



Persistent Organic Pollutants Review Committee
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Report of the Persistent Organic Pollutants Review Committee on the work of its fifteenth meeting

Addendum

Risk management evaluation on perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds

At its fifteenth meeting, by its decision POPRC-15/1, the Persistent Organic Pollutants Review Committee adopted a risk management evaluation on perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds on the basis of the draft contained in the note by the Secretariat (UNEP/POPS/POPRC.15/2), as revised during the meeting. The text of the risk management evaluation as adopted is set out in the annex to the present addendum. It has not been formally edited.

Annex

**Perfluorohexane sulfonic acid (PFHxS), its salts and
PFHxS-related compounds**

RISK MANAGEMENT EVALUATION

October 2019

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Executive summary

1. In May 2017, Norway submitted a proposal to list perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds in Annexes A, B and/or C to the Stockholm Convention. The proposal (UNEP/POPS/POPRC.13/4) was reviewed and decision POPRC-13/3 was adopted by the Persistent Organic Pollutants Review Committee (POPRC) at its thirteenth meeting in October 2017. The Committee decided to establish an intersessional working group to prepare a draft risk profile for PFHxS, its salts and PFHxS-related compounds for consideration at its fourteenth meeting in September 2018. The Committee adopted the risk profile (UNEP/POPS/POPRC.14/6/Add.1) and established an intersessional working group to prepare a risk management evaluation that includes an analysis of possible control measures for PFHxS in accordance with Annex F to the Convention for consideration at its fifteenth meeting.
2. The substances covered in this risk management evaluation include PFHxS (CAS No. 355-46-4), its salts and PFHxS-related compounds, defined as any substance that contains the chemical moiety C₆F₁₃SO₂- as one of its structural elements and that potentially degrades to PFHxS.
3. Historical production was mainly carried out by 3M, which phased out its production of C₆, C₈ and C₁₀ perfluoroalkyl sulfonic acids (PFASs) in 2002. Information on current global manufacture of PFHxS, its salts and PFHxS-related compounds is limited. A few producers located in China have been identified, however, quantitative production data are not publicly available. PFHxS, its salts and many PFHxS-related compounds have been listed on national chemical inventories indicating historical/present production, import and/or uses of products containing these substances.
4. PFHxS, its salts and PFHxS-related compounds have been intentionally used at least in the following applications: (1) Aqueous Film-Forming Foams (AFFFs) for fire-fighting; (2) metal plating; (3) textiles, leather and upholstery; (4) polishing agents and cleaning/washing agents; (5) coatings, impregnation/proofing (for protection from damp, fungus etc.); and (6) within the manufacturing of electronics and semiconductors. In addition, other potential use categories may include pesticides, flame retardants, paper and packaging, in the oil industry, and hydraulic fluids. PFHxS, its salts and PFHxS-related compounds have been used in certain per- and polyfluoroalkyl substances (PFASs) based consumer products. PFHxS is and has been unintentionally produced during the electrochemical fluorination (ECF) processes of some other PFASs. In many applications, PFHxS has been used as a replacement for perfluorooctane sulfonic acid (PFOS).
5. The limited information available on uses of PFHxS and PFHxS-related compounds indicates that these are like those for PFOS and perfluorooctanoic acid (PFOA). Assessment of alternatives to PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) as well as PFOA indicate that technically feasible alternatives are available and in use for all applications. Furthermore, no request for exemptions for PFHxS, its salts or PFHxS-related compounds has been submitted during the POPRC assessment process suggesting the switch to chemical alternatives and non-chemical technical solutions is feasible.
6. Some of the activities of the Strategic Approach to International Chemicals Management (SAICM) at the global level focus on gathering and exchanging information on perfluorinated chemicals and to support the transition to safer alternatives. In the United States (U.S.), voluntary efforts to phase out long chain PFAS and related compounds (including PFHxS) have been implemented. In 2017, PFHxS and its salts were identified in the European Union (EU) as Substances of Very High Concern (SVHC) and added to the EU Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Candidate List. In 2018, a restriction process was initiated in the EU.
7. Emissions of PFHxS to the environment occur at all its life cycle stages but are assumed to be highest during service life and in the waste phase. However, extensive releases of PFHxS have also been shown to occur from manufacturing plants.
8. Based on current knowledge it may be expected that industry can substitute PFHxS, its salts and PFHxS-related compounds without significant socioeconomic costs. In addition, as the expected benefits in terms of e.g. reduced mitigation and clean-up costs are expected to be considerable, the overall benefits of banning or restricting the use of PFHxS therefore are expected to outweigh the expected costs. High costs are estimated for remediation of fire-fighting foam training sites and airports, landfills for waste (especially those receiving industrial and hazardous waste), as well as for removal of PFASs (including PFHxS) from drinking water and water sources in the vicinity of these sites. Implementation of control measures for PFHxS, its salts and PFHxS related compounds would contribute to avoiding such future costs.
9. A positive impact on human health and the environment can be expected from a global elimination of PFHxS, its salts and PFHxS-related compounds. Therefore, the most effective control measure would be to list the substances in Annex A to the Convention with no exemptions for production and use.

1. Introduction

1.1 Chemical identity of PFHxS, its salts and PFHxS-related compounds

10. The chemical identity of PFHxS is described in the risk profile (UNEP/POPS/POPRC.14/6/Add.1) and is in line with the decision taken at the thirteenth meeting of the POPRC (decision POPRC-13/3). The chemical identity includes:

(a) Perfluorohexane sulfonic acid (CAS No. 355-46-4, PFHxS);

(b) Any substance that contains the chemical moiety $C_6F_{13}SO_2^-$ as one of its structural elements and that potentially degrades to PFHxS.

11. A number of chemicals are included in the group of PFHxS, its salts and PFHxS-related compounds including linear and branched isomers. OECD has developed a new list of per- and poly-fluorinated chemicals containing as many as 4730 substances and this list contains PFHxS-related/precursor/polymer substances ([http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV-JM-MONO\(2018\)7&doclanguage=en](http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV-JM-MONO(2018)7&doclanguage=en)). Furthermore, the restriction proposal developed under REACH contains 147 PFHxS compounds (ECHA, 2019b). This non-exhaustive list of 147 compounds was provided with the letter requesting Annex F information sent to Parties and observers by the Secretariat in September 2018. This list of PFHxS, its salts and PFHxS-related compounds, as well as polymers and mixtures, was compiled from the database of PFAS substances identified by the OECD and Appendix II (Non-exhaustive lists of perfluorohexane sulfonic acid and its related substances identified in Norwegian Environment Agency report M-792) of the annex to document UNEP/POPS/POPRC.14/INF/4.

12. Table 1 below lists the chemical identity of PFHxS and Table 2 lists selected modelled and experimental physico-chemical properties of PFHxS.

Table 1. Chemical identity of PFHxS

CAS number:	355-46-4
IUPAC name:	1,1,2,2,3,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulfonic acid
EC number:	206-587-1
EC name:	Perfluorohexane-1-sulfonic acid
Molecular formula:	$C_6F_{13}SO_3H$
Molecular weight:	400.11
Synonyms:	PFHxS PFHS Perfluorohexanesulfonic acid; 1,1,2,2,3,3,3,4,4,5,5,6,6,6-Tridecafluorohexane-1-sulfonic acid; Tridecafluorohexane-1-sulfonic acid; 1-Hexanesulfonic acid, 1,1,2,2,3,3,3,4,4,5,5,6,6,6-tridecafluoro-; 1,1,2,2,3,3,3,4,4,5,5,6,6,6-Tridecafluoro-1-hexanesulfonic acid; Tridecafluorohexanesulfonic acid
Trade names for PFHxS, its salts and PFHxS-related compounds:	RM70 (CAS No. 423-50-7), RM75 (3871-99-6), and RM570 (CAS No. 41997-13-1) (PFHxS-related compounds formerly produced by Miteni SpA, Italy). FC-95 Fluorad brand fluorochemical surfactant (CAS No. 3871-99-6) contains PFHxS-K formerly produced by 3M.

Table 2. Overview of relevant physicochemical properties of PFHxS¹

Property	Value	Reference
Physical state at 20°C and 101.3 kPa	Solid white powder for PFHxSK	As referenced in ECHA, 2017a (company provided)
Melting point	320 K (41°C)	Kim et al., 2015
Boiling point	238–239°C	Kosswig, 2000 (measured)
pK _a	-3.45 -3.3±0.5 -5.8±1.3	Wang et al., 2011a (COSMOtherm) ACD/Percepta 14.2.0 (Classic) ACD/Percepta 14.2.0 (GALAS)

¹ This refers to linear PFHxS.

