx. 560 and 480, respectively [3]  Calculation using EPISUITE BCFBAF model (using K <sub>OW</sub> = 6.5): BCF = 497.3	[2], [3], [4]
<i>BMF/TMF data</i>	n/a	
<b>Persistence</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>Environmental fate</i>	According to ECHA REACH Annex III Inventory [7]:  # Suspected persistent in the environment: The Danish QSAR database contains information indicating that the substance is predicted as non-readily biodegradable  Considered to be potentially persistent [4]	[4],[7]
<i>Water : half/life</i>	Experimental data:  t <sub>1/2</sub> = 14 days under outdoor light conditions and t <sub>1/2</sub> > 14 d under outdoor dark conditions [1]	[1],[3] [5]

	<p>Biodegradation half-lives by bacteria strains: <math>t_{1/2} = 56</math> h by <i>A. sobria</i>, <math>t_{1/2} = 61</math> h by <i>E. carotovora</i>, <math>t_{1/2} = 80</math> h by <i>Y. frederiksenii</i> and <math>t_{1/2} = 485</math> d for the control, uninoculated solution [1]</p> <p>Permethrin is quite stable, having a half-life of 51–71 days in an aqueous environment exposed to light [3]</p> <p>At pH 4, pH 5 and pH 7 (25°C), permethrin is stable towards abiotic hydrolysis; at pH 9, the abiotic hydrolysis half-life is in the range of 37–50 days. The direct photolysis half-life in water is about 23 to 37 days.</p> <p>Reaction with photo-oxidant species in natural waters can decrease the photodegradation half-life [5]</p> <p>Modelled half-life in water due to volatilisation (using EPISUITE) (based on based upon a Henry's Law constant of <math>1.87 \times 10^{-6}</math> atm-cu m/mole): 25.9 days (river water), 289 days (lake water)</p>	
Water : other data	If released into water, permethrin is expected to adsorb to suspended solids and sediment based upon its Koc values. Volatilization from water surfaces is possible based upon this compound's estimated Henry's Law constant. However, volatilization from water surfaces is expected to be attenuated by adsorption to suspended solids and sediment in the water column. [5]	
Soil : half/life	<p>Soil <math>t_{1/2} = \sim 30</math> d (range of reported values) [1]</p> <p>Field dissipation half-lives for permethrin generally fall in the range from 6 to 106 days. Under aerobic conditions, the field dissipation half-life is roughly 30 days (4-40 day range) and under anaerobic conditions, the field dissipation half-life is roughly 108 days (3-204 day range). [5]</p>	[1],[5]
Soil : other data	<p>Permethrin degrades in soil through biodegradation and abiotic hydrolysis [5]</p> <p>If released to soil, permethrin is expected to have no mobility based upon a Koc range from 10,471 to 86,000. Volatilization from moist soil surfaces is possible based upon an estimated Henry's Law constant of <math>2.4 \times 10^{-6}</math> atm-cu m/mole. However, adsorption to soil is expected to attenuate soil volatilization. [5]</p> <p>Because permethrin binds very strongly to soil particles and it is nearly insoluble in water, it is not expected to leach or to contaminate groundwater. The binding, or adsorption, of permethrin in soil may be limited to organic matter. Very little leaching of permethrin has been reported. [3]</p>	[3],[5]
Sediment : half/life	<p>Sediment: half-lives in 10 grams sediment/100 mL pesticide-seawater solution: <math>t_{1/2} &lt; 2.5</math> d for untreated sediment and <math>t_{1/2} &gt; 28</math> d for sterile sediment [1]</p> <p>The biodegradation half-life of permethrin in a sediment-seawater solution was less than 2.5 days. [5]</p>	[1]
Sediment : other data	Due to their high hydrophobicity, pyrethroids readily associated with sediment particles after entering aquatic systems and became one of the major threats to benthic invertebrates in urban waterways [3]	[3]
<b>Long-range transport</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Half-life : air (experimental)	Vapor-phase permethrin will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals and ozone; the half-	[5]

	<p>lives for these reactions in air are estimated to be 17 hours and 49 days, respectively [5].</p> <p>When applying the US Environmental Protection Agency (EPA) modelling program AOPWIN (v1.9), a half-life of about <b>5.6 hours</b> can be calculated, using a rate constant for the hydrogen abstraction (<math>K_{OH}</math>) of <math>22.88 \times 10^{-12} \text{ cm}^3/\text{s}</math> per molecule and a hydroxyl radical concentration of <math>1.5 \times 10^6 \text{ molecules/cm}^3</math>.</p>																	
LRAT, other data	<p>If released to air, a vapor pressure of <math>5.18 \times 10^{-8} \text{ mm Hg}</math> at <math>25^\circ\text{C}</math> indicates permethrin will exist in both the vapor and particulate phases in the ambient atmosphere. Particulate-phase permethrin will be removed from the atmosphere by wet and dry deposition. [5]</p>	[5]																
<b>Toxicity</b>																		
<i>Property</i>	<i>Value</i>	<i>References</i>																
Ecotoxicity hazard assessment	<p>Notified classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008 [6]:</p> <table border="1"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>Aquatic Chronic</td> <td>1</td> <td>H410</td> <td>SEVERE</td> </tr> <tr> <td>Aquatic Acute</td> <td>1</td> <td>H400</td> <td>LOW</td> </tr> </tbody> </table> <p>According to ECHA REACH Annex III Inventory [7]:</p> <p>Suspected hazardous to the aquatic environment: EPA Daphnia Magna toxicity model in VEGA (Q)SAR platform predicts that the chemical has a 48h EC50 of 0.0049 mg/L (EXPERIMENTAL value); Fathead Minnow toxicity model (EPA) in VEGA (Q)SAR platform predicts that the chemical has a 96h LC50 of 0.0246 mg/L (EXPERIMENTAL value); Fish toxicity classification (SarPy/IRFMN) model in VEGA (Q)SAR platform predicts that the chemical is Toxic-1 (less than 1 mg/L) (EXPERIMENTAL value)</p> <p>[2] notes that:</p> <ul style="list-style-type: none"> <li>• Permethrin is extremely toxic to fish and aquatic life in general</li> <li>• Permethrin is practically non-toxic to birds</li> <li>• Permethrin is extremely toxic to bees</li> </ul> <p>NOEC levels quoted in [2]:</p> <ul style="list-style-type: none"> <li>• Algae, NOEC = &lt; 3.1 µg/L</li> <li>• Invertebrates, NOEC = 0.0047 µg/L</li> <li>• Fish, NOEC = 0.41 – 10 µg/L</li> </ul> <p>Pyrethroid insecticides can be toxic to many marine and freshwater forms including aquatic invertebrates, insects and fishes (Prusty et al. 2015). The pyrethroid insecticides have been shown to affect mechanisms involved in fish reproduction [2].</p>	Classification	Category	Code	Indicative Toxicity level	Aquatic Chronic	1	H410	SEVERE	Aquatic Acute	1	H400	LOW	[6],[7]				
Classification	Category	Code	Indicative Toxicity level															
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Classification	Category	Code	Indicative Toxicity level															
Skin Sens.	1	H317	HIGH															
Acute Tox.	4	H302																
Acute Tox.	4	H332																

