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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

The annex to the present note sets out a report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride prepared by the Persistent Organic Pollutants Review Committee at its eighteenth meeting on the basis of the draft report contained in document UNEP/POPS/POPRC.18/INF/19. The present note, including its annex, has not been formally edited.

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Annex*

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

September 2022

* The studies and other information referred to in this document do not necessarily reflect the views of the Secretariat, the United Nations Environment Programme (UNEP) or the United Nations. The designations employed and the presentation of the material in such studies and references do not imply the expression of any opinion whatsoever on the part of the Secretariat, UNEP or the United Nations concerning geopolitical situations or the legal status of any country, territory, area or city or its authorities.

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Executive summary

1. At its fourth meeting in 2009, the Conference of the Parties listed perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) in Annex B to the Stockholm Convention on Persistent Organic Pollutants. At its ninth meeting in 2019, the Conference of the Parties, taking into account the reports submitted by the POPs Review Committee[1] and the Secretariat[2] and the recommendations by the Committee,[3] amended the listing for PFOS, its salts and PFOSF in Annex B to the Convention.[4]

2. The present report is an update of the report on the assessment of alternatives to PFOS, its salts and PFOSF conducted by the POPs Review Committee in 2018 (UNEP/POPS/POPRC.14/INF/13), taking into account the additional information submitted to the Secretariat by Parties and observers,[5] and the reports and recommendations previously produced by the Committee.

Insect baits with sulfluramid (CAS No. 4151-50-2) as an active ingredient for control of leaf-cutting ants from Atta spp. and Acromyrmex spp. for agricultural use only

3. The acceptable purpose for "insect baits for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp." was amended in decision SC-9/4 to "insect baits with sulfluramid (CAS No. 4151-50-2) as an active ingredient for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. for agricultural use only".

4. A wide range of commercially available alternatives (pesticides) on the market; techniques for application (e.g., dry powder formulation) have been developed. Non-chemical (mechanical, cultural, and biological) control methods have been developed but are not fully commercialised or available in all locations.

5. The Committee encourages additional research and development of alternatives and, where alternatives are available, that they be implemented, as well as additional research and development of alternatives, while maintaining the acceptable purpose for the time being.

6. 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.

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

7. Taking into account the availability of alternatives for PFOS, its salts and PFOSF and the recommendation by the Committee, the Conference of the Parties amended the exemptions for metal plating in decision SC-9/4 to limit the specific exemption under the listing to "metal plating (hard metal plating) only in closed-loop systems" and delete the acceptable purpose.

8. A 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&D activity and are less readily available. A number of process-based approaches to replace PFOS are also identified and are commercially available e.g., the High Velocity Oxygen Fuel (HVOF) process. Chromium(III) plating is available as an alternative to chromium(VI) plating for some decorative plating applications.

9. Noting that the specific exemption is time limited, the Committee recommends that Parties consider not to replace the use of PFOS, its salts and PFOSF for hard metal plating with chemicals that may exhibit persistent organic pollutant characteristic in Annex D, including the degradation products.

Fire-fighting foam

10. The industry standard for fire-fighting foams is rapidly switching from C_8 fluorinated compounds towards fluorine-free substances or toshort-chained per- and polyfluoroalkyl substances (PFASs), mainly 6:2 fluorotelomer compounds. A 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 are available for which trade names are known but chemical formulation is not, due to trade secrets. Alternative processes/practices have also been developed to minimise the release of PFOS from certain applications e.g., training operations.

11. 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 use of PFOS, its salts and PFOSF for fire-fighting foam is available a specific exemption for the use of fire-fighting foam for liquid fuel vapour suppression and liquid fuel

[1] UNEP/POPS/POPRC.14/INF/13.

[2] UNEP/POPS/COP.9/INF/12.

[3] Decision POPRC-14/3.

[4] Decision SC-9/4.

[5] http://chm.pops.int/tabid/9105/Default.aspx.

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.

12. The Committee recognized that a transition to the use of short-chain 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.

1 Introduction

1.1 Background and objectives

13. At its fourth meeting 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.

14. At its ninth meeting in 2019, the Conference of the Parties, by decision SC-9/4, amended the listing for PFOS, its salts and PFOSF in Annex B to the Convention as follows, taking into account the reports submitted by the POPs Review Committee[6] and the Secretariat[7] and the recommendations by the Committee.[8]

Chemical	*Activity*	*Acceptable purpose or specific exemption*
Perfluorooctane sulfonic acid (CAS No. 1763-23-1), its salts[a] and perfluorooctane sulfonyl fluoride (CAS No. 307-35-7) [a] For example: potassium perfluorooctane sulfonate (CAS No. 2795-39-3); lithium perfluorooctane sulfonate (CAS No. 29457-72-5); ammonium perfluorooctane sulfonate (CAS No. 29081-56-9); diethanolammonium perfluorooctane sulfonate (CAS No. 70225-14-8); tetraethylammonium perfluorooctane sulfonate (CAS No. 56773-42-3); didecyldimethylammonium perfluorooctane sulfonate (CAS No. 251099-16-8)	Production	**Acceptable purpose**: In accordance with part III of this Annex, production of other chemicals to be used solely for the use below. Production for uses listed below. **Specific exemption**: None
	Use	**Acceptable purpose**: In accordance with part III of this Annex for the following acceptable purpose, or as an intermediate in the production of chemicals with the following acceptable purpose: • Insect baits with sulfluramid (CAS No. 4151-50-2) as an active ingredient for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. for agricultural use only **Specific exemption**: • Metal plating (hard-metal plating) only in closed-loop systems • Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, in accordance with paragraph 10 of part III of this Annex

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.

16. The ultimate aim being that safer alternatives should replace the need for acceptable purposes and specific exemptions for the chemicals listed 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.

17. To assist transition to safer alternatives, at its fifth meeting, the 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.[9] At its twelfth meeting, the Committee finalized the consolidated guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals.[10]

1.2 Structure of the report

18. The present report is an update of the report on the assessment of alternatives to PFOS, its salts and PFOSF conducted by the Committee in 2018 (UNEP/POPS/POPRC.14/INF/13), taking into account the additional

[6] UNEP/POPS/POPRC.14/INF/13.

[7] UNEP/POPS/COP.9/INF/12.

[8] Decision POPRC-14/3.

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

[10] UNEP/POPS/POPRC.12/INF/15/Rev.1.

information submitted to the Secretariat by Parties and observers,[11] and the reports and recommendations previously produced by the Committee (see section 1.3).

19. In section 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.

20. 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 alternatives. The discussion of “suitability” of alternatives considers the available information on the economic viability and technical feasibility of 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.

21. In section 3, an assessment of the health and environmental effects of alternatives, including POPs characteristics (based on Annex D) and other hazards is provided. Note that 40 substances and 11 commercial brands have been 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. Furthermore, 40 substances and 11 commercial brands have been considered in document UNEP/POPS/POPRC.14/INF/13. The assessment of POPs characteristics as part of this report is not intended to imply that the Committee has fully considered whether alternative chemicals have met the Annex D criteria.

22. In section 4, a summary table of overall conclusions and recommendations is provided.

1.3 Source of information

23. In decision POPRC-17/8, the Committee invited Parties and observers to provide to the Secretariat, by 15 March 2022, information on PFOS, its salts and PFOSF using the form set out in the terms of reference for the assessment of alternatives to PFOS, its salts and PFOSF.[12] The information submitted by Parties and observers is available on the Stockholm Convention website[13] and summarized in appendix 1 to the present report.

24. In addition to the information submitted by Parties and observers, 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;

[11] http://chm.pops.int/tabid/9105/Default.aspx.

[12] UNEP/POPS/POPRC.17/INF/13/Rev.1.

[13] http://chm.pops.int/tabid/9105/Default.aspx.

(i) Guidance on best available techniques and best environmental practices for the use of perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and their related compounds listed under the Stockholm Convention (2021);[14]

(j) UNEP/POPS/POPRC.13/7/Add.2: Risk management evaluation on PFOA, its salts and PFOA-related compounds;

(k) UNEP/POPS/POPRC.14/6/Add.2: Further assessment of information on PFOA, its salts and PFOA-related compounds;

(l) UNEP/POPRC.14/INF/13: Report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride;

(m) Decision POPRC-14/3: Evaluation of perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) pursuant to paragraphs 5 and 6 of part III of Annex B to the Stockholm Convention.

25. Other publications consulted are listed in the reference section.

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

2.1 Introduction

26. 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 section 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 status of this use in the context of the Convention, and which Parties have notifications for the production or use of PFOS and related compounds for these applications.

27. The consideration of the availability, suitability and implementation of alternatives, 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 affect 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.

28. 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 expired. In these cases, a brief overview of available information is provided.

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

2.2.1 Introduction and background

29. The acceptable purpose for "insect baits for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp." was amended in decision SC-9/4 to "insect baits with sulfluramid (CAS No. 4151-50-2) as an active ingredient for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. for agricultural use only". This use is considered as open applications according to document UNEP/POPS/POPRC.7/INF/22/Rev.1.

[14] http://chm.pops.int/tabid/3170/Default.aspx.

30. As of July 2022, only Brazil is registered for production and use of this acceptable purpose.[15] Vietnam indicated in its submission on 1 July 2022 that after assessing and summing up the continued need for PFOS, Vietnam is preparing to submit the notification of acceptable purpose for PFOS to the Secretariat.[16]

31. 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.[17]

32. Leaf cutting ants are also noted for their important ecological role,[18] 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.[19]

33. 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.

34. 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.

35. The use of chemical control with toxic baits containing *N*-ethyl perfluorooctane sulfonamide (sulfluramid) is considered a practical, economical and operational approach to controlling leaf cutting ants.[20] 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.[21] 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 advertised for purchase and/or available in retail outlets noted the concentration of active ingredient ranged from 0.01% to 0.3%.

36. 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).

37. A study by Zabaleta et al. (2018) 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 was noted. Formation of other breakdown products including perfluorooctane sulfonamido acetate (FOSAA), perfluorooctane sulfonamide (FOSA), and perfluorooctanoic acid (PFOA) was also observed. However, 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.

38. The results of the Zabaleta et al. (2018) study provided evidence 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

[15] http://chm.pops.int/tabid/794/Default.aspx.

[16] http://chm.pops.int/tabid/9105/Default.aspx.

[17] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[18] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[19] https://hms.harvard.edu/news/ants-antifungals.

[20] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[21] UNEP/POPS/POPRC.12/INF/15/Rev.1.

is required.[22] The industry association ABRAISCA (2018) report that research is ongoing to evaluate with the insect bait with sulfluramid may degrade into PFOS in Brazilian soils.

39. 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 PFASs were shown to be dominated by PFOS and perfluorooctane sulfonamide (FOSA) for each environmental matrix. The mean ∑PFOS concentration measured in soils and eucalyptus leaves was 1,490 pg/g. The authors suggested, based on their observations, that sulfluramid can be considered indirect source of PFASs including PFOS to the Brazilian environment.

40. 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).

41. This section updates 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.

2.2.2 Availability of alternatives

42. 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 1. This compiles information from previously published sources (e.g., UNEP/POPS/POPRC.12/INF/15; BAT/BEP guidance) and more recent submissions from Parties and observers.

2.2.2.1 Chemical alternatives

43. 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. 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 is no longer used in insect baits in Brazil for control leaf cutting ants (Brazil, 2018).

44. The reported chemical alternatives to sulfluramid considered as pesticides for leaf cutting ants are: fipronil, deltamethrin, fenitrothion and hydramethylnon (see Table 1). In principle these pesticides are available on the world market; however, they are not all freely available everywhere.[23] 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.

45. There are two alternative chemical methods that have been developed as a complementary form insect bait to the control of leaf-cutting ants:[24]

(a) Thermonebulizable solutions (thermal fogging): generation of ultra-fine droplets in a range of 1–50μm 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.

46. 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*.