Property	Value	Reference
Vapour pressure	58.9 Pa (0.0046 mmHg)	Wang et al., 2011a (COSMOtherm)*
Water solubility	1.4 g/L (PFHxSK; 20–25°C) 2.3 g/L (non-dissociated)	Campbell et al., 2009 (measured) Wang et al., 2011a (COSMOtherm)*
Air/water partition coefficient, K_{aw} (log value)	-2.38	Wang et al., 2011a (COSMOtherm)*
<i>n</i> -Octanol/water partition coefficient, K_{ow} (log value)	5.17	Wang et al., 2011a (COSMOtherm)*
Octanol-air partition coefficient K_{oa} (log value)	7.55	Wang et al., 2011a (COSMOtherm)*
Organic carbon/water partition coefficient K_{oc} (log value) (mobility)	2.05 2.40 2.31 (range 1.8–2.76)	Guelfo and Higgins, 2013 (measured) D'Agostino & Mabury, 2017 (measured) Chen et al., 2018 (field-based)

* Estimates from Wang et al. (2011a) refer to the neutral form of PFHxS only. It should be noted that PFHxS is present in its anionic form under environmental conditions due to its low pK_a . Therefore, to describe partitioning of both the neutral and ionized species of PFHxS in the environment, estimated partition coefficients of the neutral form need to be converted to respective distribution ratios, as suggested in Schwarzenbach et al. (2002) and Wang et al. (2011a).

13. Analytical methods for the detection of PFHxS are reported in the literature which can be used to measure PFHxS and PFASs in general in almost all environmental media (see UNEP/POPS/POPRC.14/INF/4 for details). For analysis in articles and products, although there are no standardized analytical methods, it is possible to use current CEN/TS 15968 for PFOS in coated and impregnated solid articles, liquids and fire-fighting foams to determine the levels of ionic forms of PFHxS, its salts and PFHxS-related compounds. ISO 23702-1: 2018 09 15 Leather -- Organic fluorine -- Part 1 describes the detection and quantification of extractable neutral, ionic, long, medium and short chain per- and polyfluorinated substances in leather and coated leather. The ISO 25101 standard describes the analytical method for PFOA and PFOS in water. International standardization work has also been initiated for 27 PFASs for water (<https://www.anses.fr/en/system/files/EAUX2018SA0027EN.pdf>). For volatile neutral PFHxS-related compounds, Herzke et al (2012) have reported detection of PFHxS and related compounds using a different analytical instrumentation (GC/PCI-MS). Market surveillance of products is hampered by a lack of standardized methods for PFHxS and a lack of availability of analytical certified standards for PFHxS-related compounds. Standardized methods are also lacking for detecting individual PFHxS-related substances. However, non-standardized methods to detect total PFAS-precursors are commercially available, such as total extractable organic fluorine (EOF) or total oxidizable precursor (TOP) (e.g. https://www.euofins.se/media/1568225/top_precursor_short_facts_170613.pdf).

1.2 Conclusions of the POPs Review Committee, Annex E information

14. In May 2017, Norway submitted a proposal to list perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds in Annexes A, B and/or C to the Convention. At its thirteenth meeting, the Committee reviewed the proposal (UNEP/POPS/POPRC.13/4) and decided to establish an intersessional working group to prepare a draft risk profile for PFHxS, its salts and PFHxS-related compounds (decision POPRC-13/3). At its fourteenth meeting, the Committee adopted the risk profile (UNEP/POPS/POPRC.14/6/Add.1) and decided that PFHxS, its salts and PFHxS-related compounds are likely as a result of their long-range environmental transport to lead to significant adverse human health and environmental effects such that global action is warranted (decision POPRC-14/1). The Committee established an intersessional working group to prepare a risk management evaluation that includes an analysis of possible control measures for PFHxS in accordance with Annex F to the Convention for consideration at its fifteenth meeting.

1.3 Data sources

15. The risk management evaluation was developed using information contained in the risk profile (UNEP/POPS/POPRC.14/6/Add.1) and Annex F information submitted by Parties and observers. Information was submitted by the following Parties and observers: Canada, Germany, India, Japan, Republic of Korea, Sweden, United Kingdom (UK), Imaging and Printing Association Europe (I&P Europe), International POPs Elimination Network (IPEN) and Alaska Community Action on Toxics (ACAT). All submissions of Annex F information are available on the Convention website.²

16. Scientific literature obtained from scientific databases such as ISI Web of Science and PubMed was included as well as other publicly available information such as government reports, risk- and hazard assessments, industry fact sheets, etc.

² <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC14/POPRC14Followup/PFHxSInfoSubmission/tabid/7826/Default.aspx>.

1.4 Status of the chemical under international agreements and organisations

17. Perfluorinated chemicals were identified under SAICM as an issue of concern. Efforts are focused on gathering and exchanging information on perfluorinated chemicals and to support the transition to safer alternatives (<http://www.saicm.org/tabid/5478/Default.aspx>). OECD provided a recent overview on risk reduction approaches for PFASs across countries (OECD, 2015). Responses from participating countries indicated that risk reduction approaches for PFASs are mainly covered under existing national and/or regional regulatory frameworks and cover principally long chain PFASs and their precursors and salts. The type of risk reduction approaches implemented across countries varies, but there is often a combination of voluntary and regulatory approaches that are used.

1.5 National and regional risk management

18. In 2017, PFHxS and its salts were identified within the European Union as Substances of Very High Concern (SVHC) and added to the REACH Candidate List due to their persistent and bioaccumulative properties (ECHA, 2017a). PFHxS fulfilled the criteria for very persistent and very bioaccumulative (vPvB) substances. Toxicity and ecotoxicity were not subject to evaluation. Identification as a vPvB substance means that manufacturers, importers and the supply chain must minimise emissions and exposures to the environment and humans of the substances in their whole life cycle independent of further regulatory risk management. Candidate listing initiates the duty of suppliers to communicate information on PFHxS above a concentration of 0.1% in articles according to Article 33 of REACH (Germany Annex F information). As a follow-up, Norway has submitted a proposal to amend REACH Annex XVII to restrict the manufacture, use and placing on the market of PFHxS, its salts and PFHxS-related compounds, with the submission date of 12 April 2019 (ECHA, 2019 a,b).

19. Some PFHxS-related compounds (not PFHxS itself) are listed on the Canadian Domestic Substances List (DSL) (Environment Canada, 2013), an inventory of substances that are or have been manufactured in, imported into or used in Canada on a commercial scale. Any person who intends to import or manufacture a substance in Canada that is not listed on the DSL (such as PFHxS, PFHxSF or PFHxS-related compounds not yet on the DSL) must submit a notification required under the New Substances Notification Regulations. These regulations aim to ensure that new substances are not introduced into the Canadian marketplace before undergoing ecological and human health assessments. Management measures may be imposed under this process to mitigate any risks to the environment or human health. In the United States new uses of the chemicals in this group are prohibited without prior evaluation of the new use the United States Environmental Protection Agency (U.S. EPA) (United States Government, 2002; 2007). The U.S. EPA published an action plan on long-chain PFASs (defined as PFSA >C₅ and perfluorocarboxylic acids (PFCAs) >C₇), including PFHxS, and their salts and precursors in 2009. All long-chain PFAS chemicals were identified as having the potential to be persistent, bioaccumulative and toxic (U.S. EPA, 2009). The U.S. EPA published a broader PFAS Action Plan in February 2019 that lays out additional steps the EPA is taking to better understand and manage PFAS, including PFHxS (U.S. EPA, 2019). The state of Washington has recently adopted a bill banning the use of perfluorinated chemicals in food packaging (<https://www.foodpackagingforum.org/news/washington-state-bans-pfass-in-food-packaging>) as well as restricting their use in fire-fighting foam and personal protective equipment (<https://ecology.wa.gov/Waste-Toxics/Reducing-toxic-chemicals/Addressing-priority-toxic-chemicals/PFAS/Toxics-in-firefighting>).

20. In Australia, the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) has developed an action plan for assessment and management of chemicals which may degrade to PFCAs, PFSA, and similar chemicals. The primary assumption outlined in this action plan is that chemicals with a perfluorinated chain terminated by a sulfonyl group will degrade to the perfluoroalkyl sulfonate (of the same chain length) (NICNAS 2017, a, b, c and d).