Additional health hazards:		
(a) Acute toxicity	<p>Exposure to permethrin is indicated to display a low acute toxicity to terrestrial animal and plants. [5]</p> <p>The highest acute Risk Quotient is approximately 0.03 for birds feeding on short grass and 0.04 for the smallest mammals feeding on short grass. [5]</p> <p>Pyrethroids, the widely used pesticides, are highly toxic to aquatic organisms. However, little information is so far available regarding the joint toxicity of type I and type II pyrethroids to fish. While the lethal toxicity of pyrethroid insecticides to fish is well documented, their sublethal physio-behavioural effects remain poorly characterized. [5]</p> <p>Permethrin is relatively non-toxic to mammals. Acute effects of permethrin vary in accordance with the route of exposure. Through the oral route, permethrin is mostly harmless; studies in rats demonstrate a LD50 of 480 to 554 mg/kg bw. The same can be said of dermal exposure (Rat LD50 dermal &gt;2000 mg/kg bw), although the chemical has been found to cause mild skin irritation in rabbits [3]</p>	[3], [5]
(b) Mutagenicity	<p>According to ECHA REACH Annex III Inventory [7]: # Suspected mutagen: CAESAR Mutagenicity model in VEGA (Q)SAR platform predicts that the chemical is Mutagen (EXPERIMENTAL value).</p>	[7]
(c) Carcinogenicity	<p>The potential carcinogenicity of permethrin is so far inconclusive [3] and contrasting conclusions have so far been made by different Parties:</p> <p>The US Environmental Protection Agency classified permethrin as "Likely to be Carcinogenic to Humans" by the oral route. This classification was based on two reproducible benign tumour types (lung and liver) in the mouse, equivocal evidence of carcinogenicity in Long-Evans rats, and supporting structural activity relationships (SAR) information [5].</p> <p>The ECHA Assessment Report for Permethrin PT18 [4] indices: 'No carcinogenic potential'.</p>	[3], [4], [5]
(d) Toxicity for reproduction	No data available	
(e) Neurotoxicity	No data available	
(f) Immunotoxicity	No data available	
(g) Endocrine disruption	<p>Evidence so far suggests that permethrin may potentially have endocrine disrupting effects [3]</p> <p>However, the results of these studies are often contradictory and no weight-of-evidence conclusions can currently be drawn on the possible endocrine-disrupting effects of permethrin. Studies so far have indicated both oestrogenic and anti-oestrogenic effects in mammals, and it is unclear whether there is oestrogen-receptor binding.[3]</p> <p>The ECHA Assessment Report for Permethrin PT18 - Not considered to have endocrine disrupting properties. [4]</p>	
(h) Mode of action	<p>Though a lot of advance has been made in understanding the MoA and toxic effect of these pesticides on different fish species, concise information on the toxic impact of pyrethroids on various physiochemical, biological and metabolic processes is lacking [2].</p>	[2]
(i) Acceptable exposure levels	No data available	

<b>Other relevant information</b> Note	<i>References</i>
<p>According to JRC, permethrin should be a candidate for EQS derivation. However, SG-R experts during the 5th SG-R meeting suggested to suspend permethrin from the selection due to the lack of reliable data (the available records are mainly from the year 2006) and add it to the watch list instead. SG-R agreed that Permethrin is a good candidate substance for EQS derivation and consideration as potential PS or inclusion on the WL. [3]</p> <p>The cis isomer constituent is present within permethrin at amounts <math>\geq 0.1</math> % w/w then the multi-constituent substance, permethrin, should also be treated as potentially persistent. In this situation permethrin may potentially fulfil the persistency criteria and, hence, fulfil two out of the three PBT criteria. Due to this borderline status and to the difficulties pertaining to the determination of the P classification, it is the agreed opinion of the Committee that permethrin should be further assessed by the ECHA PBT Expert Group. [4]</p>	[3],[4]
<b>References</b>	
[1]	MacKay, D. et al. (2006) Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals
[2]	Joint Research Centre (2018), Review of the 1st Watch List under the Water Framework Directive and recommendations for the 2nd Watch List. <a href="http://publications.jrc.ec.europa.eu/repository/bitstream/JRC111198/wl_report_jrc_2018_04_26_final_online.pdf">http://publications.jrc.ec.europa.eu/repository/bitstream/JRC111198/wl_report_jrc_2018_04_26_final_online.pdf</a>
[3]	<a href="https://circabc.europa.eu/webdav/CircaBC/env/wfd/Library/working_groups/priority_substances/2a%20-%20Sub-Group%20on%20Review%20of%20Priority%20Substances%202014%20start/Monitoring%20based%20exercise/Factsheets/Permethrin_draft%20factsheet_annex%20monitoring%20report.pdf">https://circabc.europa.eu/webdav/CircaBC/env/wfd/Library/working_groups/priority_substances/2a%20-%20Sub-Group%20on%20Review%20of%20Priority%20Substances%202014%20start/Monitoring%20based%20exercise/Factsheets/Permethrin_draft%20factsheet_annex%20monitoring%20report.pdf</a>
[4]	ECHA (2014) Biocidal Products Committee (BPC) Opinion on the application for approval of the active substance: Permethrin, Product type: 18, ECHA/BPC/004/2014, <a href="https://echa.europa.eu/documents/10162/6d4b72f7-1f53-4787-bded-78746cb1ec5f">https://echa.europa.eu/documents/10162/6d4b72f7-1f53-4787-bded-78746cb1ec5f</a>
[5]	U.S National Libraray of Medicine, Toxicology Data Network (TOXNET) Hazardous Substances Data Bank (HSDB); <a href="https://toxnet.nlm.nih.gov/">https://toxnet.nlm.nih.gov/</a>
[6]	ECHA, Summary of Classification and Labelling, Harmonised classification - Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation), <a href="https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/59336">https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/59336</a>
[7]	ECHA REACH Annex III Inventory; <a href="https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.052.771">https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.052.771</a>

## Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)

**Overall conclusion: Class 3: Substances that are difficult for classification due to insufficient data**

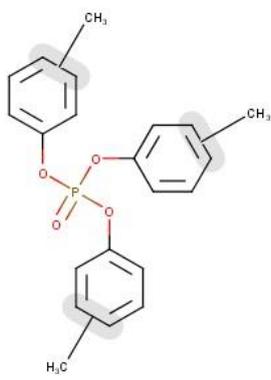
Summary		
<b>Bioaccumulation</b>		
While estimated $K_{ow}$ and BCF values suggest low level of bioaccumulation of OBS, there is insufficient data available to assess whether or not the substance will fulfil the bioaccumulation criteria according to Annex D 1 (c) (i).		
<b>Persistence</b>		
While there is evidence to suggest relatively slow rate of degradation for OBS in the environment, there is insufficient data available on half-lives in environmental compartments (water, soil, sediment) to determine if this substance is likely to meet the Annex D 1 (b) (i) criteria.		
<b>Long-range transport (LRT)</b>		
There is insufficient evidence to indicate is OBS fulfils the Annex D 1 (d) (iii) criteria.		
<b>Ecotoxicity</b>		
There is evidence to suggest OBS will display 'moderate' ecotoxicity, lower than that of PFOS. However, there is insufficient evidence to indicate is OBS fulfils the Annex D 1 (e) criteria.		
<b>Toxicity to human health</b>		
There is insufficient evidence to indicate is OBS fulfils the Annex D 1 (e) criteria.		
General Information		
CAS Name		
CAS Number	70829-87-7	
Chemical name	Sodium p-perfluorous nonenoxybenzene sulfonate	
IUPAC Name		
Structure		
Molecular formula	$C_9F_{17}OC_6H_4SO_3Na$	
Molecular weight	626.22	
Functionality & occurrence	Firefighting foam	
Physico-chemical properties		
Property	Value	References
Vapour Pressure	No data available	
Water solubility	Experimental data:	
Partition coefficient n-octanol/water (Log $K_{ow}$ )	Calculated by ECOSAR v1.10 [2] 4.48	[2]
Partition coefficient	No data available	

<i>air/octanol (Log K<sub>OA</sub>)</i>		
<i>Partition coefficient air/water Partition coefficient (Log K<sub>AW</sub>)</i>	No data available	
<i>Henry's law constant</i>	No data available	
<b>Bioaccumulation</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>BCF</i>	Calculated using BCFBAF v3.01 (EPI Suite 4.11) [2]  log BCF= 3.43  BCF (derived) = 30.88	[2]
<i>BMF/TMF data</i>		
<b>Persistence</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Environmental fate	OBS molecule presents some weak points (i.e. a double bond, an etheric bridge, and a phenylsulfonate moiety) that may cause lower stability [1]  Based on the OECD guideline 301D [2]  Test study of biotic degradation and impact on biochemical oxygen demand (BOD) evaluated by 28 days, indicate OBS is non-readily biodegraded and will potentially be persistent in the natural environment [1, 2]  In terms of abiotic degradability, OBS can be decomposed by UV/H <sub>2</sub> O <sub>2</sub> or sole UV (254 nm) systems - More than 96% OBS is degraded in aqueous solution. However, under both conditions complex by-products were formed and less than 20% of fluorine was mineralized [1].	[1]
Water : half/life	Experimental data:	
Water : other data	No data available	
Soil : half/life	No data available	
Soil : other data	No data available	
Sediment : half/life	No data available	
Sediment : other data	No data available	
<b>Long-range transport</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Half-life : air (exp)	No data available	
Half-life : air (estimated) - EpiSuite	No data available	
LRAT, other data	No data available	
<b>Toxicity</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Ecotoxicity hazard assessment	No existing classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008.  Animal studies of acute hazards to the aquatic environment, based on OECD guideline 203, using zebra fish ( <i>brachydanio rerio</i> ):  Median lethal concentration (96h-LC <sub>50</sub> ) of OBS and PFOS were 31.0 and 17.0 mg/L respectively	[2]

	OBS would therefore fall under Hazard Category 3 according to Globally Harmonized System of Classification and Labelling of Chemicals [2]  (classified as MODERATE ecotoxicity level)	
Human health hazard assessment	No data available	
Additional health hazards:	No data available	
(a) Acute toxicity	No data available	
(b) Mutagenicity	No data available	
(c) Carcinogenicity	No data available	
(d) Toxicity for reproduction	No data available	
(e) Neurotoxicity	No data available	
(f) Immunotoxicity	No data available	
(g) Endocrine disruption	No data available	
(h) Mode of action	No data available	
(i) Acceptable exposure levels	No data available	
<b>Other relevant information</b>		<i>References</i>
A preliminary assessment of acute toxicity and environmental fate indicates that OBS exhibits similar toxicity and environmental persistence to perfluorooctanesulfonic acid (PFOS). [3]		[3]
<b>References</b>		
[1]	Bao, Y. et al. (2017a) First assessment on degradability of sodium p perfluorooctanesulfonate (OBS), a high volume alternative to perfluorooctane sulfonate in fire-fighting foams and oil production agents in China. RSC Adv., 2017, 7, 46948	
[2]	Bao, Y. et al. (2017b) First report on the environmental friendliness of OBS, an alternative to PFOS in fire-fighting foams and oil production agents in China, Organohalogen Compounds Vol. 79, 678-681. Available at: <a href="http://dioxin20xx.org/wp-content/uploads/pdfs/2017/10097.pdf">http://dioxin20xx.org/wp-content/uploads/pdfs/2017/10097.pdf</a>	
[3]	Xu, L. et al., Discovery of a Novel Polyfluoroalkyl Benzenesulfonic Acid around Oilfields in Northern China, Environ. Sci. Technol., 2017, 51 (24), pp 14173–14181.	