2.2.2.2 Non-chemical alternatives/alternative technologies

47. A wide range of non-chemical methods have also been developed with the aim of controlling leaf cutting ants. 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: for example through introduction of different and more varied plant species;

[22] http://chm.pops.int/tabid/6173/Default.aspx.

[23] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[24] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

(b) Cultural control: conventional soil preparation by ploughing and harrowing leading to the mortality of newly formed Atta nests;

(c) Physical/mechanical controls: physically excavating the ant nests for queen ant removal;

(d) Barriers: 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 sapoins and flavones extracted from the plant *Tephrosia candid;*

(f) Biological controls using fungi: for example 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.

48. 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.

2.2.3 Suitability of alternatives

49. 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.

50. 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.[25] 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.

51. 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).

52. According to Brazil,[26] 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 1. 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
Chemical alternatives						
Deltamethrin (dried powder)	52918-63-5	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC. 10/INF/7/Rev.1 BAT/BEP guidance (2021)	
Fenitrothion (thermal fogging)	122-14-5	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC. 10/INF/7/Rev.1 BAT/BEP guidance (2021)	

[25] Submisison by Brazil for UNEP/POPS/POPRC.12/INF/15/Rev.1. http://chm.pops.int/tabid/6173/Default.aspx.

[26] UNEP/POPS/POPRC.12/INF/15/Rev.1.

Composition	CAS No.	Trade name	Manufacturer	Class*	Source(s)	Additional details
Fipronil	120068-37-3	Information gap	Information gap	4	Brazil (2018) UNEP/POPS/POPRC.10/INF/7/Rev.1 BAP/BEP guidance (2021)	
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, http://www.cdpr.ca.gov/docs/risk/rcd/hydrameth.pdf and http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/hydmthn.pdf).
Non-chemical/Alternative technology						
Barriers	N/A	N/A	N/A	N/A	IPEN (2018) Abraisca (2018) BAT/BEP guidance (2021)	
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
Biological controls using fungi	N/A	N/A	N/A	N/A	PAN (2018) IPEN (2018) Abraisca (2018) BAT/BEP guidance (2021)	
Cultural control	N/A	N/A	N/A	N/A	IPEN (2018) Abraisca (2018) BAT/BEP guidance (2021) UNEP/POPS/POPRC.8/INF/17/Rev.1	
Natural plant extracts	N/A	Bioisca	Cooperativa De Cafeicultores e Agropecuaristas	N/A	PAN (2018) IPEN (2018) Abraisca (2018) BAT/BEP guidance (2021)	
Physical/mechanical controls	N/A	N/A	N/A	N/A	IPEN (2018) Abraisca (2018) BAT/BEP guidance (2021) UNEP/POPS/POPRC.8/INF/17/Rev.1	

* 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).

53. The BAT/BEP guidance (2021) 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.

54. 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.[27]

55. A special formulation of hydramethylnon, sold under the trade name Amdro® Ant Block, is the only widely available bait product labelled for control of leaf cutting ants in the USA.[28] 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.

56. 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.

57. 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).

58. 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.

59. This technique can be applied to control *Atta* spp. in mature nests but cannot be used to control *Acromyrmex ssp*. It is being utilized in specific situations, such as very high infestation rates and initial land preparation for cultivation.[29]

60. For mechanical controls, the BAT/BEP guidance (2021) 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 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.

61. 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.[30]

62. 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 BAT/BEP guidance (2021) outlines different best available techniques based on a number of different specific situations (see Table 2). Available information concerning alternatives and alternatives method is different between the two strains *Atta sp.* and *Acromyrmex sp.*, the latter with less information available for control.

[27] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[28] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[29] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[30] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

63. 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 noted 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. No update of this information was available in 2022.

Table 2. Best practice for control of leaf-cutting ants from *Atta* spp. and *Acromyrmex* spp. in BAT/BEP guidance (2021)

Situation	Best available technique (BAT)
For initial large area land preparation and high infestation rate on mature *Atta* nests	Thermo-nebulization with permethrin or with fenitrothion
For small areas, such as small orchards and residential uses	Mechanical control: Excavation of the young nests and capturing the ant queens
	Barriers" fastened around tree trunks, such as plastic tape coated with grease, plastic cylinders and strips of aluminium
To control nests no larger than $5m^2$	Dried-powder dusting with deltamethrin
To control young Atta colonies and certain *Acromyrmex* species	Dried-powder dusting with deltamethrin
To control certain *Acromyrmex* species	Dried-powder dusting with deltamethrin Baits containing sulfluramid

64. PAN (2018) indicate that there is evidence to suggest that biological control agents such as using strains of *Escovopsis* parasitic fungi (Meirelles 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.

65. As noted by PAN (2018) the plant extract product Bioisca, based on an extract of the leguminous plant *Tephrosia candida* (white hoarypea) is 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 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.

66. 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 (azardirachtin) 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. Further research is required into the wider technical feasibility and operational consistency of control methods using natural plant extracts before these can be recommended for widespread use and be considered viable alternatives.

67. 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).

68. 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 in the research phase.

69. 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 on ongoing area of research.

70. A review covering a total of 691 experiments collected from 153 studies was recently published, Dionisi et al. (2021), that also evaluate the effectiveness as a function of their management efficacy, environmental and human health impacts, and their ease of application. It concluded that chemical control methods were effective but posed a danger to human health and the environment, whereas mechanical methods and integrated management were more sustainable but not always very effective. Some of the biocontrol methods were evaluated as effective and safe for the environment and human health, including the use of entomopathogenic fungi Beauveria bassiana (Bals.-Criv) Vuill. (Hypocreales: Cordycipitaceae) and Metarhizium anisopliae (Metschn.) Sorokïn (Hypocreales: Clavicipitaceae) in the form of bait or sprayed in the nest, or the application of plant mulch in the nest using Tithonia diversifolia (Hemsley) A. Gray (Asterales: Asteraceae) or Canavalia ensiformis L. DC. (Fabales: Fabaceae).[31]

71. 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.

2.2.4 Implementation of alternatives

72. According to the BAT/BEP guidance (2021) 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.

73. 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 *Acromyrrmex* 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).

74. The information 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. Additional estimates on production, use and export (up to 2019) can be found in Torres et al. (2022).

75. This suggests 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 the position stated by Brazil (2018) that there are no available alternatives for this use. According to Vietnam (2022) there are some enterprises that are using a few alternatives in Vietnam. However, Ministry of Natural Resources and Environment (MONRE) has not yet synthesized adequate information related to these alternatives.

76. While innovative chemical, biological and physical methods are available and/or being developed, it appears none of these are 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.

2.2.5 Information gaps and limitations

77. The following information gaps and limitations still remain:

(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) 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) Information on conversion rate of sulfluramid to PFOS in the environment under natural conditions is needed.

2.2.6 Concluding remarks

78. 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

[31] http://chm.pops.int/tabid/9105/Default.aspx. Submission by IPEN/ACAT in 2022.

sulfluramid suggest there has not been a significant switch to any alternative substances or techniques for this acceptable purpose.

79. The BAT/BEP guidance (2021) notes a number of alternative chemicals and approaches are available and are considered best practice for a number of specific applications.

80. 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.

81. The Committee encourages additional research and development of alternatives and, where alternatives are available, that they be implemented, while maintaining the acceptable purpose for the time being.

82. 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.

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

2.3.1 Introduction and background

83. The specific exemptions for metal plating were amended in decision SC-9/4 to “metal plating (hard metal plating) only in closed-loop systems”. It is no longer available as an acceptable purpose but as specific exemption from 20 December 2020 onwards.[32]

84. As of July 2022, Norway and Switzerland are registered the specific exemptions for the use of PFOS for hard metal plating.[33] In Switzerland, a transitional provision for this use is limited until March 2024 according to Swiss national legislation.[34] Recent national surveys indicate that use of PFOS has been phased out in Norway and Switzerland,[35] and that the specific exemption for use in metal plating (hard-metal plating) may no longer be needed. According to the register of specific exemptions, registered exemptions for all other countries have either expired or been withdrawn. However, Vietnam indicated in its submission on 1 July 2022 that after assessing and summing up the continued need for PFOS, Vietnam will submit the notification of specific exemptions for PFOS to the Secretariat.[36]

85. There are two main technologies in metal plating namely hard and decorative metal plating, where 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 for decorative surface finish.[37]

86. 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.

87. In “decorative” metal plating only a thin layer (0.05 to 0.5 µm) 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 hard metal plating, the plating bath typically consists of chromic acid (chromium(VI) acid). Chromium(VI) is a known human carcinogen and therefore minimising or eliminating its use or controlling emissions to prevent occupational and environmental exposure is essential.

88. 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.

[32] http://chm.pops.int/tabid/4644/Default.aspx.

[33] http://chm.pops.int/tabid/4644/Default.aspx.

[34] https://www.fedlex.admin.ch/filestore/fedlex.data.admin.ch/eli/cc/2005/478/20221001/fr/pdf-a/fedlex-data-admin-ch-eli-cc-2005-478-20221001-fr-pdf-a-2.pdf.

[35] https://www.bafu.admin.ch/dam/bafu/de/dokumente/chemikalien/externe-studien-berichte/verwendung-von-fluortensiden-in-der-galvanikbranche.pdf.

[36] http://chm.pops.int/tabid/9105/Default.aspx.

[37] UNEP/POPS/POPRC.12/INF/15/Rev.1.

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.

89. PFOS salts are or have been commonly used as a surfactant, wetting agent and mist suppressing agent for hard metal plating processes using chromic acid (chromium(VI) acid) 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, tine plating, zinc and zinc alloy plating, electroplating of polymers) besides hard metal plating with chromium(VI).

90. PFOS is effective in hard 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.

91. The PFOS derivative most frequently used in hard metal plating has been the quaternary ammonium salt tetraethylammonium perfluorooctane sulfonate with CAS No. 56773-42-3 (sold under trade names such as Fluorotenside-248 (abbr FT-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 potassium, lithium, diethanolamine and ammonium salts of PFOS may also be used.[38] 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.[39]

92. 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 there is no harmonised definition of closed loop systems and the definition of “closed loop” can vary dependent on different understanding. The BAT/BEP guidance (2021) states that “a closed loop system needs to be utilized when using PFOS as mist suppressants”. The document 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 chromium(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.

93. Closing the material loop for chromium(VI) hard metal 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, which is required to regain the electrolyte from the rinse water.[40] Multi-step criteria defining the characteristics of a closed loop system have been provided by Blepp et al. (2015) and the BAT/BEP guidance (2021).

[38] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[39] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[40] UNEP/POPS/POPRC.12/INF/15/Rev.1.

2.3.2 Availability of alternatives

94. 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.[41]

95. 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 metal plating applications. An overview of these different alternatives is provided in Table 3 below.

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
Fluorinated alternatives							
6:2 Fluorotelomer sulfonate (6:2 FTS) (Hard metal)	27619-97-2	Yes	No	Capstone (Chemours) FS10 Proquel OF (Kiesow) ANKOR® Dyne 30 MS (Enthone) ANKOR® Hydraulics (Enthone) ANKOR® PF1 (Enthone) Fumetrol® 21 (Atotech) Fumetrol® 21 LF 2 (Atotech) HelioChrome® Wetting Agent FF (Kaspar Walter) Maschinenfabrik GmbH & Co. KG) PROQUEL OF (Kiesow Dr. Brinkmann) Slotochrom® CR1270 (Schlötter) Wetting Agent CR (Atotech)	UNEP/POPS/POPRC.10/INF/7/Rev.1 BAT/BEP guidance (2021) Poland (2018) Germany (2018)	3	Some of the products listed are not resistant in chrome sulfuric acid pickling and chromium(VI) baths.
6:2 Fluorotelomer sulfonate (6:2 FTS) (Decorative)	27619-97-2	No	Yes	ANKOR® Dyne 30 MS (Enthone) Cancel ST-45 (Plating Resources, Inc.) FS-600 High Foam (Plating Resources, Inc.) FS-750 Low Foam (Plating Resources, Inc.) Fumetrol 21 (Atotech) SLOTOCHROM CR 1271 (SchlötterGalvanotechnik) UDIQUE® Wetting Agent PF2 (Enthone) Wetting Agent CR (Atotech)	UNEP/POPS/POPRC.10/INF/7/Rev.1 BAT/BEP guidance (2021)	3	

[41] UNEP/POPS/POPRC.12/INF/15/Rev.1.