21. No harmonized classification or labelling is available for PFHxS either in the EU or globally. However, in Australia PFHxS-related compounds are included in the Inventory Multi-Tiered Assessment and Prioritisation (IMAP) framework, which includes both human health and environmental assessments (NICNAS 2017c). Based on the NICNAS action plan to assess and manage chemicals which may degrade to perfluorinated carboxylic acids, perfluoroalkyl sulfonates and similar chemicals, where chemical specific data was not available, the PFOS hazard information was used to estimate the systemic health hazard of potassium PFHxS, ammonium PFHxS, diethanolammonium PFHxS and PFHxSF. In relation to human health risks, potassium PFHxS, ammonium PFHxS, diethanolammonium PFHxS and PFHxSF were identified as: toxic if swallowed - Cat. 3 (H301), causes serious eye irritation - Cat. 2A (H319), causes damage to organs through prolonged or repeated exposure if swallowed - Cat. 1 (H372), suspected of causing cancer - Cat. 2 (H351) using the UN Globally Harmonized System of Classification and Labelling of Chemicals (GHS). In relation to environmental risks, these chemicals were identified as chronic aquatic - Cat. 4 (H413) (NICNAS 2017a). In the EU, self-classifications have been submitted by industry with notifications to the C&L inventory under the EU legislation, for PFHxS and several PFHxS-related compounds for Acute Tox 4 (H302, harmful if swallowed; H312, harmful in contact with skin; and H332, harmful if inhaled) and Skin Corr 1B (H314, causes severe skin burns and eye damaging) (<https://echa.europa.eu/sv/information-on-chemicals/cl-inventory-database/-/discli/notification-details/10265/1400492>).

22. Australia has also identified 26 high-priority defence sites where groundwater is contaminated with PFASs including PFHxS (<http://www.defence.gov.au/Environment/PFAS/Publications/Default.asp>). For PFOS and PFHxS, Australia has implemented health-based guidance values, expressed as a tolerable daily intake (TDI) of 0.02 µg/kg bw/day (combined), while for PFOA the TDI is 0.16 µg/kg bw/day. These values are of use when investigating contaminated sites and conducting human health risk assessments (Australia Gov., 2019).
23. In Norway, PFHxS, its salts and PFHxS-related compounds were recently added to the national list of priority substances (Prioritetslista <http://www.miljostatus.no/prioritetslisten>) with a national goal to phase out their use by 2020.
24. Information concerning PFASs including PFHxS will have to be reported to the Products Register at the Swedish Chemicals Agency for the first time in February 2020. This applies regardless of the concentration of the substances, although the concentration itself doesn't need to be specified (KemI, 2018).
25. The Swedish Chemicals Agency has published a strategy for reducing the use of PFASs (KemI, 2016, 2018b). PFAS applications which could result in environmental contamination should be minimized and ultimately discontinued. Actions to achieve this aim include prioritizing the implementation of measures for uses that can result in substantial direct releases to the environment. The strategy proposed criteria on how fire-fighting foam containing PFASs can be used in Sweden and concludes that there is a need for national legislation regulating the use of fire-fighting foam that contains highly fluorinated substances.
26. In 2014, the Danish EPA published a study on groundwater contamination associated with point sources of perfluoroalkyl substances, including PFHxS and PFHxS-related compounds. Based on the findings of groundwater contamination, a study assessing and proposing health-based quality criteria was commissioned. This study led to establishing a sum criterion drinking water limit value for 12 PFASs (perfluorobutane sulfonic acid (PFBS), PFHxS, PFOS, perfluorooctanesulfonamide (PFOSA), 6:2-fluorotelomer sulfonic acid (6:2 FTS), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA)). The limit value is 0.1 µg/L drinking water and is a sum criterion for the presence of all the 12 PFASs (Denmark, 2018). The same sum criterion limit value is valid for groundwater. The Swedish National Food Agency has recommended limits of 0.09 µg/L, for drinking water based on the presence of sum of 11 PFASs (PFBS, PFHxS, PFOS, 6:2 FTS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA) (Sweden, 2018). In the proposal for a new European Drinking Water Directive, which is under discussion, a limit value is proposed for the group of PFASs. Values of 0.1 µg/L for individual PFAS, and 0.5 µg/L for the sum of per- and polyfluoroalkyl substances (chemical formula: C_nF_{2n+1}-R) has been suggested (Europe, 2018). The German Government Water and Soil Consortia have compiled 'significance thresholds' (GFS) to assess groundwater contaminated with PFASs (van der Trenck et al. 2018). The GFS serve as criteria for the decision on whether actions to remediate polluted groundwater are necessary. For PFHxS, a threshold of 0.1 µg/L was derived. In 2017, the "Trinkwasserkommission" (drinking water commission) in Germany suggested a guidance value for PFHxS in drinking water of 0.1 µg/L (Trinkwasserkommission, 2017).
27. Several US States have adopted limits that include PFHxS for drinking water. The US State of Massachusetts recommends a 0.07 µg/L limit for PFOA, PFOS, PFHxS, PFNA and PFHpA combined or individually in drinking water (Mass. Gov), the Minnesota Department of Health recommends a guidance values of 0.027 µg/L for PFHxS (MDH), and the U.S. State of Vermont recommends a drinking water limit of 0.02 µg/L for PFOA, PFOS, PFHxS, PFHpA and PFNA combined (Health Vermont). New Hampshire also has a proposed drinking water limit of 0.018 µg/L, and Michigan has drinking water screening levels for PFHxS of 0.084 µg/L (<https://www4.des.state.nh.us/nh-pfas-investigation/?p=1044>, https://www.michigan.gov/documents/pfasresponse/Health-Based_Drinking_Water_Value_Recommendations_for_PFAS_in_Michigan_Report_659258_7.pdf). In addition, Health Canada maintains a Drinking Water Screening Value of 0.6 µg/L for PFHxS (Government of Canada, 2018).
28. The U.S. EPA uses a combination of regulatory and voluntary approaches, including Significant New Use Rules and the voluntary 2010/2015 PFOA Stewardship Program (OECD, 2015). The U.S. EPA established health advisory levels for PFOA and PFOS in drinking water. Additionally, using authorities established by the Safe Drinking Water Act's Unregulated Contaminant Monitoring Rule, the U.S. EPA monitored for six PFAS in finished drinking water, including PFHxS, to understand its occurrence in U.S. drinking water systems. These occurrence data are publicly available (<https://www.epa.gov/dwucmr/third-unregulated-contaminant-monitoring-rule>).
29. Furthermore, the Republic of Korea included PFHxS along with PFOS and PFOA, as preliminary drinking water monitoring parameters in 2018. The preliminary limit values for drinking water are 0.48 µg/L for PFHxS, 0.07 µg/L for PFOS and PFOA as a sum (Republic of Korea, Annex F information). In Australia, health-based guideline values for the sum of PFOS and PFHxS are set at 0.07 µg/L for drinking water and 2.0 µg/L for recreational waters (Australian Government, 2019). The drinking water value has been adopted as interim guidance in New Zealand (<http://www.mfe.govt.nz/node/24415>).

30. The Danish government recommends not to use PFASs and organic fluoro-compounds in paper and has issued an advisory limit for PFASs in food packaging materials of 0.35 µg/decimeter² paper of organic fluorine (Denmark, 2015).
31. Lately attention has been directed to future action on PFASs. Over 200 scientists have signed the “Madrid Statement” calling for global phase-out of all PFASs (Blum et al., 2015) and in addition the “Zurich statement on the future action on PFASs” has been published (Ritscher et al., 2018). The Zurich statement paper is a result of a workshop that was held in 2017, and it contains a number of recommendations for the future assessment and management of PFASs supported by a group of more than 50 international scientists and regulators (Ritscher et al., 2018). The review of PFOA and PFOS drinking water guideline levels, presented in Cordner et al. (2019), highlights the necessity of limit value development for PFAS content as a class of chemicals (in addition to individual compounds) similarly as for polycyclic aromatic hydrocarbons and dioxins.

2. Summary information relevant to the risk management evaluation

32. The occurrence of PFHxS, its salts and PFHxS-related compounds is a result of anthropogenic production, use and disposal, since they are not naturally occurring substances. As described in the risk profile and references within, environmental monitoring shows that PFHxS is very widely found in the environment (UNEP/POPS/POPRC.14/6/Add.1). Numerous studies have reported detection of PFHxS in compartments such as surface water, deep-sea water, drinking water, wastewater treatment plant effluent, sediment, groundwater, soil, atmosphere, dust, as well as biota, and humans globally (UNEP/POPS/POPRC.14/INF/4). PFHxS is one of the most frequently detected PFASs together with PFOS, PFOA and PFNA (UNEP/POPS/POPRC.14/6/Add.1 and references within), but despite this, information on current production and use is very limited. To date, limited research has been conducted to specifically study the releases of PFHxS, its salts and PFHxS-related compounds to the environment, resulting in a lack of quantitative information on releases.