## Tricresyl phosphate (TCP)

**Overall conclusion: Class 3: Substances that are difficult for classification due to insufficient data**

Summary	
<p><b>Bioaccumulation</b></p> <p>Based on its physico-chemical properties (<math>K_{ow} &gt; 5</math>) TCP can be expected to bioconcentrate. Highly variable measured BCF values are observed and may not be representative of realistic environmental conditions. It can be concluded that TCP could potentially meet the Annex D (c) (i) criterion for bioaccumulation potential based on its physico-chemical properties but more data are required to fully assess BCF values for this substance.</p>	
<p><b>Persistence</b></p> <p>Relatively short (&lt;30 day) half-life can be expected under aerobic conditions. Under anaerobic conditions, half-life is much longer: &gt;8 weeks in soil, &gt;40 weeks in sediment have been measured. Given the observed rapid partitioning of TCP to sediments observed in the environment, the substance could potentially meet the Annex D 1 (b) (i) criteria under certain environmental conditions.</p>	
<p><b>Long-range transport (LRT)</b></p> <p>An estimated half-life in air for the reaction with OH radicals of &gt;9 hours, suggests the Annex D 1 (d) (iii) criteria may not be met, but there are no monitoring/sampling data available to fully assess the LRT potential of this compound.</p>	
<p><b>Ecotoxicity</b></p> <p>This substance is considered very toxic to aquatic organisms. Notified classification and labelling according to CLP criteria designates this substance as toxic to aquatic life. May cause long-term adverse effects in the aquatic environment, so is therefore considered likely to fulfil the Annex D 1 (e) criteria for ecotoxicity.</p>	
<p><b>Toxicity to human health</b></p> <p>According to ECHA REACH Annex III the substance is suspected as toxic for reproduction. Data is lacking on potential carcinogenic, mutagenic and neurological effects.</p>	
General Information	
CAS Name	Tris(methylphenyl) phosphate
CAS Number	1330-78-5
Chemical name	Tricresyl phosphate
IUPAC Name	Tricresylphosphate
Structure	
Molecular formula	$C_{21}H_{21}O_4P$
Molecular weight	368.36 g/mol
Functionality & occurrence	Aviation hydraulic fluids
Physico-chemical properties	

<i>Property</i>	<i>Value</i>	<i>References</i>
<i>Vapour Pressure</i>	6 x 10 <sup>-7</sup> mmHg (25°C) – experimental, EpiSuite MPBPVP 0.0121 mmHg (25°C) – estimated, EpiSuite MPBPVP  Little reliable data appear to be available for tricresyl phosphate at temperatures around 20-25°C  A vapour pressure of 3.5×10 <sup>-5</sup> Pa at 20°C and 6.6×10 <sup>-5</sup> Pa at 25°C, as obtained from analysis of available data [1]	[1]
<i>Water solubility</i>	Experimental data:  0.1 to 0.36 mg/L [1]  Calculation according to EPISUITE performed with the module WSKOW- v1.41: 0.2073 (25°C)	[1]
<i>Partition coefficient n-octanol/water (Log K<sub>ow</sub>)</i>	5.11 - Experimental value from EPISUITE: as determined by Saeger et al. (1979)  Value of 5.9 also quoted [2]  6.43 (calculation according to EPISUITE performed with the module KOWWIN, v1.68)	[2]
<i>Partition coefficient air/octanol (Log K<sub>OA</sub>)</i>	9.591 (calculated using EPISUITE KOAWIN v1.10)	
<i>Partition coefficient air/water Partition coefficient (Log K<sub>AW</sub>)</i>	No data available	
<i>Henry's law constant</i>	0.036 Pa m <sup>3</sup> /mol at 20°C and 0.068 Pa m <sup>3</sup> /mol at 25°C [1]  Calculated using EPISUITE HENRYWIN v 3.2:  5.35 x 10 <sup>-8</sup> atm m <sup>3</sup> /mole (Bond Method)	[1]
<b>Bioaccumulation</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>BCF</i>	Calculation using EPISUITE BCFBAF model (using K <sub>ow</sub> = 5.11): BCF = 163.6  According to the Justification for the selection of a candidate CoRAP substance: In a biodegradation study, 24.2% degradation was observed in a 28-day ready biodegradation test. [3]  KOWWIN predicts a log K <sub>ow</sub> of 6.3.  A wide variability in BCF values is observed in experimental animal studies (as quoted in [1])  A BCF range of 165 to 3700 is noted for fish species (fathead minnows) [2]  Including: <ul style="list-style-type: none"> <li>• 400-800 (<i>Alburnus alburnus</i>)</li> <li>• 1,589 (<i>Lepomis macrochirus</i>)</li> <li>• 784-2,768 (<i>Oncorhynchus mykiss</i>)</li> <li>• 596-2,199 (<i>Pimephales promelas</i>)</li> </ul> A BCF of 800 l/kg is used in an assessment for tricresyl phosphate [1]	[1], [3], [4]