Composition	CAS No.	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt	754925-54-7	Yes	No	F-53 (China product)	UNEP/POPS/POPRC.10/INF/7/Rev.1 BAT/BEP guidance (2021)	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	F-53B (China product)	UNEP/POPS/POPRC.10/INF/7/Rev.1 BAT/BEP guidance (2021)	3	Available in China
1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane	113507-82-7	Yes	No	No information	UNEP/POPS/POPRC.10/INF/7/Rev.1 https://pubchem.ncbi.nlm.nih.gov/compound/2776108#section=Molecular-Formula	3	
Other fluorinated alternatives	N/A	Yes	Yes	Chromnetzmittel LF (CL Technology GmbH) Netzmittel LF (Atotech) RIAG Cr Wetting Agent (RIAG Oberflächentechnik AG)	BAT/BEP guidance (2021)	N/A	No information on chemical identity is known.
Fluorine-free alternatives							
Alkane sulfonates	N/A	Yes	Yes	TIB Suract CR-H (TIB Chemicals AG))	BAT/BEP guidance (2021)	N/A	Not resistant to hard chromium plating, less effective in decorative chromium plating
Oleo amine ethoxylates	26635-93-8	No	Yes	ANKOR® Wetting Agent FF (Enthone)) Antispray S (Coventya)	BAT/BEP guidance (2021)	N/A	(Z)-Octadec-9-enylamine,ethoxylated (Oleylaminethoxylat)
Other non-fluorinated alternatives	N/A	Yes	Yes	CL-Chromeprotector BA (CL Technology GmbH) Antifog V4 (Chemisol GmbH & Co. KG) Non Mist-L (Uyemura)	BAT/BEP guidance (2021)	N/A	No information on chemical identity

Composition	CAS No.	Hard plating	Decorative plating	Trade names (manufacturer)	Information Source	Class*	Additional information
Non-chemical/alternative processes							
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 guidance (2021)	N/A	E.g. Mesh or blankets (Composite Mesh Pads) placed on top of bath Not recommender or considered BEP
Add-on air pollution control devices	N/A	Yes	Yes	Information gap	BAT/BEP guidance (2021)	N/A	E.g. Packed Bed Scrubbers
Novel plating processes	N/A	Yes	Yes	Topocrom www.topocrom.com	BAT/BEP guidance (2021)	N/A	E.g. HVOF (High Velocity Oxygen Fuel) Process
Trivalent chromium or chromium(III) plating.	N/A	No	Yes		BAT/BEP guidance (2021)	N/A	

Note: The purpose of Table 3 is to indicate alternatives to PFOS already identified and mentioned in the Stockholm Convention (SC) reports, which have been screened previously or not according to an accepted screening method (for P and B) whether they are potential POPs or not.

*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).

2.3.2.1 Chemical alternatives in metal plating

96. 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. These fluorinated substitutes are often short chain fluorinated surfactants;

(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 metal chromium(VI) 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.

97. Chemical alternatives are available for hard metal plating and decorative plating.[42] 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 3 above.

98. Non-fluorinated alternatives are also available in this sector. It is indicated[43] 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 metal plating. Canada (2018) indicated that PFOS-free fume suppressants are already in use, and that PFOS is no longer allowed for this application in Canada.

[42] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[43] UNEP/POPS/POPRC.12/INF/15/Rev.1.

99. The German electroplating industry association (ZVO, 2018) indicated the availability of PFOS-free alternative products from 10 German suppliers. 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.

100. One chemical alternative to PFOS, as identified in the BAT/BEP guidance document, are oleo amine ethoxylates (CAS No. 26635-93-8). This substance was not covered in the previous alternates assessment and will be considered in more detail in section 3.

2.3.2.2 Non-chemical alternatives/alternative processes

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

102. There is no drop in alternatives for hard metal plating, providing that all the required properties to the surfaces of all articles needed are industrially available There are several coating technologies with no use of fluorinated surfactants, that are considered to replace hard chrome plating with chromium (VI), depending on the requirements for the certain application.

103. These alternative processes are as follows:[44,45]

(a) Electroless plating, nickel and nickel alloy electroplating;

(b) Case hardening for carburizing or carbonitriding;

(c) Cyaniding;

(d) Nitriding;

(e) Boronizing;

(f) Chemical vapour deposition (CVD);

(g) Nanocrystalline cobalt phosphorus alloy coating;

(h) High velocity thermal process;

(i) Chromium(III) plating;

(j) Physical vapour deposition (PVD);

(k) Plasma spraying;

(l) Stainless steel & high-speed steel (HSS);

(m) Thermal spray coatings.

104. For decorative plating, the BAT/BEP guidance (2021) noted that parts of the decorative chrome plating industry have adopted the use of trivalent chromium, chromium(III) in plating, which is intrinsically less toxic than chromium (VI). The use of chromium(III) represents the BAT for the applications in which it is feasible, and it is indicated that, where used, it has eliminated the use PFOS as mist suppressant. It is also suggested that the use of trivalent chromium (chromium(III)) could also be applied in hard metal plating in some applications. In principle, the use of PFOS would not be strictly necessary if chromium(VI) was not used; however, chromium(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 chromium(III) to chromium(VI) during the plating process is unclear and will require further investigation.

105. Novel plating techniques for hard metal 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 (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.

106. Another alternative process has also been developed where no surfactants are required[46] 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.

[44] Submission by Sweden in 2022. http://chm.pops.int/tabid/9105/Default.aspx.

[45] CROMOMED S.A, “ANALYSIS OF ALTERNATIVES - Functional chrome plating” Public Version (2017) https://echa.europa.eu/documents/10162/ece8b65e-aec0-4da8-bf68-4962158a4952.

[46] http://www.topocrom.com/content/pdf/Artikel_Verfahren_k_muell.pdf.

107. 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.

108. Germany (2018) outlined a number of alternative technologies for the prevention of chromium(VI) release during plating processes, including the use of PTFE-coated balls on top of bath, and mesh or blanket covers for plating baths.[47] 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.[48] It has been indicated that there are no factors limiting the accessibility of these control devices, and they are commercially available in Canada.[49]

2.3.3 Suitability of alternatives

109. 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 chromium(VI) 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.[50]

110. 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.[51] 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.[52]

111. 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:[53]

(a) The performance is not equal to PFOS based suppressants, particularly for fluorine-free alternatives;[54]

(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.[55] 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 chromium(VI) to chromium(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 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;

(f) Fluorinated alternatives to PFOS could potentially have similar properties to PFOS and could therefore lead to regrettable substitutions Germany (2018).

112. 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).

113. The BAT/BEP guidance (2021) notes 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.

[47] http://www.subsport.eu/case-stories/179-de/?lang=de.

[48] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[49] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[50] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[51] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[52] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[53] BAT/BEP guidance (2021); UNEP/POPS/POPRC.12/INF/15/Rev.1.

[54] BAT/BEP guidance (2021); UNEP/POPS/POPRC.12/INF/15/Rev.1.

[55] BAT/BEP guidance (2021); UNEP/POPS/POPRC.12/INF/15/Rev.1.

No information is available on the shorter chain alternatives developed in China. 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.

114. ZVO (2018) express concern that alternatives may be able to pass such filters significantly., According to the case study by Blepp et al. (2020) on 6:2 FTS used in Cr(VI) coating plants, the additional treatment of the overall wastewater flow is necessary. Due to the detected carry-over of the 6:2 FTS in the electroplating machine by adsorption and desorption processes, a partial flow treatment of the chromium(VI)-containing waste water is not sufficient (Blepp et al. 2020).

115. 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.

116. 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.

117. 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 (2021), the use of fluorine-free alternative substances should be considered on a case-by-case basis.

118. 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.

119. 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.[56] However, layers deposited using this method may be more porous and less resistant to corrosion (German Environment Agency, 2017).

120. 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 USD 1,000 per kilogram.

2.3.4 Implementation of alternatives

121. The BAT/BEP guidance (2021) stated "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.

122. The use of chromium(III) instead of chromium(VI) for certain decorative metal plating processes has made PFOS use in decorative metal plating obsolete.[57] 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.

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

124. National Implementation Plans (2017, 2018) indicate that PFOS may still be in use in hard metal plating in the EU, at least in the Czech Republic and Germany. Netherlands and Germany have reported the use for PFOS in hard metal plating (POPRC-11 follow-up). Norway (2022) and Switzerland (2022) are registered for specific exemptions

[56] See also https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2017-11-01_texte_95-2017_pfos_en_0.pdf.

[57] UNEP/POPS/POPRC.12/INF/15/Rev.1.

of the use of PFOS for hard metal plating.[58] In Switzerland, a transitional provision for this use is limited until March 2024 according to Swiss national legislation.[59] Recent national surveys indicate that use of PFOS has been phased out in Norway[60] and Switzerland, and that the specific exemption for use in metal plating (hard-metal plating) may no longer be needed. 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 chromium(VI) mist suppressant in China has also been indicated by a CAFSI Survey in 2012 (Huang et al., 2013). China has since then stopped the use of PFOS in chromium mist suppressant. PFOS is not produced in Vietnam, however, it is imported into the country and used in many sectors such as industries, business and households. Major PFOS uses in Vietnam are likely firefighting foams and metal plating according to Vietnam updated NIP (2017).[61]

125. The United Kingdom of Great Britain and Northern Ireland (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. All of the volume used in 2017 was for use in metal plating. UK (2022) reported that there is no use of PFOS since 2020 in this sector which could indicate a full switch to non-PFOS alternatives.[62]

126. Canada reported declining use of PFOS in hard metal plating in closed loop systems until 2014 when the use was 0 kg. Canada has no specific exemption for this use, since PFOS is domestically prohibited for this use since 29 May 2013.[63]

127. Vietnam indicated that the Decree No. 08/2022/ND-CP regulates exemption register of PFOS in metal plating (hard-metal plating) only in closed-loop systems.[64]

2.3.5 Information gaps and limitations

128. The following information gaps and limitation still remain:

(a) The detailed specification of the “closed loop” process for PFOS as set out in the BAT/BEP Guidance (2021) is needed in to be applied among industry stakeholders and competent authorities to enable harmonised conditions for this use;

(b) More information on the degradation products of potential alternatives is needed to establish the environmental performance of different alternatives. If the use of 6:2 FTS cannot be replaced the recommended BAT is to treat the total wastewater flow by specific ion exchangers;

(c) Knowledge gaps exist concerning novel plating practices, including details of the processes themselves, identity of chemicals used, best practices and levels of market acceptance. Currently the BREF document on surface treatment of metals and plastics is reviewed that will increase the knowledge of BEP/BAT for these technologies.[65]

2.3.6 Concluding remarks

129. Fluorinated alternatives, fluorine-free alternatives and alternative technologies in hard metal plating and decorative plating are globally available. Fluorine-free products are not considered equally effective in all applications and more information about their areas of application and their limitations is required. Fluorinated alternatives or their degradation products might be very persistent. There are environmental and health concerns regarding emissions of PFASs from manufacturing companies that perform hard chrome plating with chromium(VI). This means that it will be increasingly important to replace hard chrome plating with chromium(VI) with other processes where chromium(VI) is not used and thus likely no need for mist suppressants.

130. Taking into account the availability of alternatives for PFOS, its salts and PFOSF and the recommendation by the Committee, the Conference of the Parties amended the exemptions for metal plating in decision SC-9/4 to limit it to “metal plating (hard metal plating) only in closed-loop systems”, no longer available as an acceptable purpose but as a specific exemption. The reason for now being a specific exemption is that there are several drop in chemical alternatives (both fluorinated and non-fluorinated), and non-chemical or alternative process approaches are industrially available for use that are considered to replace hard chrome plating with chromium(VI), depending on the requirements for the certain application.