33. Historically, 3M was the biggest global manufacturer of PFHxS, its salts and PFHxS-related compounds, with an annual production of about 227 tonnes of PFHxSF in the U.S. in 1997 (3M, 2000a). In 2000 – 2002, 3M ceased its production of PFHxS, its salts and PFHxS-related compounds (3M, 2000a). Some manufacturers in China and Italy (following bankruptcy in the company, manufacture in Italy ceased in November 2018) have reportedly produced PFHxS and its precursors (Stockholm Convention, 2012; Miteni, 2018; Pan et al., 2018) potentially as a replacement for PFOS and its precursors (Löfstedt et al., 2016; Huang et al., 2015; Ma et al., 2018; Zhou et al., 2019). The information on production in China corresponds well with environmental data, such as high levels of PFHxS in lakes and rivers in Asia (Ma et al., 2018; Pan et al., 2018; Cui et al., 2018). For example, in a study by Ma et al., (2018), PFHxS was the predominant PFAS compound in Taihu Lake and flow-in river waters. Levels of PFHxS (45.9–351 ng/L) exceeded PFOS levels in Taihu Lake and this increase of PFHxS was linked to production and use of PFHxS as an alternative due to recent regulation of PFOS in China (Ma et al., 2018). The flux of total PFASs to the Lake was 1255 kg/year and was mainly contributed by PFHxS (611 kg/year), PFOS (227 kg/year), PFOA (182 kg/year), and PFHxA (84.4 kg/year). A different study reported increased concentrations in rivers and nearby lakes (Tai and Chao Lakes) in China. The estimated load of PFHxS to these rivers was 21.6 tonnes in 2016, up from 0.09 tonnes in 2013 (Pan et al., 2018). Recently it was reported, from two rivers (Fen and Wei) in China, that the mean contribution of PFHxS was distinctly higher than PFOS, which could be due to PFHxS being increasingly produced and applied as an alternative to PFOS (Zhou et al., 2019). Among the PFASs, PFHxS had the highest mass discharge rate at 116 and 37 kg/year in the two rivers. Furthermore, it was stated that the relative high ratio of PFHxS to PFOS, could be due to the use of PFHxS as a substitute for PFOS in manufacture of textiles, protective coating for carpets and fluoropolymers (Zhou et al., 2019).

34. PFHxS, its salts and/or many PFHxS-related compounds have been listed on chemical inventories (Australia, New Zealand, Canada, China, EU, Japan, Nordic countries³ and U.S.) indicating historical/present production, import and/or uses of products containing these substances (see risk profile UNEP/POPS/POPRC.14/6/Add.1). PFHxS, its salts and PFHxS-related compounds have been intentionally used at least in the following applications: (1) AFFFs for fire-fighting; (2) metal plating; (3) textiles, leather and upholstery; (4) polishing agents and cleaning/washing agents; (5) coatings, impregnation/proofing (for protection from damp, fungus etc.); and (6) within the manufacturing of electronics and semiconductors. Other potential use categories may include pesticides, flame retardants, paper and packaging, in the oil industry, and hydraulic fluids (UNEP/POPS/POPRC.14/6/Add.1).

35. For the uses in categories (4) and (5) there is a lack of information, but there are indications that these uses could be related to cleaning, polishing, sealers, coatings, etc., both in the building and car maintenance sectors. Recent information from the Republic of Korea and further investigations have revealed use of a polymer containing PFHxS (most likely unintentional as a constituent in a PFOS-polymer, CAS No.127133-66-8) in a car coating spray product produced in the EU and imported to the Republic of Korea (RPA 2019). It was reported in 2016 that 20 tonnes of the polymer in the product were imported into the country from 2013 to 2015 (Republic of Korea, Annex F information).

³ Norway, Sweden, Denmark, Finland, Iceland, Greenland and Faroe Island.

Furthermore, during the work on the risk profile for PFHxS, its salts and PFHxS-related compounds it was revealed that a PFHxS-related compound was contained in a floor sealer- and finisher product available from a North American company, however this product is no longer available (see risk profile UNEP/POPS/POPRC.14/6/Add.1). There are indications that PFHxS or its salts or PFHxS-related compounds (the CAS No. is not known) are used in the additive of solar cell texturing solution. According to the Annex F information of the Republic of Korea, the sudden increase of PFHxS concentrations were monitored at a water treatment and purification plant adjacent to a manufacturing plant using the solar cell texturing solution. The Republic of Korea has monitored PFAS at 70 water treatment and purification plants nationwide since 2012. PFHxS concentrations ranged from 0.002 ug/L to 0.013 ug/L in 2016, but PFHxS suddenly increased up to 0.454 ug/L at the plant in the streams of the Nakdong River in 2017 (Republic of Korea, Annex F information). This is in line with detection of PFHxS in tap water samples originating from the same river in a study in which PFHxS was in the highest concentrations ranging from not detected (n.d.) to 190 ng/L (Park et al., 2018). After corrective actions including the replacement of the texturing solution at the plant, the PFHxS concentrations dropped to the levels of previous years. The solution was imported into the country and there has been no production of PFHxS, its salts and PFHxS-related compounds in the country (Republic of Korea, Annex F information).

36. Furthermore, high concentrations of PFHxS have been detected in several samples of Chinese PFOS substitute products. As stated in this report https://www.switchmed.eu/en/documents/huang_pfos-substtution-in-china.pdf (Huang et al., 2015), "These products are mainly used in surfactants for AFFF, e.g. VF-230 (5,082 mg/L), VF-9126 (1771 mg/L), and VF-9128 (583 mg/L). Actually, the producer of the above AFFF products purchased the "non-PFOS" fluorocarbon surfactants that they used to produce AFFF from other vendors with the guarantee of a non-PFOS containing product. However, the content of PFHxS in these products was not noticed and no such information was provided upon sale of this product that was later used in AFFF (VF-230, VF-9126 and VF-9128) (https://www.switchmed.eu/en/documents/huang_pfos-substtution-in-china.pdf; Huang et al., 2015).

37. PFHxS, its salts and PFHxS-related compounds are not registered under the European Chemicals legislation REACH. However, since there are about 68 classification, labelling and packaging (C&L) notifications/self-classifications registered for the substance group of PFHxS, its salts and PFHxS-related compounds in the European Chemicals Agency C&L inventory⁴ this information suggests that the use of each notified compound of PFHxS, its salts and PFHxS-related compounds in Europe is in quantities less than 1000 kg/year. However, registration and evaluation of polymers of chain length ≥ 3 (monomers) is exempted under REACH which could mean that there is a substantial additional source of releases of PFHxS from the use of polymers containing PFHxS-related compounds (as side chains or unintentionally present) in various applications. Monomers or other unintentional compounds present in the polymer and exceeding 2 % weight by weight (w/w) or more, and the total quantity makes up 1 tonne or more per annum, must be registered under REACH (Article 6(3)). However, future control of polymers on the market are being reviewed as described in the REACH regulation (Article 138(2)). Such uses of polymers have been reported in the Republic of Korea (Annex F information) as polymers containing PFHxS-related compounds were used in car coating sprays.

38. Annex F information submitted by the UK reported that a waste company responded to the request for information that PFHxS, its salts and PFHxS-related compounds is used in textiles, carpet protectors, leather, papermaking, pesticides, electroplating, fire-fighting foams, photosensitive material and some synthetic materials. It has also been found in printing inks and sealants. Although according to the UK Annex F information, while no use or production of the chemical as a raw product takes place in the UK, it is assumed that there will be some embedded in everyday materials (UK Annex F information).

39. Furthermore, it should be noted that information on the volumes and uses of PFHxS, its salts and PFHxS-related compounds has been reported to the competent authorities in Denmark, Sweden and Norway, but most of such information has been claimed as confidential business information (SPIN, 2018; Norwegian Environment Agency M-961/2018). A recent source analysis in coastal areas of Bohai Bay in China, showed that PFHxS was associated with hydraulic fluid formulations, AFFF factories, metal plating, manufacturing and processing of fluoropolymer and food contact material (Liu et al., 2019). In addition, PFHxS has been detected in several consumer products such as various forms of textile including upholstery, carpets, electrical items and building material (Becanova et al., 2016).