	<p>TCP has, because of its physico-chemical properties, a high potential for bioaccumulation. Taking into account the ready biodegradability of TCP, these data should be viewed as probable overestimates, and it is suggested that little bioaccumulation would occur with environmentally realistic TCP exposure. [4]</p> <p>None of the exposures were considered to be representative of realistic environmental levels. More-over the bioconcentration factor (BCF) measured in the laboratory must be considered as a bioaccumulation potential rather than an absolute bioaccumulation factor [4].</p>	
<i>BMF/TMF data</i>	n/a	
<b>Persistence</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Environmental fate	<p>According to the Justification for the selection of a candidate CoRAP substance:</p> <p>The P status of the substance is uncertain [3]</p> <p>Many studies have shown that tricresyl phosphate degrades rapidly in a variety of aerobic test systems. In standard tests, tricresyl phosphate can be considered to be readily biodegradable [3]</p> <p>Indicated that volatilisation from water is likely to be limited [1]</p>	[1], [3]
Water : half/life	<p>Experimental data:</p> <p>Biodegradation half-lives - 15 days [1]</p> <p>Relatively rapid (&lt;30 day) degradation noted for aerobic conditions; very slow &gt;8 week) degradation noted for anaerobic conditions (although no half-life data presented). [1]</p> <p>The second-order alkaline hydrolysis rate constant for tricresyl phosphate has been reported to be <math>0.27 \text{ k/M}^{-1} \text{ sec}^{-1}</math> at 27°C which corresponds to half-lives of 319 days at pH 7, 31.9 days at pH 8 and 3.19 days at pH 9 [2]</p> <p>Based on hydrolysis data for similar triaryl phosphates, the neutral hydrolysis half-life for tricresyl phosphate at 20-25°C is on the order of 1 month or longer [2].</p> <p>Modelled half-life in water due to volatilisation (using EPISUITE) (based on based upon a Henry's Law constant of <math>8.08 \times 10^{-7} \text{ atm-cu m/mole}</math>) 58 days (river water), 640 days (lake water)</p> <p>The estimated volatilization half-life from a model pond is greater than 20 years when adsorption is considered [2].</p> <p>Tricresyl phosphate does not absorb UV wavelengths &gt;290 nm and, therefore, is not expected to be susceptible to direct photolysis by sunlight [2].</p>	[1], [2]
Water : other data	<p>The available information indicates that tricresyl phosphate undergoes hydrolysis However, since the pH in the environment is generally outside the range where rapid hydrolysis would be expected, and since other biotic removal mechanisms are likely to be much more important than hydrolysis for tricresyl phosphate at lower pH, the rate of hydrolysis of tricresyl phosphate will be assumed to be zero.</p>	[1]

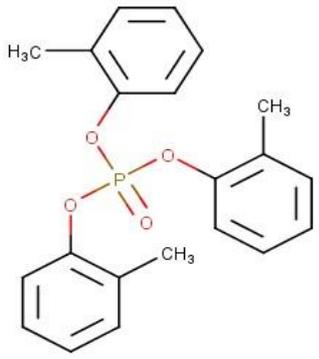
	The rate of photolysis of tricresyl phosphate can assumed to be zero.													
Soil : half/life	Biodegradation half-lives - 30 days [1]	[1]												
Soil : other data	Estimated Koc value ( $4.5 \times 10^4$ ) suggests that tricresyl phosphate is expected to be immobile in soil [2]  Henry's Law constant indicates that volatilization from moist soil surfaces or dry soil is not expected to be an important fate process.													
Sediment : half/life	Biodegradation half-lives - 300 days (deeper sediment layers are anaerobic, assumes no anaerobic degradation)	[1]												
Sediment : other data	Using bottom sediment from a river, the tricresyl phosphate isomers were found to adsorb strongly to the sediment; it was further observed that tricresyl phosphate in the water column adsorbed to sediment and precipitated to the bottom.  A sediment sorption constant (Kd) of 400 has been reported for tricresyl phosphate in a marine sediment. In aquatic persistence studies, tricresyl phosphate and other aryl phosphates have been observed to partition rapidly from the water column to sediment; concentrations in the sediment become much greater than concentrations in the water column.	[2]												
<b>Long-range transport</b>														
<i>Property</i>	<i>Value</i>	<i>References</i>												
Half-life : air (experimental)	A rate constant for reaction of tricresyl phosphate with atmospheric hydroxyl radicals of $1.44 \times 10^{-11}$ cm <sup>3</sup> /molecule s can be estimated from its structure  Using an atmospheric hydroxyl radical concentration of $5 \times 10^5$ molecules/cm <sup>3</sup> , a half-life for the reaction in air is estimated to be <b>27.5 hours</b> [1]  When applying the US Environmental Protection Agency (EPA) modelling program AOPWIN (v1.9), a half-life of about <b>9.4 hours</b> can be calculated, using a rate constant for the hydrogen abstraction (K <sub>OH</sub> ) of $13.7 \times 10^{-12}$ cm <sup>3</sup> /s per molecule and a hydroxyl radical concentration of $1.5 \times 10^6$ molecules /cm <sup>3</sup> .	[1]												
LRAT, other data	No sampling/monitoring data available													
<b>Toxicity</b>														
<i>Property</i>	<i>Value</i>	<i>References</i>												
Ecotoxicity hazard assessment	Notified classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008 [5]:  <table border="1" data-bbox="497 1512 1209 1675"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>Aquatic Chronic</td> <td>1</td> <td>H410</td> <td>SEVERE</td> </tr> <tr> <td>Aquatic Acute</td> <td>1</td> <td>H400</td> <td>LOW</td> </tr> </tbody> </table> According to the classification provided by companies to ECHA in REACH registrations this substance is very toxic to aquatic life [1]  Acute toxicity data are available for fish, invertebrates and algae. The lowest results from the more reliable standard tests are a 96-hour LC50 of 0.26 mg/L for fish ( <i>Oncorhynchus mykiss</i> ), a 48-hour EC50 of 0.27 mg/L for <i>Daphnia magna</i> and a 96-hour EC50 of 1.5 mg/l for the algae <i>Scenedesmus pannonicus</i> [1].	Classification	Category	Code	Indicative Toxicity level	Aquatic Chronic	1	H410	SEVERE	Aquatic Acute	1	H400	LOW	[1], [5]
Classification	Category	Code	Indicative Toxicity level											
Aquatic Chronic	1	H410	SEVERE											
Aquatic Acute	1	H400	LOW											