[58] http://chm.pops.int/tabid/4644/Default.aspx.

[59] https://www.fedlex.admin.ch/filestore/fedlex.data.admin.ch/eli/cc/2005/478/20221001/fr/pdf-a/fedlex-data-admin-ch-eli-cc-2005-478-20221001-fr-pdf-a-2.pdf).

[60] Submisison by Norway in 2022. http://chm.pops.int/tabid/9105/Default.aspx.

[61] Submission by Vietnem in 2022. http://chm.pops.int/tabid/9105/Default.aspx.

[62] Submisison by UK in 2022. http://chm.pops.int/tabid/9105/Default.aspx.

[63] Submisison by Canada in 2022. http://chm.pops.int/tabid/9105/Default.aspx.

[64] Submission by Vietnem in 2022. http://chm.pops.int/tabid/9105/Default.aspx.

[65] https://eippcb.jrc.ec.europa.eu/reference/surface-treatment-metals-and-plastics.

131. Noting that the specific exemption is time-limited, the Committee recommends that Parties consider replacement hazard characteristics and not to replace the use of PFOS, its salts and PFOSF for hard metal plating with chemicals that may exhibit persistent organic pollutant characteristic in Annex D, including the degradation products.

2.4 Fire-fighting foam

2.4.1 Introduction and background

132. In decision SC-9/4, the Conference of the Parties removed fire-fighting foam from acceptable purpose and listed it as a specific exemption as "fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, in accordance with paragraph 10 of part III of this Annex".[66,67] The condition for the use of fire-fighting foam set in paragraph 10 of part III of Annex B is similar to the condition provided for the specific exemption for the use of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds listed in Annex A to the Convention. This use is considered as an open application according to document UNEP/POPS/POPRC.7/INF/22/Rev.1. As of July 2022, no Party is currently registered for this specific exemption.[68]

133. Fire-fighting foam concentrates usually contain general classes of compounds, such as surfactants, solvents, stabilisers and thickeners. However, each foam formulation is unique and even foams with the same name differ over time in the combination of specific ingredients.

134. The main function of fluorinated substances in firefighting foams is to act as a surfactant, that is to form a film over the surface of a burning liquid in order to prevent flammable gases from being released from it as well as from reigniting. Different types of PFAS-containing foams are available on the market, mainly as:

(a) "Aqueous Film Forming Foam" (AFFF) which form an aqueous film on the surface of the flammable liquid by the foam solution as it drains from the foam blanket;

(b) "Alcohol Resistant-Aqueous Film Forming Foam" (AR-AFFF) which are resistant to polar solvent and alcohol liquids;

(c) "Fluoro Protein" foams (FP);

(d) "Film Forming Fluoro-Protein" foams (FFFP);

(e) Other types of PFAS-containing foams also exist, such as "Alcohol-Resistant FilmForming Fluoro-Protein" foams (AR-FFFP) and "Fluoro-Protein Alcohol-Resistant" foams (FPAR).[69]

135. Fluorine-free fire-fighting foams are based on the following compositions:

(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 (e.g., Hi Combat ATM from AngusFire);

(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. Protein based foams were commonly used until the 1960s/70s before being replaced in favour of fluorinated surfactants.[70]

136. 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.[71] 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.

137. 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

[66] Vietnam indicated that the Decree No. 08/2022/ND-CP regulates exemption register of PFOS in Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, in accordance with paragraph 10 of part III of Annex.

[67] PFOS is not produced in Vietnam, however, it is imported into the country and used in many sectors such as industries, business and households. Major PFOS uses in Vietnam are likely firefighting foams and metal plating.

[68] http://chm.pops.int/tabid/4644/Default.aspx.

[69] ECHA restriction dossier Firefigthing foams, March 2022, rest_pfas_fff_axvreport_annex_23593_en.pdf.

[70] ECHA restriction dossier Firefigthing foams, March 2022, rest_pfas_fff_axvreport_annex_23593_en.pdf.

[71] UNEP/POPS/POPRC.12/INF/15/Rev.1.

fires).[72] In the past, industry has favoured the use of C_8-based[73] perfluorinated compounds, including those containing PFOS, which are developed specifically for use on liquid (Class B) fires.[74] As discussed in subsequent sections, industry indicates that C_8-based foams have been largely displaced by C_6-based[75] foams, as well as other non-fluorinated substances.

138. 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) commented that C_6 technologies (i.e., C_6 fluorotelomer based AFFF) were 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_8 perfluorinated compounds, including PFOA, as a contaminant within C_6 species. The Swedish Chemicals Agency (2015) noted studies indicating some goods marketed as C_6 fluorotelomer products contain concentrations of C_8 (including PFOA/PFOS) significantly above trace residual concentrations, in some cases at concentrations with equal amounts of C_6 and C_8. 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%).

139. 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.[76] 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.

140. 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.[77] 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).[78]

141. Canada (2018) noted that the use of PFOS has been 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_8 fluorosurfactants in their production process.

2.4.2 Availability of alternatives

142. It was noted over a decade ago that a number of alternatives to the use of PFOS-based fluorosurfactants in fire-fighting foams are available, including C_6-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.[79]

143. Non-PFOS based AFFFs are widely commercially available from all major suppliers of fire-fighting equipment and have been in use for several years.[80] For example, suppliers in North America and Norway include but are not limited to, Ansul and Chemguard (both Tyco companies), Chemours, Kidde, and Solberg.

144. There are two key categories of alternatives to consider in this section: short-chained fluorinated alternatives, and non-fluorine containing alternatives. An overview of available fluorinated and non fluorinated alternatives is presented in Table 4 below.

[72] 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/.

[73] C_8 means fire-fighting foams based on the PFOA or the PFOS chemistry.

[74] UNEP/POPS/POPRC.13/7/Add.2.

[75] C_6 means fire-fighting foams based on the PFHxA or the PFHxS chemistry.

[76] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[77] UNEP/POPS/POPRC.12/INF/15/Rev.1.

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

[79] UNEP/POPS/POPRC.3/20/Add.5, UNEP/POPS/POPRC.12/INF/15/Rev.1.

[80] UNEP/POPS/POPRC.12/INF/15/Rev.1.

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

Composition	CAS No.	Trade Names	Manufacturer	Information Source	Class*	Additional details
Fluorinated alternatives						
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_6 fluorotelomer sulfonamide compounds	Information gap	National Foam Ansulite; 3M lightwater	Chemours 3M National Foam Ansul	https://www.chemours.com/Capstone/en_US/products/Index.html ECHA, 2022b	N/A	
Perfluorohexane ethyl sulfonyl betaine	161278-39-3	Capstone™ products	Chemours	UNEP/POPS/POPRC.10/INF/7/Rev.1 https://www.chemours.com/Capstone/en_US/products/Index.html https://www.diva-portal.org/smash/get/diva2:1128873/FULLTEXT01.pdf	3	Perfluorohexane ethyl sulfonyl betaine and C6-fluorotelomers often used in combination with hydrocarbons
5:1:2 fluorotelomer betaine	171184-14-8		3M Buckeye	ECHA, 2022b	Not screened	
6:2 Fluorotelomer sulfonamide betaine	34455-29-3	Chemours, STHAMEX® - AFFF 3% F-15 #4341 Dupont Forafac 1157 Dr. Sthamer, 3M National Foam F-500, Hazard Control Tech., 1997 (Foam 1) Angus Fire, 2004 Tridol S Angus Fire, 2000 Niagara 1-3 Chemours	Chemours STHAMER DuPont National Foam Angus	ECHA, 2022b	Not screened	
7:1:2 fluorotelomer betaine	171184-03-5	Buckeye 2009	3M Buckeye	ECHA, 2022b	Not screened	
7:3 fluorotelomer betaine	171184-15-9	Buckeye Ansul, 2002 Ansulite 3% AFFF DC-3	Buckeye Ansul	ECHA, 2022b	Not screened	

Composition	CAS No.	Trade Names	Manufacturer	Information Source	Class*	Additional details
Carboxymethyldimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl] amino]propylammonium hydroxide[81]	34455-29-3	Capstone product B[82]	Chemours	UNEP/POPS/POPRC.10/INF/7/Rev.1	3	
A fluorosynthetic versatile AR foam concentrate containing 5-10% 2-(2-butoxyethoxy) ethanol	112-34-5	BIO HYDROPOL 6	Bio Ex	UNEP/POPS/POPRC.12/INF/15/Rev.1	Not screened	
Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)	70829-87-7	Information gap	Information gap	Bao et al. (2017)	Not screened	Commercially available in China
Fluorotelomer Sulfonates(4:2 Fluorotelomer sulfonic acid)	757124-72-4	Angus Fire, 2004 Tridol S 3% Ansul 2002 Anslite 3% AFFF-DC-6 Hazard Control Tech 1197 F-500 National Foam	Angus National Foam	ECHA, 2022b	Not screened	
6:2 Fluorotelomer sulfonate	27619-97-2	Dr. Richard Sthamer GmbH & Co. KG STHMEXAFFF 3% Hazard Control Tech., 1997 F-500 Angus Fire, 2004 Tridol S 3 % Angus Fire, 2000 ; Niagara 1-3, Angus Fire, 1997; Forexpan Angus Fire, 2004 Tridol S 3 % Ansul, 2002 Ansulite 3 % AFFF - DC-4 Ansul, 2006; Ansul Anulite ARC National Foam 2005 National Foam 2007	Stahmer Angus Ansul National Foam	ECHA, 2022b	3	

[81] 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.

[82] https://www.lgcstandards.com/FR/en/p/DRE-C11041300.

Composition	CAS No.	Trade Names	Manufacturer	Information Source	Class*	Additional details
		National Foam 2008 (slightly different shares				
4:2 fluorotelomer thioamido sulfonates	1432486-88-8	Ansul AFFF formulations Angus Fire, 2004 Tridol S Ansul, 2002 Ansulite 3% AFFF DC-3 Ansul, 2006 Ansul Anulite ARC Hazard Control Tech., 1997 F-500 Chemguard Ansul Angus	Ansul Angus	ECHA, 2022b	Not screened	
6:2 fluorotelomer thioether amido sulfonic acid	88992-47-6	Angus Fire, 2004 Tridol S Ansul 1986 Ansul 1987 Angus Fire, 2000 Niagara 1-3 Ansul, 2002 Ansulite 3% AFFF DC-3 Ansul 2009 Ansul 2010 Chemguard 2008 F-500, Hazard Control Tech., 1997	Angus Ansul	ECHA, 2022b	Not screened	
6:2 fluorotelomer sulfonamide amine	1383438-86-5		3M, National Foam	ECHA, 2022b	Not screened	
N-[3-(Dimethyloxidoamino) propyl] - 3,3,4,4,5,5,6,6,7,7,8,8, 8-Tridecafluoro-1-octanesulfonamide	80475-32-7	Dupont, Forafac® 1183	DuPont	ECHA, 2022b	Not screened	
(Carboxymethyl)dimethyl [3- (gamma-omega perfluoro-1-C6-14-alkansulfonamid)propyl)ammonium (inner salt)	133875-90-8	Dupont, Forafac® 1203	DuPont	ECHA, 2022b	Not screened	
6:2 fluorotelomer thio hydroxy ammonium	88992-46-5		3M	ECHA, 2022b	Not screened	
Perfluoroheptane sulfonamidoethanol	167398-54-1	OR Ansul (telomer based foam)	Ansul	ECHA, 2022b	Not screened	
Others (unidentified)	Information gap	See Table 5	See Table 5		N/A	See Table 5