40. The raw material used for manufacture of PFHxS, its salts and PFHxS-related compounds, PFHxSF (CAS No. 423-50-7), is potentially available from several providers (https://www.lookchem.com/product_High-quality-Perfluorohexane-Sulphonyl-Fluoride/14315526.html) and is advertised for the following uses; "this product is one of the most essential raw materials for preparing fluorine-containing surfactants. The fluorine-containing surfactant can be widely used in textile, leather, papermaking, pesticide, electroplating, oilfield, fire control, photosensitive material, synthetic material and other fields". A total of six manufacturers or downstream suppliers are established in China (<https://www.lookchem.com/newsell/search.aspx?key=423-50-7&countryId=1&businessType=Manufacturers>, accessed on 1 October 2019) showing potential for production of PFHxSF. Moreover, a number of manufacturers

⁴ <https://echa.europa.eu/information-on-chemicals/cl-inventory-database>.

and/or suppliers of PFHxS (CAS No. 355-46-4) are registered on the following web page (<https://www.lookchem.com/newsell/search.aspx?p=1&key=355-46-4&ad=>, accessed on 1 October 2019) suggesting potential use and availability.

41. PFHxSF may be unintentionally produced as a by-product during the electrochemical fluorination (ECF) process to produce perfluorooctane sulfonyl fluoride (PFOSF) (Gramstad and Haszeldine, 1957; Jiang et al., 2015; 3M 2000b). Unless manufacturers remove PFHxSF from PFOSF, it would remain as a contaminant and potentially react to form PFHxS, as shown in, e.g., 3M, 2015; Herzke et al., 2012; Huang et al., 2015. It is likely that the ratios of PFHxSF yields to PFOSF yields in the production of PFOSF are between 4% (Gramstad and Haszeldine, 1957) and 14.2% (reported by a Chinese manufacturer; Ren, 2016). This is supported by measured ratios of PFHxS to PFOS in commercial PFOS product, namely 3.5%–9.8% in 3M's FC-95 (3M, 2015) and 11.2%–14.2% in three products from China (Jiang et al., 2015). Of the PFHxS impurities from the 3M ECF production process for PFOS, branched isomers of PFHxS were also detected e.g. 18% branched of the 4.7% PFHxS impurity in one batch (Benskin et al., 2010). To our knowledge, it is not clear whether PFHxSF is a by-product in the ongoing manufacture of PBSF. Boucher et al. 2019 indicated that unintentionally produced PFHxSF (after clean-up of PFOS products) were converted into products and used as specified in paragraph 31.

42. A global emission inventory of C₄–C₁₀ PFASs and related precursors was recently published (Boucher et al., 2019). It reviews and integrates existing information on the life cycle of the raw material PFHxSF and its derivatives using historical production data. Using the same methodology to develop and validate an emission inventory as was used for an earlier study on PFOSF (Wang et al., 2017), an inventory for PFHxSF was developed and used as inputs for the global mass-balance environmental fate model, CliMoChem, to estimate environmental concentrations, which were then compared to field measurements. Past and ongoing intentional production of PFHxSF and its derivatives are not quantified and included here because no public information about their production volumes could be found. The estimated emission inventories included the range of global total emissions from the life cycle for PFHxSF-based products. The global emission from individual source categories for different time periods is reported. In the time-period 2016–2030, a total global emission of 2–89 tonnes of PFHxS from production, use and disposal, degradation of PFHxS-related compounds and from degradation of PFHxSF, is estimated. Highest emissions of PFHxS over this period were estimated to occur from use and disposal (1–21 tonnes), and from degradation of PFHxS-related compounds (1–66 tonnes). The lack of quantitative data for the substances in the inventory calculations made it necessary to make estimations and assumptions which have in turn introduced uncertainties into the results (Boucher et al., 2019).

43. The reported field concentrations fit well with the modelled concentrations of PFHxS. The results show that elevated environmental concentrations of PFHxSF and its derivatives (such as PFHxS and PFHxS-related compounds) are expected to continue for decades, and that areas far from the source regions have not yet reached their estimated peak concentrations. These estimated trends are likely to be widely representative on a large geographical scale; however, the currently non-quantifiable emissions resulting from the intentional production of PFHxSF-based products in China (and possible other countries) may increase levels of local exposure in some areas and are not captured by the current study (Boucher et al., 2019).

44. In summary, the information in this section shows that PFHxS is very widely distributed in the environment globally (see also UNEP/POPS/POPRC.14/6/Add.1 and UNEP/POPS/POPRC.14/INF/4 for details). Historically, major emissions of PFHxS and PFHxS-related compounds were most likely due to its unintentional presence in PFOS manufactured by ECF. There are probably still ongoing emissions and releases of PFHxS from production and use of PFOS. In addition, PFHxS might also be present in stockpiles of PFOS or products/chemical mixtures containing PFOS, that are still not disposed of. However, recent information especially from Asia suggests that PFHxS has replaced PFOS in many applications. This is shown by the many new publications reporting detection of PFHxS as the main PFAS discharged in rivers and lakes, especially in urban areas and in the proximity to industrial facilities in Asia. It is reported that activities such as textile treatment (Park et al., 2018; Ma et al., 2018; Zhou et al., 2019), electronic and chemical industries (Park et al., 2018), semiconductor industry (Lin et al., 2010), photographic film production plant (Cui et al., 2018), protective coating for carpets (Zhou et al., 2019), and manufacture of fluoropolymers (Zhou et al., 2019) might be connected to these releases of PFHxS. These studies suggest that PFHxS is intentionally used in these applications and industry processes and not present as an unintentional contaminant in PFOS manufacture. Furthermore, PFHxS has been used in AFFF, and recently marketed as a PFOS-substitution product in Asia. Quantitative data on intentional production of PFHxSF, the raw material for production of PFHxS, its salts and PFHxS-related compounds, are not publicly available. Therefore, it is not possible to estimate an emission inventory for the intentional production, use and disposal of PFHxS, its salts and PFHxS-related compounds. The emission inventory presently in Boucher et al., (2019) only covers unintentional production, use and disposal of PFHxS, its salts and PFHxS-related compounds.

2.1 Identification of possible control measures

45. For identification of possible control measures throughout their life-cycle the most relevant applications and the possible routes of emission should be considered. Emission of PFHxS can appear by three possible routes:

- (a) Production, use and disposal of PFHxS, its salts and PFHxS-related compounds;
- (b) Presence as an impurity in other perfluoroalkyl sulfonic acids (e.g. PFOS); and
- (c) As a degradation product of PFHxS-related compounds including from polymers with side chains containing the $C_6F_{13}SO_2$ -moiety.

46. As mentioned in paragraph 34, the following applications have been identified: (1) AFFFs for fire-fighting; (2) metal plating; (3) textiles, leather and upholstery; (4) polishing agents and cleaning/washing agents; (5) coatings, impregnation/proofing (for protection from damp, fungus, etc.); and (6) within the manufacturing of electronics and semiconductors. Other potential use categories may include pesticides, flame retardants, paper and packaging, in the oil industry, and hydraulic fluids. From available information it is likely that the application in AFFF, treatment of textiles, leather and upholstery, and manufacturing of electronics and semiconductors are the main applications from where PFHxS, its salts and PFHxS-related compounds are released. This conclusion is supported by work presented under the Basel Convention by China (2013) which reported that PFHxS was identified and detected as an alternative to PFOS in the following applications; (1) AFFF; (2) water-proofing agents; (3) textile finishing agents (Huang et al., 2015). However, releases from other usage such as domestic and professional use of e.g. polishing agents and cleaning/washing agents cannot be excluded.

47. Under the Convention, there are different approaches that can be applied to achieve “prohibition or restriction of production, use, import and export” as required by Article 3:

- (a) PFHxS, its salts and PFHxS-related compounds may be listed in Annex A, with or without specific exemptions accompanied with a specific part of Annex A that details specific actions; or
- (b) PFHxS, its salts and PFHxS-related compounds may be listed in Annex B, with acceptable purposes/specific exemptions accompanied with a specific part of Annex B that details specific actions; and/or
- (c) PFHxS, its salts and PFHxS-related compounds may be listed in Annex C as an unintentional persistent organic pollutant (POP) to capture potential formation and unintentional release from anthropogenic sources e.g. due to possible unintentional formation of PFHxS from incineration.