	<p>The algal result is above the water solubility of the test substance. Based on these data the following classification is appropriate: N: Dangerous for the environment.</p> <p>R50/53: Very toxic to aquatic organisms. May cause long-term adverse effects in the aquatic environment. [1]</p>																													
Human health hazard assessment	<p>Notified classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008 [5]:</p> <table border="1"> <thead> <tr> <th>Classification</th> <th>Category</th> <th>Code</th> <th>Indicative Toxicity level</th> </tr> </thead> <tbody> <tr> <td>Repr.</td> <td>2</td> <td>H361</td> <td>HIGH</td> </tr> <tr> <td>Skin Sens.</td> <td>1B</td> <td>H317</td> <td></td> </tr> <tr> <td>STOT SE</td> <td>1</td> <td>H370</td> <td></td> </tr> <tr> <td>STOT RE</td> <td>2</td> <td>H373</td> <td></td> </tr> <tr> <td>Eye Irrit.</td> <td>2</td> <td>H319</td> <td></td> </tr> <tr> <td>Acute Tox.</td> <td>4</td> <td>H302</td> <td></td> </tr> </tbody> </table> <p>According to the Justification for the selection of a candidate CoRAP substance [3]:</p> <p>For human health, our primary concern relates to the potential neurotoxic effects of (isomers of) TCP, especially due the use of TCP as additive in oils used in airplane engines and subsequent exposure of TCP, or breakdown products, to cabin crew, pilots and passengers [3]</p> <p>The lowest NOEC value from the available tests is 0.0032 mg/l; it may also be classifiable as a Category 2 reprotoxin. The substance therefore meets the T criterion [1]</p>	Classification	Category	Code	Indicative Toxicity level	Repr.	2	H361	HIGH	Skin Sens.	1B	H317		STOT SE	1	H370		STOT RE	2	H373		Eye Irrit.	2	H319		Acute Tox.	4	H302		[1], [3], [5]
Classification	Category	Code	Indicative Toxicity level																											
Repr.	2	H361	HIGH																											
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Eye Irrit.	2	H319																												
Acute Tox.	4	H302																												
Additional health hazards:	No additional data																													
(j) Acute toxicity	No additional data																													
(k) Mutagenicity	Numerous animal testing studies, negative for mutagenicity	[2], [6]																												
(l) Carcinogenicity	Numerous animal testing studies, negative for carcinogenicity	[2], [6]																												
	TCP is not listed by the IARC																													
(m) Toxicity for reproduction	<p>According to ECHA REACH Annex III:</p> <p>#Suspected toxic for reproduction: Recommended for R category 2 by IMAP</p> <p># Suspected to meet STOT RE classification: Recommended for STOT RE 2 by IMAP</p>	[7]																												
(n) Neurotoxicity	Some experimental data in animal tests suggest limited neurological effects but relatively scarce data on these effects is available	[2]																												
(o) Immunotoxicity	No additional data																													
(p) Endocrine disruption	No additional data																													
(q) Mode of action	No additional data																													

(r) Acceptable exposure levels	GESTIS International Limit Values : 0.1 mg/m <sup>3</sup> - eight hours 2 mg/m <sup>3</sup> – short term (15 minutes average value)	[8]
<b>Other relevant information</b>		<i>References</i>
According to the Justification for the selection of a candidate CoRAP substance [3]  Information on toxicological properties, use and exposure may be needed to clarify the concern on, amongst others, the neurotoxic potential of (isomers of) TCP and other potential neurotoxic substances formed during intended use of TCP as additive in oils used in airplane engines. Furthermore, there is (amongst others) as yet insufficient information in the dossier regarding the exposure of air cabin crew, pilots and passengers to TCP, or breakdown products, during intended use of TCP as additive in oils used in airplane engines.		[3]
<b>References</b>		
[1]	Environment Agency (2009) Environmental risk evaluation report: Tricresyl phosphate (CAS no. 1330-78-5) <a href="https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/290861/scho0809bquj-e-e.pdf">https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/290861/scho0809bquj-e-e.pdf</a>	
[2]	U.S National Libraray of Medicine, Toxicology Data Network (TOXNET) Hazardous Substances Data Bank (HSDB); <a href="https://toxnet.nlm.nih.gov/">https://toxnet.nlm.nih.gov/</a>	
[3]	ECHA (2014) Justification for the selection of a candidate CoRAP substance: Tris(methylphenyl)phosphate – UPDATE – <a href="https://echa.europa.eu/documents/10162/2eee808e-98ca-4a03-80e7-4c05859fb18f">https://echa.europa.eu/documents/10162/2eee808e-98ca-4a03-80e7-4c05859fb18f</a>	
[4]	WHO (1990) International Programme on Chemical Safety, Environmental Health Criteria 110, Tricresyl Phosphate, <a href="http://www.inchem.org/documents/ehc/ehc/ehc110.htm">http://www.inchem.org/documents/ehc/ehc/ehc110.htm</a>	
[5]	ECHA, Summary of Classification and Labelling, Harmonised classification - Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation), <a href="https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/72582">https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/72582</a>	
[6]	U.S National Libraray of Medicine, Toxicology Data Network (TOXNET) Hazardous Substances Data Bank (HSDB); <a href="https://toxnet.nlm.nih.gov/">https://toxnet.nlm.nih.gov/</a>	
[7]	ECHA REACH Annex III Inventory: <a href="https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.014.136">https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.014.136</a>	
[8]	IFA, Institut für Arbeitsschutz der Deutschen Unfallversicherung. GESTIS International Limit Values <a href="http://limitvalue.ifa.dguv.de/">http://limitvalue.ifa.dguv.de/</a>	