Composition	CAS No.	Trade Names	Manufacturer	Information Source	Class*	Additional details
Non-fluorinated alternatives						
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. https://www.epa.gov/greenchemistry/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
Poly(oxy-1,2-ethanediyl),α-hydro-ω-hydroxy- Ethane-1,2-diol, ethoxylated	25322-68-3	Fomtec AFFF 1% F, Fomtec AFFF 3% S, Fomtec AFFF 3%	Dafo Fomtec AB	ECHA, 2022b	Not screened	
Allyloxy(polyethylenEoxide), methyl Ether (9-12 eo)	27252-80-8	1% AFFF Denko 3% AFFF Denko 6% AFFF Denko Alcohol AFFF 3–6% Single or Double Strength Denko		ECHA, 2022b	Not screened	
Poly(oxy-1,2-ethanediyl), α-sulfo-ω-(dodecyloxy)-, ammonium salt (1:1)	32612-48-9	Orchidex BlueFoam 3x3	Orchidee Fire	ECHA, 2022b	Not screened	
Poly(oxy- 1,2-ethanediyl), .alpha.-sulfo-.omega.-hydroxyC6-10-alkyl ethers, sodium salts	73665-22-2	STHAMEX® 2% F6 Multipurpose detergent foam, STHAMEX® 3% F6 Multi-purpose detergent foam, STHAMEX® K 1% F-15 #9143, STHAMEX-SV/HT 1% F-5	Dr. Sthamer	ECHA, 2022b	Not screened	

Composition	CAS No.	Trade Names	Manufacturer	Information Source	Class*	Additional details
		#9142, TRAINING FOAM-N 1% F-0 #9141				
Poly(oxy-1,2-ethanediyl), α-sulfo-ω-hydroxy-, C9-11-alkyl ethers, sodium salts	96130-61-9	Dafo Brand AB: ARC Miljö Dafo Fomtec AB: Fomtec AFFF 1% A, Fomtec AFFF 1% F, Fomtec AFFF 1% Plus, Fomtec AFFF 1% Ultra LT, Fomtec AFFF 3%, Fomtec AFFF 3%ICAO, Fomtec AFFF 3% S, Fomtec Askum	Dafo Fomtech AB	ECHA, 2022b	Not screened	
2-6% Hexylene glycol (CAS No. 107-41-5, EC 203489-0); hydrolysed protein [70-80%], metallic salt: $NaCl+MgCl_2$ [8-15%]; $FeSO_4*7H_2O$[0-2%]	107-41-5 Hydrolysed protein is N/A	PROFOAM 806G	Gepro Group	UNEP/POPS/POPRC.12/INF/15/Rev.1	Not screened	
1-Dodecanol Tetradecanol	112-53-8 112-72-1	Respondol ATF 3-6% LS xMax F6Multi-purpose detergent Foam STHAMEX-SV/HT 1% F-5 #9142	Angus Fire National Foam Dr. Sthamer Dafo Foamtec	ECHA, 2022b	Not screened	
Alcohols, C9-11, ethoxylated, sulphates, ammonium salts	160901-27-9	OneSeven Foam Concentrate Class A	OneSeven of Germany GmbH.	ECHA, 2022b	Not screened	
Alcohols, C10-16, ethoxylated, sulfates, ammonium salts	67762-19-0	Meteor Allround Ma-13	Kempartner AB	ECHA, 2022b	Not screened	
Tetradecan-1-ol	67762-41-8	Expandol (aka Expandol 1-3), Expandol LT (aka Expanol 1-3LT)	Angus Fire	ECHA, 2022b	Not screened	
Alcohols, C12-15, ethoxylated	68131-39-5	Micro-Blaze Out	Verde Environmental Inc (Micro Blaze)	ECHA, 2022b	Not screened	
Xanthan gum	11138-66-2	Phos-Chek 3×6 Fluorine Free (aka UNIPOL-FF 3/6); Phos-Chek Training Foam 140 Moussol-FF® 3/6 Eco-Gel Unifoam Bio Yellow	Auxquimia Dr Sthamer FireRein Kempartner AB Verde Environmental Inc	ECHA, 2022b	Not screened	

Composition	CAS No.	Trade Names	Manufacturer	Information Source	Class*	Additional details
		Micro-Blaze Out	(Micro Blaze):			
Cyamopsis gum; Cyanopsis tetragonoloba	9000-30-0	Eco-Gel	FireRein	ECHA, 2022b	Not screened	
Starch	9005-25-8	US20080196908	Solberg	ECHA, 2022b	Not screened	
Canola Oil	120962-03-0	Eco-Gel	FireRein	ECHA, 2022b	Not screened	
Alkylpolyglycoside C10-16	110615-47-9	Orchidex BlueFoam 3x3	Orchidee Fire	ECHA, 2022b	Not screened	
(3R,4S,5S,6R)-2-(decyloxy)-6-(hydroxymethyl)oxane 3,4,5-trio	54549-25-6	Unifoam Bio Yellow	Kempartner AB	ECHA, 2022b	Not screened	
Alkyl polyglucoside	68515-73-1	Dafo Brand AB: ARC Miljö Enviro 3x3 Plus, Enviro 3x3 Ultra, Enviro 3x6 Plus, Environ 6x6 Plus, LS aMax, MB -20, Trainer E-lite, Fomtec AFFF 1% A, Fomtec AFFF 1% F, Fomtec AFFF 1% Plus, Fomtec AFFF 1% Ultra LT, Fomtec AFFF 3% ICAO, Fomtec AFFF 3% S, Fomtec AFFF 3% OneSeven ®	Dafo Fomtech AB OneSeven of Germany GmbH:	ECHA, 2022b	Not screened	
Alkyl polyglucoside	N/A	US20080196908	Solberg	ECHA, 2022b	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	

Note: The purpose of Table 4 is to indicate alternatives to PFOS already identified and mentioned in the Stockholm Convention (SC) reports, which have been screened previously or not according to an accepted screening method (for P and B) whether they are POPs or not.

* 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).

2.4.2.1 Short-chained fluorinated alternatives

145. 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.[83] The Fire Fighting Foam Coalition Inc (FFFC, 2018) indicate that most foam manufacturers have transitioned to the use of only short-chain (C_6) fluorotelomer surfactants. DuPont (Chemours), for example, have previously commercialised two AFFFs based on 6:2 fluorotelomer

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

sulfonamidealkylbetaine (6:2 FTAB) or 6:2 fluorotelomer sulfonamideaminoxide (Wang et al., 2013).[84] Chemours markets a range of fluorosurfactant-based firefighting foams on their website.[85]

146. As discussed in the previous section, the Swedish Chemicals Agency (2015) comments that C_6 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_8 perfluorinated compounds, including PFOS, as a contaminant within C_6 species.[86]

147. 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. According to the European Committee of the Manufacturers of Fire Protection Equipment and Fire Fighting Vehicles (Eurofeu) as well as FCCC, PFASs presently used in firefighting foam technology in the EU exclusively consist of PFHxA related substances. FFFC has further indicated that PFASs based on <C6-chemistry have never been used as an active ingredient for firefighting foams as the chemistry is not suitable. (ECHA, 2022). Perfluorohexane sulfonate (PFHxS) is considered as a long chain PFSAs according to the OECD definition, biomonitoring measurements in fire-fighters have shown highler 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, Rotander et al., 2015). Note that at its tenth meeting, the Conference of the Parties listed PFHxS, its salts and PFHxS-related compounds in Annex A to the Convention without specific exemptions.

148. There is still limited publicly available information on the chemical structure or properties of the AFFF products containing fluorinated alternatives. Canada (2018) noted that the actual C_6 (or below) fluorosurfactants contained in AFFF formulations are considered proprietary by AFFF manufacturers.

149. 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)[87]

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

150. 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).

151. Bao et al. (2017) reported that the aromatic compound sodium p-perfluorous nonenoxybenzene 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 sodium p-perfluorous nonenoxybenzene sulfonate (OBS) may be a desirable alternative to PFOS as it can be readily treated by H_2O_2/UV.

2.4.2.2 Fluorine-free alternatives

152. 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[88] i.e., formulations that do not use any fluorine-based chemistry, including as surfactants or other components.

[84] Note that Chemours has replaced DuPont on the market. https://www.chemours.com/Capstone/en_US/uses_apps/fire_fighting_foam/index.html.

[85] https://www.chemours.com/Capstone/en_US/products/Index.html.

[86] UNEP/POPS/POPRC.13/7/Add.2.

[87] See UNEP/POPS/POPRC.12/INF/15/Rev.1, annex 5.

[88] UNEP/POPS/POPRC.12/INF/15/Rev.1.

153. 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.

154. It has been indicated that non-fluorinated foams exist and are available commercially in the market.[89] The FFFC (2018) note that most foam manufacturers also produce fluorine-free foams. For example, fluorine-free foams certified to different ICAO levels,[90] required for use at civilian airports, are available on the market and are already introduced at airports in practice (FFFC, 2018).

155. There is still limited 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.[91]

Table 6. Commercially available non-fluorinated alternatives for fire-fighting foams (chemical composition not disclosed)

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%, Shtamex-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

156. The FFFC (2018) noted that the Solberg Company developed Re-Healing Foam™ RF,[92] a high-performance fluorine-free foam concentrate for use on Class B hydrocarbon fuel fires. Airservices Australia reportedly use the Solberg Re-Healing RF6 6% foam as the preferred operational fire-fighting foam at the 23 capital and major regional

[89] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[90] International Civil Aviation Organisation specifications – see http://www.firefightingfoam.com/knowledge-base/international-standards/icao/.

[91] https://files.chubbfiresecurity.com/chubb/en/uk/contentimages/CFAR6%20MOUSSOL%20APS.pdf.

[92] https://www.solbergfoam.com/getattachment/41e509c4-63cd-4b7a-b734-fda67d7642f9/SOLBERG-Expands-Product-Certifications-on-Foam-1.aspx.

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 to 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 PFASs 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).

157. 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 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 PFASs and fluorinated telomers and use of fluorine-free alternatives is also being developed in this sector.

158. Based on information provided by Eurofeu and additional manufacturers, it has been estimated that at least some 7 000 tonnes, but probably around 9 000 tonnes of fluorine-free firefighting foams are sold in the EU annually, representing around 32% of the market. The split by sector of use varies considerably from that of PFAS-based foams, with a much larger share used by municipal fire brigades but a much smaller share in the chemical/petrochemical sectors. A breakdown by chemical group of alternatives is not available, but consultation responses suggest that the main alternatives used are based on hydrocarbon surfactants and detergents (ECHA, 2022b).

2.4.2.3 Reducing the environmental impacts of using AFFFs

159. One key aspect of fire-fighting foam usage that has been highlighted previously[93] 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 BAT/BEP guidance (2021) 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”.

160. 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 available for training and other uses.

161. As reported in the PFOA Risk Management Evaluation (RME) addendum,[94] the FFFC provided details of best practice for use of Class B fire-fighting foams, which includes AFFF (PFOA/PFOS and C_6 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

[93] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[94] See UNEP/POPS/POPRC.13/7/Add.2.

provisions of the Stockholm Convention to destroy POPs in an environmentally sound manner. For contaminated fire-water 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).

162. The UNEP (2017) BAT/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.

163. It is indicated that there is no available information on alternative technology for this use.[95]

164. 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 section 3.

2.4.3 Suitability of alternatives

165. 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.

166. The available testing information indicates that both C_6-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.

167. As presented in the discussion below, and previously,[96] there is some conflicting evidence and opinion regarding the relative efficacy of foams based on short-chained PFASs 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.

168. 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.[97]

169. 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) BAT/BEP guidance states that “non-PFOS fluorinated surfactants based on short-chain fluorotelomers should be used for Class B fire-fighting foam concentrates”.

170. According to the Annex XV report (ECHA, 2022) for restricting the use of PFASs in fire-fighting foams under REACH, alternatives to PFAS-based fire fighting foams are generally considered to be technically feasible in most applications. However, further testing is required to confirm the technical feasibility of alternatives for specific applications, particularly in the oil and chemical sector with installations with large atmospheric storage tanks and sites using multiple types of flammable liquids.