48. No requests for exemptions have been raised by any Party or observer during the preparation of this risk management evaluation. No requests for exemptions have been made and technically feasible alternatives appear to be available and in use for all applications. Hence there are no identified reasons to list PFHxS, its salts and PFHxS-related compounds in Annex B of the Convention. Further, no information that PFHxS is unintentionally produced from incineration are presented or available at present suggesting that a listing in Annex C is not required. This suggests that a complete phase-out of PFHxS from all uses is possible and that exemptions for production and use are not necessary. Therefore, the possible control measure would be to list PFHxS, its salts and PFHxS-related compounds in Annex A to the Convention with no exemptions for production and use.

49. The control measures related to an Annex A listing without exemptions for PFHxS, its salts and PFHxS-related compounds may be achieved by (1) prohibition of production, use, import and export, (2) remediation of contaminated sites, (3) environmentally sound management of waste and obsolete stockpiles, (4) prohibition of reuse and recycling of wastes or stockpiles.

50. Listing of PFHxS, its salts and PFHxS-related compounds in Annex A without exemptions would be subject to note (i) of Annex A. This would mean that the presence of PFHxS, its salts and PFHxS-related compounds in other substances can only occur as an unintentional trace contaminant.

51. One of the highest estimated emission sources of PFHxS are from use and disposal (Boucher et al., 2019). An overview of possible routes in the waste streams that can result in emissions of PFHxS to the environment are given in the Supplementary information in Boucher et al (Figure S6). In addition to direct emission from use, waste water (gases, effluent and sludge) and through solid wastes (landfill, land treatment) are shown to be major routes of emission of PFHxS to the environment. Remediation of contaminated soil from PFHxS is with today’s technology very difficult, if at all possible (Naturvardsverket, 2019; CRC Care, 2017). In addition, when users are switching to an alternative chemical, they need to wash out their manufacturing and storage equipment and there will be a need to dispose of this waste liquid in an environmentally sound manner. Many studies have detected PFHxS in effluent from waste water treatment plants (WWTPs) and from industry (Lin et al., 2010; Eriksson et al., 2017; UNEP/POPS/POPRC.14/INF/4. Table 1.5). In addition, degradation of PFHxS-related compounds to give PFHxS in the WWTPs have been reported (Eriksson et al., 2017) as well as content of PFHxS emission from WWTP effluents (Norwegian Environment Agency, M-806/2017). If emissions are high through effluents, control measures at WWTP should be implemented as described in section 2.4.1.

52. Following a listing of PFHxS, its salts and PFHxS-related compounds in the Convention, the provisions of paragraph 1 (d) (ii) of Article 6 must be fulfilled. This means that waste shall be disposed of in such a way that the POP content is destroyed or irreversibly transformed so that it does not exhibit the characteristics of POPs, or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option, or the POP content is low. Parties should also consider emission reduction measures and the use of best available techniques and best environmental practices (BAT/BEP) in the waste management phase (UNEP, 2007). In addition, Parties shall endeavour to develop appropriate strategies for identifying sites contaminated with PFHxS. If contaminated sites are identified and remediation is undertaken, it shall be performed in an environmentally sound manner.

2.2 Efficacy and efficiency of possible control measures in meeting risk reduction goals

53. To reduce PFHxS emissions, control measures at all life cycle stages need to be considered. Emissions of PFHxS to the environment occur at all its life cycle stages but are assumed to be highest during service life and in the waste phase. However, extensive releases of PFHxS have also been shown to occur from manufacturing plants especially in China (see e.g. Cui et al., 2018; Ma et al., 2018). Hence, the most effective control measure for PFHxS, its salts and PFHxS-related compounds is the prohibition of all production, use, import and export. This will be best accomplished by listing PFHxS, its salts and PFHxS-related compounds in Annex A to the Stockholm Convention with no exemptions. Measures under Article 6 would address environmentally sound management of stockpiles and wastes and clean-up of contaminated sites (if undertaken) such as at or near manufacturing facilities, airports, military bases and other sources.

54. According to the Annex F information submitted by Parties and observers, no critical uses of PFHxS, its salts and PFHxS-related compounds have been identified and no requests for exemptions have been raised. Therefore, it should be possible to discontinue production and use and consequently stop emissions and releases from manufacturing facilities and from facilities that use PFHxS, its salts and PFHxS-related compounds in their products (such as textile and leather treatment, semiconductor manufacture, etc.).

55. According to a survey performed by the OECD/UNEP Global PFC Group, two important drivers for PFAS risk reduction are growing scientific knowledge and the increasing number of international initiatives supporting a transition to safer alternatives (OECD, 2015). A number of challenges can appear during development and implementation of risk reduction measures for PFASs (OECD, 2015). Some of these challenges may apply to the control measures that need to be implemented to meet the risk reduction goal for PFHxS, its salts and PFHxS-related compounds. There is a lack of information on the sources (production and use) of PFHxS and especially the PFHxS-related compounds. This will in turn make it difficult to identify industrial processes (i.e. textile, leather and other surface treatments, electronics and semiconductor industry, etc.) and products where these chemicals are used. The targeted industry has not provided adequate information on the sources (production and use), and industrial processes and products using PFHxS. Furthermore, standardized analytical methods to detect and quantify individual PFHxS-related compounds are at present lacking and this makes it difficult to identify the compounds in chemical mixtures and products (analytical methods for PFHxS and its salts and PFHxS-related substances are described in section 1.1). The lack of information on the content of chemicals in products, in general, will make it difficult to separate these products in the waste stream and during waste treatment. To improve the exchange of information on chemicals contained in products a programme has been developed under SAICM <http://www.saicm.org/Implementation/EmergingPolicyIssues/ChemicalsinProducts/tabid/5473/language/en-US/Default.aspx>.

56. In addition, PFASs are very often added to products in low concentrations with the result that the obligation of reporting the content of the substance might not apply. Examples are, under the REACH registration in the EU where the suppliers have an obligation to communicate information on substances above a concentration of 0.1% in articles (see section 1.5) as well as the 1000 kg/year threshold for registrations under REACH that may not be reached if the concentration in product in questions contain PFAS in very low concentrations (see section 2, para 34), and where the registration of polymers are exempted. Kotthoff et al. (2015) reported that some consumer products (cleaning agents, food-contact material) had low contents of PFAAs while other products such as ski wax, leather samples, and outdoor textiles had higher levels.

57. As discussed earlier and in the next section, PFHxS, its salts and PFHxS-related compounds are used in many of the same applications as PFOS (see section 2 for details). Experience, guidelines and inventories developed under the work program for PFOS can be very useful in implementing control measures for PFHxS, its salts and PFHxS-related compounds.

58. Establishment of market surveillance and environmental monitoring activity will need to be considered to monitor the effectiveness of the control measures implemented.

2.2.1 Technical feasibility

59. Although no clear overview of the use of PFHxS, its salts and PFHxS-related compounds is available, many of the intentional uses are expected to be similar to PFOS (see risk profile for PFHxS for more detailed information; UNEP/POPS/POPRC.14/6/Add.1) and in some cases PFOA. This is also elaborated on in the summary of section 2. Therefore, “The report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF)” (UNEP/POPS/POPRC.14/4 and UNEP/POPS/POPRC.14/INF/8) can give useful information on possible alternatives/alternative techniques also for PFHxS, its salts and PFHxS-related compounds. The assessment report indicates that technically feasible alternatives are available for all PFOS-applications, suggesting the switch to chemical and non-chemical alternatives are feasible. Many of the suggested alternatives may also apply to PFHxS. However, it should be noted that previously, for some applications (fire-fighting foam and treatment of textiles and leather), PFHxS has been used and included as an alternative to PFOS (UNEP/POPS/POPRC.12/INF/15/Rev.1).

60. From the POPRC-process on PFOS, its salts and PFOSF, information from industry indicates that a substitution process for PFOS is ongoing and that only a few uses are identified for which PFOS is still needed. These are related to the use of PFOS (or PFOS-related compounds) as a mist suppressant in hard metal plating in closed-loop systems, and insect baits for control of leaf cutting ants. The 9th meeting of the Conference of the Parties (COP-9) decided to move mist suppression in hard metal plating into a time limited specific exemption and keep the insect baits for control of leaf cutting ants as an acceptable purpose but limited its scope to agricultural uses (decision SC-9/4). Also, the acceptable purpose for the production and use of PFOS, its salts and PFOSF for fire-fighting foam was converted to a time-limited 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. The same decision was also adopted for PFOA, its salts and PFOA-related compounds used in AFFF (decision SC-9/12). For PFOA several other time-limited exemptions were agreed, e.g. a specific exemption was granted for the use of PFOA, its salts and PFOA related compounds in textiles for oil- and water-repellence for the protection of workers from dangerous liquids that comprise risks to their health and safety (decision SC-9/12), but also here transition to other chemical and non-chemical substitutions is ongoing.