## o-Tolyl phosphate

**Overall conclusion: Class 2: Substances considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data**

Summary	
<p><b>Bioaccumulation</b></p> <p>A calculated BCF value of &gt; 1000, and <math>K_{OW} &gt; 5</math> suggest a potential for bioaccumulation, so it is likely this substance can meet the Annex D (c) (i) criterion for bioaccumulation potential, however more data would be required to assess if the cut-off value of 5000 would be met under environmental conditions.</p>	
<p><b>Persistence</b></p> <p>This substance is, according to ECHA Annex III inventory, suspected persistent in the environment.</p> <p>Relatively long half lives up to &gt; 1 year in water are observed for volatilisation and hydrolysis, with shorter half lives (&lt;1 month) for biodegradation. There is a lack of information available for half-life in soil and sediment. Overall, there is evidence to indicate that the Annex D 1 (b) (i) could be met, but more data are required to carry out a full assessment against Annex D criteria.</p>	
<p><b>Long-range transport (LRT)</b></p> <p>A relatively short (&lt;10 hour) estimate half-life in air for the reaction of o-Tolyl phosphate with OH radicals, suggests the Annex D 1 (d) (iii) criteria is not likely to be met, but there are no monitoring/sampling data available to fully assess the LRT potential of this compound.</p>	
<p><b>Ecotoxicity</b></p> <p>This substance is, according to ECHA Annex III inventory the substance is suspected hazardous to the aquatic environment. Notified classification and labelling according to CLP criteria designates this substance as toxic (chronic) to aquatic life, so can therefore be considered likely to fulfil the Annex D 1 (e) criteria for ecotoxicity.</p>	
<p><b>Toxicity to human health</b></p> <p>Notified classification and labelling according to CLP criteria designates this substance as mutagenic (1B). This substance is, according to ECHA Annex III inventory, suspected mutagenic and toxic for reproduction, so can therefore be considered likely to fulfil the Annex D 1 (e) criteria for human health.</p>	
General Information	
CAS Name	o-Tolyl phosphate (TOCP, TOTP)
CAS Number	78-30-8
Chemical name	o-Tolyl phosphate (three tricresyl phosphate isomers)
IUPAC Name(s)	Phosphoric acid, tris(2-methylphenyl) ester ; Tri-o-cresyl Phosphate; Tri-o-tolyl Phosphate; tris(2-methylphenyl) phosphate
Structure	
Molecular formula	$C_{21}H_{21}O_4P$

Molecular weight	368.37 g/mol	
Functionality & occurrence	Aviation hydraulic fluids	
<b>Physico-chemical properties</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>Vapour Pressure</i>	EPI SUITE Vapour Pressure Estimations (MPBPVP v1.43):  0.0121 (mm Hg, 25°C): (Mean VP of Antoine & Grain methods) 1.62 (Pa, 25°C): (Mean VP of Antoine & Grain methods)  Experimental database) 6.00 x 10 <sup>-7</sup> mm Hg (8.0 x 10 <sup>-5</sup> Pa) at 25°C [1]	[1]
<i>Water solubility</i>	Estimated using US EPA; Estimation Program Interface (EPI) Suite (WSKOW v1.41):  0.2073 mg/L (at 25°C)  Experimental value: 0.36 mg/L	
<i>Partition coefficient n-octanol/water (Log K<sub>OW</sub>)</i>	log K <sub>ow</sub> = 6.34 Estimated US EPA; Estimation Program Interface (EPI) Suite (KOWWIN v1.68) [1]  Experimental database: log K <sub>ow</sub> = 5.11	[1]
<i>Partition coefficient air/octanol (Log K<sub>OA</sub>)</i>	Estimation Program Interface (EPI) Suite. KOAWIN v1.10 (25°C): 9.591	
<i>Partition coefficient air/water Partition coefficient (Log K<sub>AW</sub>)</i>	No data available	
<i>Henry's law constant</i>	Estimation Program Interface (EPI) Suite. HENRYWIN v3.20: 5.35 x 10 <sup>-8</sup> atm m <sup>3</sup> /mole	
<b>Bioaccumulation</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
<i>BCF</i>	Estimated based on EpiSuite BCFBAF model:  Arnot-Gobas method: BCF=1280  An estimated BCF of 1060 was calculated in fish for tri-o-cresyl phosphate(SRC), using an estimated log K <sub>OW</sub> of 6.34 (1) and a regression-derived equation  According to a classification scheme, this BCF suggests the potential for bioconcentration in aquatic organisms is very high, provided the compound is not metabolized by the organism(SRC)  Bioconcentration factors for C <sub>14</sub> tri-m-cresyl phosphate, determined by total radioactivity, in rainbow trout and fathead minnows using short-term static exposure were 784 and 596, respectively  A maximum concentration of 7.3 µg/g C <sub>14</sub> tri-m-cresyl phosphate was observed in fathead minnows 8 hours after the chemical's application to the artificial pond, this represents a concentration factor of about 348.	[1]
<i>BMF/TMF data</i>	n/a	
<b>Persistence</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Environmental fate	According to the ECHA REACH Annex III inventory [2]	[2]

	# Suspected persistent in the environment: The Danish QSAR database contains information indicating that the substance is predicted as non-readily biodegradable.	
Water : half/life	<p>Volatilisation from water (estimated using EPISUITE model; <math>8.08 \times 10^{-7}</math> atm m<sup>3</sup>/mole)</p> <p>Half-life from model lake: 58 days Half-life from model river: 640 days</p> <p>Estimated hydrolysis half-lives are 1.2 years, 43 days and 4.3 days at pH 7, pH 8 and pH 9, respectively at 25°C</p> <p>Biodegradation is an important fate process .The half-life of tri-o-cresyl phosphate in lake water, river water and sediment bottoms has been observed to range from less than 3 to 12 days.</p>	
Water : other data	<p>Tri-o-cresyl phosphate does not absorb UV wavelengths &gt;290 nm and, therefore, is not expected to be susceptible to direct photolysis by sunlight.</p> <p>If released into water, tri-o-cresyl phosphate is expected to adsorb to suspended solids and sediment based upon the estimated K<sub>oc</sub>.</p>	[1]
Soil : half/life	No data available	
Soil : other data	<p>If released to soil, tri-o-cresyl phosphate is expected to have no mobility based upon an estimated K<sub>OC</sub> of <math>4.7 \times 10^4</math>. Volatilization from moist soil surfaces is expected to be an important fate process based upon an estimated Henry's Law constant of <math>1.9 \times 10^{-6}</math> atm-cu m/mole.</p> <p>Biodegradation in soil is expected to be an important fate based upon observed ready biodegradability in water and sediment</p>	[1]
Sediment : half/life	No data available	
Sediment : other data	Biodegradation in soil is expected to be an important fate based upon observed ready biodegradability in water and sediment	[1]
<b>Long-range transport</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Half-life : air (exp)		
Half-life : air (estimated) - EpiSuite	<p>Estimated using EPISUITE AOPWIN:</p> <p>9.37 hours (based on overall OH rate constant <math>13.7 \times 10^{-12}</math> cm<sup>3</sup>/molecules/sec ; OH concentration of <math>1.5 \times 10^6</math> OH/cm<sup>3</sup>, 12 hour day)</p> <p>If released to air, an estimated vapor pressure of <math>1.9 \times 10^{-6}</math> mm Hg at 25°C indicates tri-o-cresyl phosphate will exist in both the vapor and particulate phases in the atmosphere. Vapor-phase tri-o-cresyl phosphate will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 1.2 days.</p>	[1]
LRAT, other data	Monitoring studies have observed that tri-o-cresyl phosphate is removed from the atmosphere by both wet and dry deposition.	[1]
<b>Toxicity</b>		
<i>Property</i>	<i>Value</i>	<i>References</i>
Ecotoxicity hazard assessment	Notified classification and labelling according to CLP criteria [3]:	[3], [4]