171. Fluorine-free foams behave differently to PFAS-containing foams and show more variability in their performance. However, large-scale tests have also demonstrated satisfactory technical performance under certain conditions. Since large fire incidents are rare and large fire testing is costly,limited practical experience has been gained until now in such challenging fire scenarios. Importantly, it is not only the foam itself which needs to be

[95] Guidance on BAT/BEP for the use of PFOS, PFOA and their compounds under the Stockholm Convention. http://chm.pops.int/tabid/3170/Default.aspx.

[96] UNEP/POPS/POPRC.12/INF/15/Rev.1.

[97] https://www.solbergfoam.com/Technical-Documentation/Technical-Bulletins.aspx.

considered, but the performance of the foam in combination with (i) the flammable liquid to be tackled and (ii) the foam application method (application system and application parameters) (ECHA, 2022).

172. 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 fires on fuels with lower flash points are more difficult to control with fluorine-free foams.

173. 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 PFOSFoam.

174. As noted in the PFOA RME,[98] 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 minutes).[99] 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.[100] 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).

175. 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),[101] proved to be as effective and efficient as the used AFFFs.[102] 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).

176. As noted in the PFOA RME[103] 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.

177. 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).

178. However, 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

[98] See UNEP/POPS/POPRC.13/7/Add.2.

[99] 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.

[100] https://theintercept.com/2018/02/10/firefighting-foam-afff-pfos-pfoa-epa/.

[101] 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.

[102] https://www.internationalairportreview.com/article/11655/ensuring-a-safer-future-for-the-aviation-industry/.

[103] See UNEP/POPS/POPRC.13/7/Add.2.

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.

179. 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.

180. 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_6-fluorinated alternatives perform better than all fluorine-free alternatives and vice versa.

181. 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.

182. 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.

183. 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.

184. 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 USD 1,000 per kilogram. However, it is indicated that the cost of remediation could be well over USD 10,000 per kilogram.

2.4.4 Implementation of alternatives

185. Over the past 20 years, the use of PFOS in fire-fighting foams has declined substantially, with the use of non-PFOS containing foams 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.

186. According to the estimated inventory of PFOS-based AFFF by FFFC (2011) in the USA, 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 bases fire-fighting foams.[104]

187. According to FFFC (FFFC, 2020), currently about 85-95% of their class B foam sales are fluorinated foams, while whereas Eurofeu's data indicates that PFAS-containing foams represent around 68% of the market in the EU (ECHA, 2022b).

188. Canada (2018) indicated that foams containing PFOS have not been manufactured in the U.S. or Europe since 2002. However, 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.[105]

[104] 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.

[105] UNEP/POPS/POPRC.12/INF/15/Rev.1.

189. In Europe, the use of fire-fighting foams containing PFOS has been banned since 27 June 2011. The use of PFOA, its salts and PFOA-related compounds in FFF for Class B fires in already installed in systems is permitted under the Regulation (EU) 2019/1021[106] until 4 July 2025 [107].

190. In 2021 the Committee for Risk Asssessment (RAC) and Committee for Socio-economic Analysis (SEAC) have adopted their opinion on the proposal to restrict under REACH the manufacturing, placing on the market and use of PFHxA, its salts and related substances (ECHA, 2021). The restrictions on PFHxA proposed by the Dossier Submitter include transitional periods for concentrated fire-fighting foam mixtures (i) that are placed on the market before 18 monts after the entry into force and are used or are to be used in the production of other fire-fighting foam mixtures for cases of class B fires (5 years);[108] (ii) for cases of class B fires in tanks with a surface area above 500 m^2 (12 years);[109] (iii) for defence applications (until successful transition to military operable fluorine free foams can be achieved).[110]

191. A proposal to restrict the use of all PFASs in fire-fighting foams under REACH is currently discussed in ECHA's scientific commites.[111] The restriction option proposed by ECHA as a Dossier Submitter includes different transitional periods per type of use, with a long transition period (10 years after the entry into force) for certain applications (notably for large atmospheric storage tank fires and industries dealing with numerous different flammable liquids at the same site) where further testing is required to determine the technical feasibility of alternatives, and where potential fire-safety risks from using inappropriate alternatives may be higher (ECHA, 2022).

192. The FFFC (2018) indicated that over the past few years most manufacturers have transitioned to short-chain (C_6) fluorosurfactants and that fluorotelomer-based foams are available on the market and accessible by foam users anywhere in the world.

193. Airports in a number of countries (including Norway and Denmark) as well as Australia have phased out the use of PFOS-containing firefighting foams in favour of fluorinated and fluorine-free alternatives.[112]

194. Continued use of PFOS as surfactants in AFFF in China has been indicated by a CAFSI Survey (Huang et al., 2013). However, it is unclear whether China still uses fire-fighting foams that contain PFOS.

195. 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.

196. Vietnam (2022) reports that there are some enterprises that are using a few alternatives in Vietnam. However, Ministry of Natural Resources and Environment (MONRE) has not yet synthesized adequate information related to these alternatives.

2.4.5 Information gaps and limitations

197. The following information gaps and limitations still remain:

(a) More information on technical performance of fluorine-free alternatives is needed. Continued R&D effort is required to improve the performance and capability of fluorine-free alternatives;

[106] Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants (recast) (Text with EEA relevance.). *OJ L 169, 25.6.2019, p. 45–77.* http://data.europa.eu/eli/reg/2019/1021/oj.

[107] Excluding testing unless all releases are contained, and training. From 1 January 2023, uses shall only be allowed in sites where all releases can be contained.

[108] SEAC proposes that the derogation applies to firefighting foam mixtures for class B fires placed on the market before the entry into force of the restriction plus 36 months. RAC did not support the derogation and concluded that emissions cannot be minimised by means other than a restriction, e.g., due to wide-dispersive uses.

[109] SEAC proposes that the derogation for class B fires is expanded to tanks is with a surface area above 400 m2 and the bunded areas. According to RAC, there are significant uncertainties on minimisation of emissions and is uncertain if derogation justified.

[110] SEAC considers that it has not been sufficiently demonstrated in the Background Document that alternatives to fluorinated firefighting foams considered suitable for civilian uses are not also applicable for military uses over the transition period of 5 years proposed for firefighting foams for class B fires in general. Therefore, SEAC does not support a separate derogation for defence purposes. SEAC recalls that according to REACH Article 2(3), Member States may allow for exemptions from the REACH Regulation in the interests of defence. RAC did not support the derogation and concluded that emissions cannot be minimised by means other than a restriction, e.g., due to wide-dispersive uses.

[111] https://echa.europa.eu/es/registry-of-restriction-intentions/-/dislist/details/0b0236e1856e8ce6.

[112] https://ipen.org/sites/default/files/documents/IPEN_F3_Position_Paper_POPRC-14_12September2018d.pdf.

(b) More information on the composition of alternative commercial fire-fighting foams is needed in order to asses potential environmental and health risks.

2.4.6 Concluding remarks

198. 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 use of PFOS, its salts and PFOSF for fire-fighting foam is available as 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.

199. The Committee recognized that a transition to the use of short-chain 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.

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

3.1 Introduction and background

200. A report on the assessment of alternatives to PFOS, its salts and PFOSF was published in 2014 (UNEP/POPS/POPRC.10/INF/7/Rev.1). The assessment conducted 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. The assessment of POPs characteristics as part of this report is not intended to imply that the Committee has fully considered whether alternative chemicals have met the Annex D criteria. An overview of results from the assessment carried out in 2014 and an excerpt of the annex to decision POPRC-10/4 are available in appendix 2 and 3 to the present report, respectively.

201. Further assessment was carried out in 2018 as reported in document UNEP/POPS/POPRC.14/INF/13. The output of screening results for the additional alternatives assessed in 2018 and the conclusions of the screening assessment reported in that document are set out in appendix 4 and 5 to the present report, respectively.

202. 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).

203. The present report is an update of the report published in 2018 (UNEP/POPS/POPRC.14/INF/13). 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

204. Many of the alternative substances previously screened (see appendix 2) are discussed in the sections on individual uses in section 2, i.e., many of the substances identified as potential alternatives were screened for POPs characteristics in the previous assessment conducted in 2014. The results of the previous assessment are set out in appendix 3, 4, 5 and 6 to the present report.

205. In this assessment, the principal source of information was a review of the inputs provided by Parties and observers[113] and any literature/additional information sources referenced therein; including company websites and safety data sheets.

206. 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.[114] 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

[113] http://chm.pops.int/tabid/9105/Default.aspx.

[114] 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).

resources and time available for its preparation of the current report. Table 7 below provides an overview of PFOS alternatives identified for screening and assessment for POPs characteristics.

Table 7. Overview of PFOS alternatives identified for screening and assessment for POPs characteristics

Substance/Brand name	CAS No.	Applications	Class*
Carbaryl	63-25-2	Insecticides for control of leaf-cutting ants	Not screened
Chlorpyrifos	2921-88-2	Insecticides for control of leaf-cutting ants	2
Metaflumizone	139968-49-3	Insecticides for control of leaf-cutting ants	Not screened
Methoprene	40596-69-8	Insecticides for control of leaf-cutting ants	Not screened
Permethrin (pyrethroid)	52645-53-1	Insecticides for control of leaf-cutting ants	Not screened
D-Limonene (citrus oil extract)	5989-27-5	Insecticides for control of leaf-cutting ants	Not screened
Fenvalerate	51630-58-1	Insecticides for control of leaf-cutting ants	Not screened
Metaflumizone	139968-49-3	Insecticides for control of leaf-cutting ants	Not screened
6:2 Fluorotelomer sulfonate (6:2 FTS)	27619-97-2	Metal plating	3
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt	754925-54-7	Metal plating	3
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	Metal plating	3
1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane	113507-82-7	Metal plating	3
Alkane sulfonates	N/A	Metal plating	N/A
Oleo amine ethoxylates	26635-93-8	Metal plating	Not screened
Fluorinated alternatives			
Dodecafluoro-2-methylpentan-3-one	756-13-8	Fire-fighting foams	3
Perfluorohexane ethyl sulfonyl betaine	N/A	Fire-fighting foams	3
5:1:2 fluorotelomer betaine	171184-14-8	Fire-fighting foams	Not screened
6:2 Fluorotelomer sulfonamide betaine	34455-29-3	Fire-fighting foams	Not screened
7:1:2 fluorotelomer betaine	171184-03-5	Fire-fighting foams	Not screened
7:3 fluorotelomer betaine	171184-15-9	Fire-fighting foams	Not screened
Carboxymethyldimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl] amino]propylammonium hydroxide	34455-29-3	Fire-fighting foams	3
A fluorosynthetic versatile AR foam concentrate containing 5-10% 2-(2-butoxyethoxy) ethanol	11234-5	Fire-fighting foams	Not screened
Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)	70829-87-7	Fire-fighting foams	Not screened
4:2 Fluorotelomer sulfonic acid	757124-72-4	Fire-fighting foams	Not screened
6:2 Fluorotelomer sulfonate	27619-97-2	Fire-fighting foams	Not screened
4:2 fluorotelomer thioamido sulfonates	1432486-88-8	Fire-fighting foams	Not screened
6:2 fluorotelomer thioether amido sulfonic acid	88992-47-6	Fire-fighting foams	Not screened
6:2 fluorotelomer sulfonamide amine	1383438-86-5	Fire-fighting foams	Not screened