61. As set out in section 2.3, there are a wide number of non-fluorinated chemical alternatives for all possible uses of PFHxS, its salts and for PFHxS-related compounds including some technical solutions for elimination of PFHxS.

2.2.2 Cost and benefits of implementing control measures

62. As there are no requests for exemptions it is anticipated that costs associated with the implementation of control measures on production and use would be limited. Control measures at a high cost taken for PFOS or PFOA could also be effective for PFHxS due to the assumed similar uses (e.g. substitution and destruction of AFFF). Furthermore, expected volumes of existing stocks should be minimal and PFHxS as an unintentional byproduct in PFOS products would be eliminated due to phase-out of PFOS. As the costs of remediating PFASs from drinking water and contaminated sites is known to be very high, implementation of control measures for PFHxS, its salts and PFHxS related compounds would contribute to avoiding such future costs (see section 2.4.3 for more information on costs).

2.3 Information on alternatives (products and processes) where relevant

63. In general terms there is a lack of published data on the identity, properties and efficiency of the alternatives to PFASs for most applications because the data usually are protected by confidential business information. Despite several attempts, the relevant industry has not submitted information about production and use of PFHxS (Norwegian Environment Agency M-961/2018, ECHA, 2019b). However, alternatives exist and are used in many applications indicating that they have been approved by the industry and hence should be usable alternatives (UNEP/POPS/POPRC.14/6/Add.1). This assessment of alternatives to PFHxS is therefore based on the general uses mentioned in the Risk Profile (UNEP/POPS/POPRC.14/6/Add.1) and the assumption that the functions of PFHxS in these uses are the same or very similar to those of PFOS and in some cases of PFOA.

2.3.1 Application-specific alternative substances

64. Alternatives to PFHxS, its salts and PFHxS-related compounds include substitute chemicals and alternative techniques including non-chemical alternatives such as design or product changes. All effort should be made to ensure substitution with other persistent and/or toxic chemicals is avoided.

65. Regrettable substitution has been defined as occurring “when a toxic chemical is replaced by another chemical that later proved unsuitable because it, too, turned out to be a persistent, bioaccumulative and toxic (PBT) substance, or because of other concerns” (U.S. National Research Council, 2014). Reducing the likelihood of regrettable substitution of PFHxS and related compounds with similar perfluoroalkyl acids (PFAAs) and related compounds is challenging because this is a large class of chemicals (OECD 2018) and for the majority of these substances

information about their properties is very limited. This challenge of dealing with a large class of chemicals can be dealt with using a grouping approach, which has been found to be an important method for reducing the likelihood of regrettable substitution, has been proposed by ECHA (ECHA; 2017b), as well as by national policy makers in several countries (Ritscher et al., 2018; Cordner et al., 2016). In many cases, long-chain PFAAs, their salts and related compounds can be replaced by short-chain PFAAs, their salts and related compounds (short-chain PFAAs defined as C₂–C₇ perfluorocarboxylic acids (PFCAs) and C₃–C₅ PFSA) and other fluorinated alternatives which are considered safe for their intended uses by the industry (Fluorocouncil, 2015). Although PFAAs with shorter chain are in general less bioaccumulative, they are persistent, have higher water solubility and high mobility, which makes it even more difficult to retain and control the spreading of these substances within the environment than longer-chain PFAAs (Arp et al., 2017; Neumann et al., 2017; Kotthoff and Bücking, 2018).

66. Some short-chain PFAAs and other fluorinated alternatives have similar toxic potency compared to PFOA and PFOS when corrected for bioavailability (Gomis et al., 2018). Short-chain PFASs (C₂–C₇ PFCAs and C₄ PFSA) contributed to over 80% of the detectable PFASs in rain samples and the C₂–C₃ PFASs alone accounted for over 40% of the total sum of PFASs in rain and water samples in Toronto (Yeung et al., 2017). Novel fluorinated compounds have emerged on the market to replace the long-chain PFAAs, its salts and related compounds. Occurrences of several novel perfluoro ether carboxylic and sulfonic acids (PFECAs and PFESAs), including hexafluoropropylene oxide dimer and trimer acids (HFPO-DA, also known by the trade name GenX, and HFPO-TA), ammonium 4,8-dioxo-3-*H*-perfluorononanoate (also known by its tradename ADONA), chlorinated polyfluorinated ether sulfonic acid (6:2 Cl-PFESA), and its hydrogen-substituted analogue (6:2 H-PFESA) have been observed in surface waters worldwide (Pan et al., 2018). ADONA has also been detected in human blood in populations receiving tapwater contaminated with the substance (Fromme et al., 2017). Contamination of water sources with short-chain PFAAs has been observed (Gebbinck et al., 2017; Braunig et al., 2019). PFCAs, other PFASs such as PFECAs and PFESAs were detected in natural waters collected from locations with historical perfluorinated compound contamination (Strynar et al., 2015).

67. Several short-chain alternative substances are currently under substance evaluation under REACH suspected as PBT or vPvB substances (e.g. ADONA and PFHpA-related compounds (ECHA CoRAP list)) and/or under preparation for regulatory risk management (PFHpA, PFBS, PFHxA (ECHA Registry of Intentions and Public Activities Coordination Tool PACT)). HFPO-DA was considered in July 2019 as a Substance of Very High Concern because of its persistency, mobility, potential for long range environmental transport, observed adverse effects, low absorption potential and high water solubility rendering the substance full bioavailable for uptake via (drinking) water⁵. It is therefore possible that restrictions on use of some of these substances will be implemented in the future. Furthermore, these compounds are often less efficient in the application resulting in use of larger volume and increased emissions from the user- and disposal-phase of the product (Schellenberger et al. 2019).

68. POPRC has previously addressed the issue of regrettable PFAS substitutes for both PFOA and PFOS in the recommendations for alternatives to PFOS (decision POPRC-14/3) and the recommendations for the listing of PFOA (decision POPRC-14/2) under the Stockholm Convention. At COP-9 it was decided that since short-chain PFASs are a large class of chemistries with varying chemical and physical properties and since POPRC had not reviewed data from this large class, specific reference to avoiding short-chain PFASs (in fire-fighting foams) would not be made. Instead the following language was adopted: ‘Encourages Parties and others to use alternatives to PFOA, its salts and PFOA-related compounds, where available, feasible and efficient, while considering that fluorine-based fire-fighting foams could have negative environmental, human health and socio-economic impacts due to their persistency and mobility (Decision SC-9/5 (PFOS) and Decision SC-9/12 (PFOA)). The alternative short-chain PFASs show higher water solubility and increased environmental mobility than long-chain PFASs (Baduel et al., 2017; Barzen-Hanson and Field, 2015). To avoid regrettable substitution to other PFAAs, the following sections mainly focus on non-fluorinated chemical alternatives and non-chemical alternative techniques.

69. Table 3 gives an overview of the identified use categories and the available alternatives to PFHxS followed by separate sections with information on each application and its alternatives in cases where the main focus is on non-fluorinated chemical- and technical solutions. (Fluorinated alternatives are only indicated for applications where non-fluorinated chemical alternatives and alternative techniques has not been proven viable for all applications in the user category).

⁵ <https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1833efc3e>.

Table 3. Overview of alternatives

Application	Alternative available	Type of alternative
Fire-fighting foam	Yes	Non-fluorinated and fluorinated chemical alternatives
Metal plating	Yes	Chemical alternatives (non-fluorinated and fluorinated chemical alternatives), and technical solutions
Textiles	Yes	Chemical alternatives (non-fluorinated and fluorinated chemical alternatives), and technical solutions
Polishing, cleaning- and washing agents	Yes	Non-fluorinated chemical alternatives
Coating, impregnation/proofing	Yes	Non-fluorinated chemical alternatives
Electronic and semiconductors	Yes	Non-fluorinated and fluorinated chemical alternatives

2.3.1.1 Fluorinated fire-fighting foams

70. Fluorinated fire-fighting foams, including aqueous film-forming foams (AFFF) are highly effective foams intended for fighting high-hazard flammable liquid fires. AFFF produce a thin layer separating highly flammable liquid or combustible solids from the oxygen rich air. The water film, which is located between the fuel and the foam, cools the surface of the fuel, acts as a vapor barrier, and supports the spreading of the foam on the fuel. AFFFs have typically been formulated by combining synthetic hydrocarbon surfactants with fluorinated surfactants and used as Class B fire-fighting foams formulated to extinguish liquid hydrocarbon fuel fires. The fluorinated foams in this class are called AFFF, fluoroprotein foams (FP) or film-forming fluoroprotein foams (FFFP). The fluorine-free (F3) Class B fire-fighting foams are based on proprietary mixtures of hydrocarbon surfactants.