	<b>Classification</b>	<b>Category</b>	<b>Code</b>	<b>Indicative Toxicity level</b>	
	Aquatic Chronic*	2	H411	HIGH	
	* Classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008  According to the ECHA REACH Annex III inventory [4]:  # Suspected hazardous to the aquatic environment: Fish Acute Toxicity model (KNN/Read-Across) in VEGA (Q)SAR platform predicts that the chemical has a 96h LC50 of 0.8375 mg/L (EXPERIMENTAL value); The Danish QSAR database contains information indicating that the substance has a 96h EC50 to green algae of <1 mg/L				
Human health hazard assessment	Notified classification and labelling according to CLP criteria [3]:				
	<b>Classification</b>	<b>Category</b>	<b>Code</b>	<b>Indicative Toxicity level</b>	
	Mutagenicity	1B	H340	SEVERE	
	STOT SE*	1	H370		
	Acute Tox. 2	2	H330		
	Acute Tox. 4	4	H302		
	* Classification according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Regulation (EC) No 1272/2008.				
Additional health hazards:					
(a) Acute toxicity	Human toxicity studies:  LD (human oral) = 1.0 g/kg				[1]
(b) Mutagenicity	According to the ECHA REACH Annex III inventory [2]: # Suspected mutagen: CAESAR Mutagenicity model in VEGA (Q)SAR platform predicts that the chemical is Mutagen (EXPERIMENTAL value); mutagen according to ISSSTY  Mutagenicity indicated in animal test studies using rat (liver)				[1], [2]
(c) Carcinogenicity	Not classifiable as a human carcinogen				[2]
(d) Toxicity for reproduction	According to the ECHA REACH Annex III inventory [2] # Suspected toxic for reproduction: Developmental/Reproductive Toxicity library (PG) in VEGA (Q)SAR platform predicts that the chemical is Toxicant (moderate reliability)  Is known to have a deleterious effect on the male reproductive system in animals, but the precise mechanism is yet to be elucidated [1]  TOCP produced toxic effects on both male and female Reproductive Systems when Long-Evans rats were given doses of 0 to 400 mg/kg [1]				[1], [2]
(e) Neurotoxicity	Reported to induce delayed neurotoxicity in humans and animals – wide number of studies  Most commercial isopropylated triaryl phosphates lacked urotoxic in both acute and subchronic hen OPIDN studies.				[1], [4]

	<p>As an example, when 3% TCP in aviation oil was dosed acutely at 5000 mg/kg, or for 90 days at 1000 mg/kg/day, no delayed neurotoxicity was noted</p> <p>Ingested TOCP was the cause of "ginger jake paralysis" or "jake leg," a form of organophosphate induced delayed neuropathy (OPIDN). The minimum paralytic dose in humans by ingestion is approximately 10 to 30 mg/kg.</p> <p>Reported adverse effects after occupational exposure include reduced plasma cholinesterase activity and peripheral neuropathy. No neurological abnormalities were found after careful examination of workers exposed over several months to hydraulic fluid containing 21% TOCP and air concentrations of 1.5 mg/m<sup>3</sup>[4].</p>	
(f) Immunotoxicity	No data available	
(g) Endocrine disruption	No data available	
(h) Mode of action	No data available	
(i) Acceptable exposure levels	<p>GESTIS International Limit Values – 8 hour Limit Value 0.1 mg/m<sup>3</sup> [5]</p> <p>NIOSH Recommended Exposure Limit: 10 Hour Time-Weighted Average: 0.1 mg/cu m, skin [6]</p> <p>OSHA Permissible Exposure Limit - 8-hr Time Weighted Avg: 0.1 mg/cu m. [1]</p>	[1],[5],[6]
<b>Other relevant information</b>		<i>References</i>
None		
<b>References</b>		
[1]	U.S National Libraray of Medicine, Toxicology Data Network (TOXNET) Hazardous Substances Data Bank (HSDB); <a href="https://toxnet.nlm.nih.gov/">https://toxnet.nlm.nih.gov/</a>	
[2]	ECHA REACH Annex III Inventory: <a href="https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.001.003">https://echa.europa.eu/information-on-chemicals/annex-iii-inventory/-/dislist/details/AIII-100.001.003</a>	
[3]	ECHA, Summary of Classification and Labelling, Harmonised classification - Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation), <a href="https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/17760">https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/17760</a>	
[4]	U.S National Libraray of Medicine, Haz-Map: <a href="https://hazmap.nlm.nih.gov/category-details?table=copytblagents&amp;id=669">https://hazmap.nlm.nih.gov/category-details?table=copytblagents&amp;id=669</a>	
[5]	IFA, Institut fur Arbeitsschutz der Deutschen Unfallversicherung. GESTIS International Limit Values <a href="http://limitvalue.ifa.dguv.de/">http://limitvalue.ifa.dguv.de/</a>	
[6]	NIOSH. NIOSH Pocket Guide to Chemical Hazards. Department of Health & Human Services, Centers for Disease Control & Prevention. National Institute for Occupational Safety & Health. DHHS (NIOSH) Publication No. 2010-168 (2010). Available from: <a href="http://www.cdc.gov/niosh/npg">http://www.cdc.gov/niosh/npg</a>	