Substance/Brand name	CAS No.	Applications	Class*
N-[3-(Dimethyloxidoamino)propyl] -3,3,4,4,5,5,6,6,7,7, 8,8,8-Tridecafluor 1-octanesulfonamid	80475-32-7	Fire-fighting foams	Not screened
(Carboxymethyl)di methyl [3-(gamma-omega perfluoro-1-C6-14-alkansulfonamid)propyl)ammonium (inner salt)	133875-90-8	Fire-fighting foams	Not screened
6:2 fluorotelomer thio hydroxy ammonium	88992-46-5	Fire-fighting foams	Not screened
Perfluoroheptane sulfonamidoethanol	167398-54-1	Fire-fighting foams	Not screened
Non-fluorinated alternatives			
Poly(oxy-1,2- ethanediyl),α-hydro-ω-hydroxy- ethane-1,2- diol, ethoxylated	25322-68-3	Fire-fighting foams	Not screened
Allyloxy(polyethylen e oxide), methyl ether (9-12 EO)	27252-80-8	Fire-fighting foams	Not screened
Poly(oxy-1,2- ethanediyl), α-sulfo-ω-(dodecyloxy)-, ammonium salt (1:1)	32612-48-9	Fire-fighting foams	Not screened
Poly(oxy- 1,2- ethanediyl), .alpha.-sulfo-.omega.-hydroxyC6-10-alkyl ethers, sodium salts	73665-22-2	Fire-fighting foams	Not screened
Poly(oxy-1,2-ethanediyl), α-sulfo-ω-hydroxy-, C9-11-alkyl ethers, sodium salts	96130-61-9	Fire-fighting foams	Not screened
2-6% Hexylene glycol (CAS No. 107-41-5, EC 203489-0); hydrolysed protein [70-80%], metallic salt: NaCl+MgCl2 [8-15%]; FeSO4*7H2O[0-2%]	See column “Substance/Brand name”	Fire-fighting foams	Not screened
1-Dodecanol	112-53-8	Fire-fighting foams	Not screened
Tetradecanol	112-72-1	Fire-fighting foams	Not screened
Alcohols, C9-11, ethoxylated, sulphates, ammonium salts	67762-19-0	Fire-fighting foams	Not screened
Tetradecan-1-ol	67762-41-8	Fire-fighting foams	Not screened
Alcohols, C12-15, ethoxylated	68131-39-5	Fire-fighting foams	Not screened
Xanthan gum	11138-66-2	Fire-fighting foams	Not screened
Cyamopsis gum; cyanopsis tetragonoloba	9000-30-0	Fire-fighting foams	Not screened
Starch	9005-25-8	Fire-fighting foams	Not screened
Canola Oil	120962-03-0	Fire-fighting foams	Not screened
Alkylpolyglycoside C10-16	110615-47-9	Fire-fighting foams	Not screened
(3*R*,4*S*,5*S*,6*R*)-2-(decyloxy)-6-(hydroxymethyl)oxane-3,4,5-trio	54549-25-6	Fire-fighting foams	Not screened
Alkyl polyglucoside	68515-73-1	Fire-fighting foams	Not screened

207. 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 and acceptable purposes in Annex B to the Convention.

208. As noted in the previous assessment report, 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. Alternatives with known chemical composition and CAS numbers were prioritised for the assessment.

3.3 Methodology for the assessment of POPs characteristics

209. 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 sections 3 and 4 of the previous alternatives assessment report.[115] This previous assessment was undertaken by applying and adapting the methodology previously used by the Committee in the assessment of alternatives to endosulfan.[116] An overview of the methodology used is described here.

210. 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

211. 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.

212. Due to the time constraints of carrying out the assessment, the screening step was carried out using the PB-score tool, developed at RIVM[117]. 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.[118] 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 validly of results generated from this screening tool.

213. The overall PB-score varies between 0 and 2. Cut-off values complying with the formal screening criteria in Annex D are ≥0.5 for the P-score as well as the B-score. Thus, substances with a PB score of ≥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.

214. 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).

215. 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.

[115] UNEP/POPS/POPRC.10/INF/7/Rev.1.

[116] UNEP/POPS/POPRC.8/INF/28.

[117] 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.

[118] Raw materials meaning parent precursors, manufacturing intermediates and final functional chemicals such as fluorosurfactants are included in the assessment, but not transformation chemicals that are formed and consumed during the synthesis.

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 ≤0.5 (for fluorinated substances) and/or persistence: half-life (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

216. As described in the previous PFOS alternatives assessment[119] (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).

217. 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**.

218. 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;

(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;

(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) Macckay, D. et al. (2006) Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals.

219. The following priorities were considered:

(a) Substance identity: CAS number, IUPAC name, molecular weight, chemical structure, chemical group;

[119] UNEP/POPS/POPRC.10/INF/7/Rev.1.

(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;

(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[120] (only European harmonized classifications were considered)[121] 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 33 (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

220. Additionally, the following hazards were considered:

(a) Acute toxicity;

(b) Mutagenicity;

(c) Carcinogenicity;

(d) Toxicity for reproduction;

(e) Neurotoxicity;

(f) Immunotoxicity;

[120] http://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev04/English/ST-SG-AC10-30-Rev4e.pdf.

[121] 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

221. In assessing potential alternatives that are suitable substitutes for persistent organic pollutants (POPs), the criteria in paragraph 1 of Annex D to the Convention 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 PFOS, its salts and PFOSF. 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.

222. 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.

223. Parties may use this report when choosing alternatives to PFOS, its salts and PFOSF as an initial source of information. 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 Assessment of POPs characteristics

3.5.1 Results of the initial screening of alternatives to PFOS

224. 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. See Table 8 below.

225. 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”.

226. 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. 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 utlilised in the interpretation B-values in this assessment is justified.

227. The substance sodium p-perfluorous nonenoxybenzene sulfonate (OBS) did not undergo screening using the RIVM tool[122] 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 8. Results of the initial screening exercise

Screening categories	Substances
Screening category I: potential persistent organic pollutants	1. Metaflumizone 2. Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)[123] 3. Tolyl phosphate (TOCP, TOTP) 4. Tricresyl phosphate (TCP)
Screening category II: candidates for further assessment	1. Methoprene 2. Permethrin (pyrethroid)
Screening category III: candidates for further assessment with limited data	1. Cyfluthrin (pyrethroid) 2. Diphenyl-2-ethylhexyl phosphate 3. Diphenyl isopropylphenyl phosphate 4. Fenvalerate 5. *p-tert*-Butylphenyl diphenyl phosphate 6. Trixylyl phosphate (TXP)
Screening category IV: not likely to fulfil the criteria on persistence and bioaccumulation in Annex D	1. Acephate 2. Alcohols, C12-16 3. Alkylpolyglycoside 4. Amyl acetate 5. Anisole 6. 2-Butoxyethanol 7. 1-Butoxy-2-propanol; propylene glycol butyl ether; 3-butoxy-2-propanol 8. n-Butyl acetate 9. Carbaryl 10. Cycltriphosphazene 11. Decylsulfate 12. Dibutyl phenyl phosphate 13. Diethylene glycol monobutyl ether; 2-(2-butoxyethoxy)-ethanol 14. Diphenyl tolyl phosphate 15. D-Limonene (citrus oil extract) 16. 1,2-Ethandiol 17. Ethyl lactate 18. Hexylene glycol; 2-methyl-2,4-pentanediol; methyl-3-methoxypropionate 19. Isodecyldiphenylphosphate 20. Isopropylphenyl phosphate 21. Methyl-3-methoxypropionate 22. Nonylphenyl dipenyl phosphate 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

[122] 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.

[123] Categorisation based on a manual calculation of P and B values, strongly indicating high P (1.00) and B (0.69) characteristics.

Screening categories	Substances
	31. Tri-*tert*-butyl phenyl phosphate
Screening category V: substances and products that are difficult to classify due to insufficient data (i.e., chemical composition or structure unknown)	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

3.5.2 Results of the initial detailed assessment of alternatives to PFOS

228. 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 in Table 9 below.

229. 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 Tolyl phosphate (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 9. 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
Tolyl phosphate (TOCP, TOTP)	Yes	Yes	Insufficient data	Yes	Yes	2
Tricresyl Phosphate (TCP)	Yes	Yes	Insufficient data	Yes	Yes	2
Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)	Insufficient data	Insufficient data	Insufficient data	Insufficient data	Insufficient data	3
Methoprene	Insufficient data	Yes	Insufficient data	Yes	No	4
Permethrin	Yes	No	Insufficient data	Yes	Insufficient data	4

3.6 Data availability and uncertainties

230. 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 3.3. Where data from these sources was limited, a wider search of publicly available primary literature.

231. As discussed in the previous PFOS alternatives assessment[124] 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.

232. 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

[124] UNEP/POPS/POPRC.10/INF/7/Rev.1.

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.

233. As noted in the previous assessment,[125] 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.

234. As noted previously, for fluorinated substances, no data on BMF or TMF was available from the sources consulted. The bioaccumulation potential of fluorinated chemicals is overestimated in the RIVM model which uses Kowwin 1.67. The underlying US-EPA models, such as Kowwin1.68,[126] have been updated for the fluorinated substances. These 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. EPISuite generates 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 initial screening assessment on persistent organic pollutants characteristics of alternatives to PFOS

235. 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.

236. 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 tolyl 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 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 to meet all Annex D criteria

0 substances	
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

3 substances	
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

7 substances	
CAS No.	**Substance**
70829-87-7	Sodium p-perfluorous nonenoxybenzene sulfonate (OBS)
1241-94-7	Diphenyl-2-ethylhexyl phosphate

[125] UNEP/POPS/POPRC.10/INF/7/Rev.1.

[126] https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface.

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)

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.

33 substances	
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

33 substances	
CAS No.	**Substance**
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.

8 products	
CAS No.	**Substance**
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

237. 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	**Availability (*Commercial availability on the market; geographic, legal or other limiting factors.)***	**Suitability (*Technically feasibility, economic viability, cost-effectiveness)***	**Implementation (*Trends in use of PFOS and related compounds, extent to which alternatives are already used.)***	**Data gaps/limitations (*Key areas where information is lacking)***	**Specific exemption/acceptable purpose should be retained until further notice**
Insect baits for control of leaf-cutting ants	Wide range of commercially available alternatives (pesticides) on the market; techniques for application (e.g., dry powder formulation) have been developed. Non-chemical (mechanical, cultural, and biological) control methods have been developed but are not fully commercialised or available in all locations.	Sulfluramid is still 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. BAT/BEP guidance indicates in general, chemical control with toxic baits containing sulfluramid seems often more practical, economical and operational to control the pests. 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. A number of promising biological and physical control methods are outlined. The level of implementation of these techniques is unknown. It is not 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.	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. Because of variations in the efficacy data between laboratory and field tests for alternatives to sulfuramid, is would be of value to evaluate these control methods through field studies with different leaf-cutting ant species and under different environmental conditions for possible implementation.	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. 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. Information on conversion rate of sulfluramid to PFOS in the environment under natural conditions is needed.	Acceptable purpose should be retained.

Measure	**Availability (*Commercial availability on the market; geographic, legal or other limiting factors.)***	**Suitability (*Technically feasibility, economic viability, cost-effectiveness)***	**Implementation (*Trends in use of PFOS and related compounds, extent to which alternatives are already used.)***	**Data gaps/limitations (*Key areas where information is lacking)***	**Specific exemption/acceptable purpose should be retained until further notice**
Metal-plating	A 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&D activity and are less readily available. A number of process-based approaches to replace PFOS are also identified and are commercially available e.g., High Velocity Oxygen Fuel (HVOF) process. Chromium(III) plating is available as an alternative to chromium(VI) plating for some decorative plating applications.	PFOS-free alternatives are considered to be less stable and durable in the chrome bath than PFOS due to a number of limitations, including the potential for degradation to hazardous products in the environment. Use of identified alternatives in a closed loop process may be more problematic due to potential issues with preventing release to the environment. 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.	Use of chromium(III) instead of chromium(VI) for certain decorative chrome plating processes has made PFOS use in decorative plating obsolete. No continuous need for PFOS use for hard metal plating is indicated by any Party, which means that the specific exemption for use of chromium(VI) in metal plating (hard-metal plating) may no longer be needed, indicating the viability and feasibility of alternatives.	A harmonised definition of “closed loop” process is needed in order to establish a common understanding among industry stakeholders and competent authorities to enable harmonised conditions for this use. More information on the degradation products of potential alternatives is needed to establish the environmental performance of different alternatives. Knowledge gaps exist concerning novel plating practices, including details of the processes themselves, identity of chemicals used, best practices and levels of market acceptance	Specific exemption should be retained.
Fire-fighting foam	The industry standard for fire-fighting foams is rapidly switching from C_8 fluorinated compounds towards fluorine-free substances or to short-chained PFASs and fluorinated telomers. 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. Alternative processes/practices have also been developed to minimise the release of PFOS from certain applications e.g., training operations.	Alternative foam formulations, both fluorinated and fluorine-free are shown to be technically and economically viable for a number of applications. 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. 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.	The use of non-PFOS containing foams widespread across Europe, North America and Australia. Available information from Parties and industry indicates use of PFOS in this sector is declining rapidly. Industry indicate that most manufacturers have transitioned to only short-chain (C_6) fluorosurfactant foams and fluorine-free foams, where these meet the required standards.	More information on technical performance of fluorine-free alternatives is needed. Continued R&D effort is required to improve the performance and capability of fluorine-free alternatives. More information on the composition of alternative commercial fire-fighting foams is needed in order to asses potential environmental and health risks.	Specific exemption should be retained.

