

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

The Persistent Organic Pollutants Review Committee,

Recalling decision SC-6/4, by which the Conference of the Parties adopted a process, set out in the annex to that decision, 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,

Having completed the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride in accordance with paragraph 3 of decision SC-6/4 and having reviewed the draft report of the Secretariat for the evaluation of information on perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride¹ in accordance with the terms of reference set out in the annex to decision POPRC-9/5,

1. *Decides* to submit the summary of the report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride set out in the annex to the present decision, together with the full assessment report² and fact sheets on nine of the alternatives assessed,³ to the Conference of the Parties for consideration at its seventh meeting;

2. *Requests* the Secretariat to finalize its report for the evaluation of information on perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride on the basis of comments and suggestions provided by the Committee⁴ and to submit it to the Conference of the Parties for consideration at its seventh meeting;

3. *Recommends* that the Conference of the Parties encourage parties that have registered or will register for specific exemptions for the production and use of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride pursuant to Article 4 of the Stockholm Convention to take measures necessary to ensure that articles containing perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride that are allowed to be produced and used can be easily identified by labelling or other means throughout their life cycles;

4. *Also recommends* that the Conference of the Parties encourage parties that have registered or will register for the production and use of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride for an acceptable purpose by notifying the Secretariat in accordance with Annex B to the Convention to take measures necessary to ensure that articles containing perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride that are allowed to be produced and used can be easily identified by labelling or other means throughout their life cycles.

¹ UNEP/POPS/POPRC10/INF/10.

² UNEP/POPS/POPRC.10/INF/7/Rev.1.

³ UNEP/POPS/POPRC.10/INF/8/Rev.1.

⁴ UNEP/POPS/POPRC.10/INF/18.

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)⁵ 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.⁶ 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 observers⁷ using a format developed by the Committee.⁸ 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 chemicals⁹ 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.¹⁰ 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.¹¹
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.

⁵ UNEP/POPS/POPRC.10/INF/7/Rev.1.

⁶ UNEP/POPS/POPRC.8/INF/28.

⁷ The information, submitted by 11 parties and 3 others, is available on the website of the Stockholm Convention at:
<http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/tabid/3565/Default.aspx>.

⁸ UNEP/POPS/POPRC.9/INF/10/Rev.1.

⁹ UNEP/POPS/POPRC.9/INF/11/Rev.1.

¹⁰ UNEP/POPS/POPRC.8/INF/17/Rev.1.

¹¹ 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>.

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 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.

<p>Screening category I: potential persistent organic pollutants</p> <p>Cut-offs: bioaccumulation: experimental bioconcentration factor (BCF) > 5000 and/or experimental log Kow > 5 and/or biomagnification factor or trophic magnification factor (BMF/TMF) > 1 (for fluorinated substances). Persistence: half-life (experimental) in water greater than two months (60 days), in soil greater than six months (180 days) or sediment greater than six months (180 days). The substances identified in this screening category fulfilled both bioaccumulation and persistence criteria.</p>
<p>Screening category II: candidates for further assessment</p> <p>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).</p>
<p>Screening category III: candidates for further assessment with limited data</p> <p>Cut-offs: bioaccumulation: no experimental data for BCF and log Kow and for BMF/TMF (for fluorinated substances).</p>
<p>Screening category IV: not likely to fulfil the criteria on persistence and bioaccumulation in Annex D</p> <p>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).</p>

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	Octamethyl cyclotetrasiloxane (D4)*

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

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

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

Fluorinated alternatives (20 substances)	
CAS No.	Substance
29420-49-3	Perfluorobutane sulfonate potassium salt
3871-99-6	Perfluorohexanesulfonate potassium salt*
647-42-7	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol*
27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulfonate
355-86-2	Tris(octafluoropentyl) phosphate
563-09-7	Tris(heptafluorobutyl) phosphate
40143-77-9	Sodium bis(perfluorohexyl) phosphinate
34455-29-3	Carboxymethyldimethyl-3-[[[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)sulfonyl]amino]propylammonium hydroxide
358-63-4	Tris(trifluoroethyl) phosphate
163702-07-6	Methyl nonafluorobutyl ether
163702-08-7	Methyl nonafluoro-isobutyl ether
59587-38-1	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctane-1-sulphonate potassium salt
2043-47-2	1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -Perfluorohexanol or 3,3,4,4,5,5,6,6-nonafluorobutyl ethanol*
	2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate
	1,1,2,2,-tetrafluoro-2-(perfluorohexyloxy)-ethane sulfonate
	Perfluorohexane ethyl sulfonyl betaine
756-13-8	Dodecafluoro-2-methylpentan-3-one
40143-76-8	Perfluorohexyl phosphonic acid

	1-chloro-perfluorohexyl phosphonic acid
2144-53-8	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester*
Non-fluorinated alternatives (four substances)	
541-02-6	Decamethyl cyclopentasiloxane (D5)*
577-11-7	Di-2-ethylhexyl sulfosuccinate, sodium salt
4261-72-7	Stearamidomethyl pyridine chloride
67674-67-3	(Hydroxyl) Terminated polydimethylsiloxane
Commercial brands (11 brands)	
	Polyfox®
	Emulphor® FAS
	Enthone®
	Zonyl®
	Capstone®
	Nuva®
	Unidyne®
	Rucoguard®
	Oleophobol®
	Asahiguard®
	Solvera®

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

Non-fluorinated alternatives (nine substances)	
CAS No.	Substance
540-97-6	Dodecamethyl cyclohexasiloxane (D6)*
107-46-0	Hexamethyl disiloxane (MM or HMDS)*
107-51-7	Octamethyl trisiloxane (MDM)*
141-62-8	Decamethyl tetrasiloxane (MD2M)*
141-63-9	Dodecamethyl pentasiloxane (MD3M)*
25640-78-2	1-Isopropyl-2-phenyl-benzene
38640-62-9	Diisopropyl-naftalene (DIPN)
35860-37-8	Triisopropyl-naftalene /TIPN)
69009-90-1	Diisopropyl-1,1'-biphenyl
Pesticides (eight substances)	
CAS No.	Substance
52315-07-8	Cypermethrin
52918-63-5	Deltamethrin
95737-68-1	Pyriproxyfen
138261-41-3, 105827-78-9	Imidacloprid
120068-37-3	Fipronil
122-14-5	Fenitrothion

71751-41-2	Abamectine
67485-29-4	Hydramethylnon

*Manufacturing intermediate for alternatives to PFOS.

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 K_{ow} 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, fire fighting foams), articles (for example, electric and electronic parts for some colour printers and colour copy machines) and processes (for example, chemically driven oil production) for which PFOS, its salts and PFOSF can have a variety of uses. The lack of information about the precise use and function of PFOS, its salts and PFOSF in these applications makes it difficult to identify corresponding alternatives with a high degree of certainty. Where possible, the functionality and application of alternative substances have been indicated in the table in appendix 1 to the full report.

19. Obtaining precise and detailed information about alternatives to the use of PFOS, its salts and PFOSF and their properties is necessary for the assessment of those alternatives by the Committee. It is recommended that the format for collecting information from parties and others be revised to facilitate the provision of such information by, for example, specifying the functionality of PFOS, its salts and PFOSF under the use categories listed as specific exemptions and acceptable purposes. Parties and others should also be encouraged to provide additional information to support the assessment of alternatives to PFOS, its salts and PFOSF.