5 References

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Appendix 1: Overview of information provided by Parties and observers

Submitter	Title	Date
Parties		
Brazil	Alternatives to PFOS information	14/03/2022
Canada	Alternatives to PFOS information	14/03/2022
European Union	Alternatives to PFOS information	14/03/2022
Monaco	Response	04/02/2022
Netherlands	Form	14/03/2022
Norway	Alternatives to PFOS information	14/03/2022
Republic of Korea	Alternatives to PFOS information	16/03/2022
Sweden	Alternatives to PFOS information	14/03/2022
Sweden	Hard chrome metal plating - use of PFOS as mist suppressant and its alternatives	14/03/2022
Türkiye	Alternatives to PFOS information	15/03/2022
UK	Alternatives to PFOS information	16/03/2022
Vietnam	Alternatives to PFOS information	01/07/2022
Observers		
International Pollutants Elimination Network/Alaska Community Action on Toxics (IPEN/ACAT)	Alternatives to PFOS information	16/03/2022
Le Grand Puissance de Dieu ONG	Alternatives to PFOS information	14/03/2022
Leaf-cutting Ant Baits Industries Association (ABRAISCA)	Alternatives to PFOS information	14/03/2022

Appendix 2: Overview of results from the alternatives assessment in UNEP/POPS/POPRC.10/INF/7/Rev.1 (assessed in 2014)[127]

Substance/Brand name	CAS No.	Type	Functionality	Applications
Class 1: Substances that the committee considered met all Annex D criteria[128]				
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
Class 2: Substances that the committee considered might meet all Annex D criteria but remained undetermined due to equivocal or insufficient data				
Chlorpyrifos[129]	2921-88-2	Pesticides		
Class 3: Substances that are difficult for classification due to insufficient data				
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)[130]	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
Carboxymethyldimethyl-3-[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl] amino]propylammonium hydroxide[131]	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[132]	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

[127] For these previously assessed substances, more information is currently available.

[128] POPRC-17 concluded that D4 meets the screening criteria as a potential POP.

[129] Chlorpyrifos has been proposed for listing in Annex A, B or C to the Stockholm Comvention.

[130] 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.

[131] See above.

[132] See above.

Substance/Brand name	CAS No.	Type	Functionality	Applications
sulphonate potassium salt (6:2 FTS K)				
1*H*,1*H*,2*H*,2*H*-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)	73606-19-6, 83329- 89-9	Fluorinated substance	Fluorosurfactant	Metal plating
1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate (F-53)	68136-88-9	Fluorinated substance	Fluorosurfactant	Metal plating
Perfluorohexane ethyl sulfonyl betaine	161278-39-3	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)[133]*	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®	N/A	Commercial brand	Polymer coating	Coating and coating additives
Emulphor® FAS	N/A	Commercial brand	Polymer coating	Coating and coating additives Metal plating
Enthone®	N/A	Commercial brand	Polymer coating	Coating and coating additives Metal plating
Zonyl®[134]	N/A	Commercial brand	Polymer coating	Coating and coating additives Metal plating
Capstone®	N/A	Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Nuva®	N/A	Commercial brand	Polymer coating	Coating and coating additives, carpets, leather and apparel, textiles and upholstery, and metal plating

[133] There is ongoing work through which new information is becoming available to further support the assessment of these substances.

[134] According to FluoroCouncil, production of Zonyl® was discontinued in 2014.

Substance/Brand name	CAS No.	Type	Functionality	Applications
Unidyne®	N/A	Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Rucoguard®	N/A	Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Oleophobol®	N/A	Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Asahiguard®	N/A	Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Solvera®	N/A	Commercial brand	Polymer coating	Carpets, leather and apparel, textiles and upholstery
Class 4: Substances that are not likely to meet all Annex D criteria (b), (c), (d) and (e)				
Dodecamethyl cyclohexasiloxane (D6)*	540-97-6	Non-fluorinated substance	Manufacturing intermediate for the production of silicone polymers[135]	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[136]	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.[137]	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-phenyl-benzene	25640-78-2	Non-fluorinated substance	Waxes and resins	Coating and coating additives
Diisoproplynaphthalene (DIPN)	38640-62-9	Non-fluorinated substance	Waxes and resins	Coating and coating additives
Triisopropylnaphthalene (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 *Atta* spp. and *Acromyrmex* spp.
Pyriproxyfen	95737-68-1	Pesticide	Pesticide	Insecticides for control of red imported fire ants and termites

[135] 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.

[136] http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f.

[137] http://echa.europa.eu/documents/10162/c98c53e1-7228-4985-8f87-6e202788106f.

Substance/Brand name	CAS No.	Type	Functionality	Applications
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 *Atta* spp. *and Acromyrmex* spp.
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 *Atta* spp. and *Acromyrmex* spp.
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 *Atta* spp. and *Acromyrmex* spp.
Not classified; Not prioritised*				
Perfluorohexanoic acid (PFHxA)[138]	307-24-4	N/A	N/A	N/A
Perfluorohexanoic acid sodium salt (PFHxA-Na)	2923-26-4	N/A	N/A	N/A
Perfluorobutanoic acid (PFBA)	375-22-4	N/A	N/A	N/A
Perfluoroheptanoic acid (PFHpA)	375-85-9	N/A	N/A	N/A

* Substances not classifies/not prioritised as they are degradation products

[138] 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, 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)[139] 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.[140] 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[141] using a format developed by the Committee.[142] 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[143] 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.[144] 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.[145]

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 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

[139] UNEP/POPS/POPRC.10/INF/7/Rev.1.

[140] UNEP/POPS/POPRC.8/INF/28.

[141] 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.

[142] UNEP/POPS/POPRC.9/INF/10/Rev.1.

[143] UNEP/POPS/POPRC.9/INF/11/Rev.1.

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

[145] 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; 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.

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_{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). The substances identified in this screening category fulfilled both bioaccumulation and persistence criteria.
Screening category II: candidates for further assessment Cut-offs: bioaccumulation: experimental BCF >1000 and/or experimental log Kow > 4 and/or BMF/TMF > 0.5 (for fluorinated substances). Persistence: A PB-score >1 (P-score >0.5) and/or half-life (experimental and/or estimated) in water greater than two months (60 days), in soil greater than six months (180 days) or in sediment greater than six months (180 days).
Screening category III: candidates for further assessment with limited data Cut-offs: bioaccumulation: no experimental data for BCF and log Kow and for BMF/TMF (for fluorinated substances).
Screening category IV: not likely to fulfil the criteria on persistence and bioaccumulation in Annex D Cut-offs: bioaccumulation: experimental BCF< 1000 and/or experimental log Kow < 4.0 (for non-fluorinated substances) and BMF/TMF values ≤ 0.5 (for fluorinated substances) and/or persistence: half-life (experimental) in water less than two months (60 days), in soil less than six months (180 days) and in sediment less than six months (180 days).

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

Non-fluorinated alternatives (one substance)	
CAS No.	**Substance**
556-67-2	Octamethylcyclotetrasiloxane (D4)*

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

Pesticides (one substance)	
CAS No.	**Substance**
2921-88-2	Chlorpyrifos

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

Fluorinated alternatives (20 substances)	
CAS No.	**Substance**
29420-49-3	Perfluorobutane sulfonate potassium salt
3871-99-6	Perfluorohexanesulfonate potassium salt
647-42-7	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol*
27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulfonate
355-86-2	Tris(octafluoropentyl) phosphate
563-09-7	Tris(heptafluorobutyl) phosphate
40143-77-9	Sodium bis(perfluorohexyl) 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*H*,1*H*,2*H*,2*H*-Perfluorohexanol or 3,3,4,4,5,5,6,6,6-nonafluorobutyl ethanol*
	2-(6-Chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
	1,1,2,2,-Tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate
	Perfluorohexane ethyl sulfonyl betaine
756-13-8	Dodecafluoro-2-methylpentan-3-one
40143-76-8	Perfluorohexyl phosphonic acid
	1-Chloro-perfluorohexyl phosphonic acid
2144-53-8	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester*
Non-fluorinated alternatives (four substances)	
541-02-6	Decamethylcyclopentasiloxane (D5)*
577-11-7	Di-2-ethylhexyl sulfosuccinate, sodium salt
4261-72-7	Stearamidomethyl pyridine chloride
67674-67-3	(Hydroxyl) terminated polydimethylsiloxane
Commercial brands (11 brands)	
	Polyfox®
	Emulphor® FAS
	Enthone®
	Zonyl®
	Capstone®
	Nuva®
	Unidyne®
	Rucoguard®
	Oleophobol®

	Asahiguard®
	Solvera®

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

Non-fluorinated alternatives (nine substances)	
CAS No.	**Substance**
540-97-6	Dodecamethylcyclohexasiloxane (D6)*
107-46-0	Hexamethyldisiloxane (MM or HMDS)*
107-51-7	Octamethyltrisiloxane (MDM)*
141-62-8	Decamethyltetrasiloxane (MD2M)*
141-63-9	Dodecamethylpentasiloxane (MD3M)*
25640-78-2	1-Isopropyl-2-phenyl-benzene
38640-62-9	Diisoproplynaphthalene (DIPN)
35860-37-8	Triisopropylnaphthalene (TIPN)
69009-90-1	Diisopropyl-1,1'-biphenyl
Pesticides (eight substances)	
CAS No.	**Substance**
52315-07-8	Cypermethrin
52918-63-5	Deltamethrin
95737-68-1	Pyriproxyfen
138261-41-3, 105827-78-9	Imidacloprid
120068-37-3	Fipronil
122-14-5	Fenitrothion
71751-41-2	Abamectine
67485-29-4	Hydramethylnon

*Manufacturing intermediate for alternatives to PFOS.

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.

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 reported in document UNEP/POPS/POPRC.14/INF/13

Name	CAS No.	P-Score	B-Score[146]	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	-
Cycltriphosphazene	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	-

[146] 0.5 represents BCF = 5000 and 0.33 represents BCF = 2000.

Name	CAS No.	P-Score	B-Score[146]	PB-Score	PB category
Propylene glycol methyl ether acetate	108-65-6	0.03	0.00	0.03	-
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: Conclusions of the screening assessment on persistent organic pollutants characteristics of alternatives to PFOS reported in document UNEP/POPS/POPRC.14/INF/13

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.

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 tolyl 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 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

0 substances	
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

3 substances	
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

7 substances	
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)

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.

33 substances	
CAS No.	**Substance**
30560-19-1	Acephate

33 substances	
CAS No.	**Substance**
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.

8 products	
CAS No.	**Substance**
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

8 products	
CAS No.	**Substance**
107028-44-4	Reolube HYD46
50815-84-4	Skydrol 500B-4
55962-27-1	Skydrol LD-4