71. The perfluorinated substances (such as PFOS and PFHxS) used in AFFFs have been intentionally produced using ECF, with hydrogen fluoride used as a feedstock alongside organic material (Buck et al., 2011). The ECF production of fluorinated substances may produce both branched and linear products as well as products with different chain length (Buck et al., 2011). PFOS products may contain 1–10% PFHxS (Wang et al., 2017 (supplementary); reviewed in the risk profile; UNEP/POPS/POPRC.14/6/Add.1), unless it is cleaned-up and the unintentional PFHxS removed. A complete phaseout of AFFF containing PFOS will also contribute to reduced emissions of PFHxS and PFHxS-related compounds to the environment.

72. PFHxS and PFHxS-related compounds have been detected in AFFF (D'Agostino and Mabury 2014; Keml, 2015; Favreau et al., 2017) and have been found in soil and groundwater impacted by AFFF training activities most often as a result of use of PFOS-containing foam with unintentional amounts of PFHxS (Barzen-Hanson et al., 2017; Gobelius et al., 2018; Banzhaf et al., 2017). However, AFFF with PFHxS as the active perfluorinated compound has also been on the market in the past (Table 8, ECHA, 2019b). Due to the long shelf-life of 10–20 years of AFFF concentrates, stocks of already installed AFFF may still contain PFHxS. In addition, some AFFF produced in 2015 in China contains PFHxS as a substitute to PFOS (https://www.switchmed.eu/en/documents/huang_pfos-substitution-in-china.pdf). According to Eurofeu (the European Committee of the Manufacturers of Fire Protection Equipment and Fire Fighting Vehicles), the European and North American fire-fighting foam industry has fully implemented the U.S. EPA Stewardship Program with a total phaseout of production of C₈-based AFFF although stockpiles still exist (<http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC13FU-SUBM-PFOA-FFFC-3-20180112.En.pdf>). This indicates that fluorinated foams manufactured up to 2015 may contain C₈ perfluorinated substances; after that 'C₆ Pure' policies have been implemented (Eurofeu, 2018). 'C₆ Pure' foam contains fluorosurfactants produced by the telomerisation method and should therefore not contain PFHxS (FFFC, 2017).

Alternatives to PFHxS in fire-fighting foam for Class B fires

73. There are two key categories of alternatives to consider in this section, a) fluorine-free alternatives and b) short-chained fluorinated alternatives.

a) Fluorine-free alternatives:

74. Several fire-fighting foam manufacturers provide fluorine-free foams that can meet Class B standard fire-fighting performance certifications (see Table 6 in UNEP/POPS/POPRC.14/INF/8). The only exception is the U.S. Mil Spec (MIL-F-24385), that does not only relate to performance standards but also specifies the inclusion of fluorochemicals. However, the U.S. Department of the Navy, the custodian of Mil-Spec, has for some years been considering changing the Mil-Spec standard to be based around performance rather than referencing specific chemical content and properties (IPEN, 2018). In October 2018, the U.S. Senate approved a five-year reauthorization for the Federal Aviation Administration which changed the performance standards for fire-fighting foams to allow the use of fluorine-free foams at civilian airports (U.S. Congress, 2018).

75. Fluorine-free foams are now being used at civilian airports in Australia, Denmark, Norway, Sweden, and at major hub airports e.g. London Heathrow and Gatwick, Dubai, Stuttgart, Edinburgh, Auckland (IPEN, 2018). At civilian airports in Norway this substitution covers both fixed- and mobile-systems. In Norway, several military properties have phased in fluorine-free foams. In addition, the oil and gas sector are in the process of phasing in fluorine-free foam (both offshore and onshore) in Norway, and the sector is satisfied and confident with its performance (personal communication with Equinor and Norwegian Oil and Gas Association, Norwegian Environment Agency, 2019).

76. 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 that can be constituents of biodiesel (Keutel and Koch, 2016). The authors concluded 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, reports 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.

77. LASTFIRE, which is a consortium of 16 oil companies, initiated a project in the late 1990s to review the risks associated with large diameter (greater than 40 m) open top floating roof fuel storage tanks. In 2018, LASTFIRE tested six new C₆ pure AFFF and two fluorine-free foams on large scale tanks, and from their experiences (based on the selected foams included in the test), it was concluded 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 formulation and the type of application equipment used. Hence it is not possible to state that all C₆-fluorinated alternatives perform better than all fluorine-free alternatives and vice versa (Ramsden, 2018).

78. There is relatively little publicly available information on the chemical structure or properties of the fluorine-free alternatives. A number of manufacturers and commercial products of safety certified fluorine-free foams have been identified, where the details of the precise formulations are not divulged due to confidential business information (see Table 6 in UNEP/POPS/POPRC.14/INF/8). However, patents for fluorine-free foams provide more insights. For example, in the Solberg patent the following ingredients are listed: Diethylene glycol butyl ether, xanthan gum, starch, carbonized sugar, diethanolamine lauryl sulfate, sodium decyl ethoxy sulfate, cocamidopropyl betaine, cocamidopropyl hydroxysultaine, sodium octyl sulfate, sodium decyl sulfate, alkyl polyglucoside (Patent-US20080196908). (Simplified: carbonised saccharide composition, a cross-linking agent or inorganic salt, a surfactant, and water).

79. The benefits from using fluorine-free foams are related to the reduction of long-term impact on the environment, while short-term impact related to acute toxicity due to biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are not significantly different from the fluorine-containing foams (IPEN, 2018). Fluorine-free-foams are biodegradable while AFFF contain persistent fluorinated substances (<https://echa.europa.eu/fluorine-free-foams>).

b) Short-chain fluorinated alternatives:

80. According to the Fire Fighting Foam Coalition (FFFC, 2017), all modern AFFF agents contain fluorotelomer-based fluorosurfactants, and the short-chain (C₆) fluorosurfactants (i.e. short-chain PFASs with <C₇ PFCAs or <C₆ PFSAs) have been the predominant fluorochemicals used in fluorotelomer-based AFFF for the last 25 years. Telomerisation, which besides ECF is an important process for manufacturing perfluorinated substances, makes a product that normally contains two non-fluorinated carbons between the functional-group and the perfluoroalkyl chain (Buck et al., 2011). Studies indicate that fluorotelomers eventually degrade to perfluorinated acids in nature, and e.g. 6:2 FTS are known to degrade to PFHpA and PFHxA but not PFHxS (Wang et al., 2011b). There are several Class B certified AFFF on the market based on fluorosurfactants made by telomerisation (see Table 5 in UNEP/POPS/POPRC.14/INF/8). (Please note that several perfluorinated substances in the short-chain category are under scrutiny for regulation in the EU (reviewed in section 2.3 paragraph 68)). Compared to the C₈-foams, increased concentrations of C₆ fluorosurfactants, or oligomeric surfactants, have to be used for efficient firefighting effect (Tyco patent 2014).

81. The aquatic environment, both surface- and groundwater are in many regions polluted with PFASs (including PFHxS) and consequently pose a risk to both human health and the environment. Fire training sites where PFAS-containing AFFFs have been used (often located at airports and military training grounds) have been recognized as one of the major PFAS-contamination sources (Gobelius et al., 2018; Banzhaf et al., 2017; Hu et al., 2016; IPEN 2018). Impact on the environment and the remediation costs are high at these hot spot sites. Furthermore, the alternative short-chain PFASs with <C₇ PFCAs or <C₆ PFSAs (including their precursors) show relatively higher water solubility and increased environmental mobility (Baduel et al., 2017; Barzen-Hanson and Field, 2015). There is

also increased focus on a “Cradle to Grave approach” (Ramsden, 2017). In Queensland, Australia, also C6 pure foam ($\leq C_6 = 99.995\%$ of PFASs) substances are now increasingly regulated (Queensland Government, Australia 2016). In Queensland, Australia, they are not allowed to be released directly to the environment, must be fully contained on site, and must be disposed of as a regulated waste (Queensland Government, Australia 2018).

82. Best practice guidelines have been developed by the foam industry (FFFC, 2016) for use of fluorine containing foam due to concerns over environmental pollution and include, for instance, the following advice:

- (a) Fluorinated Class B foams should only be used in situations that present a significant flammable liquid fire hazard;
- (b) Before deciding to use fluorinated Class B foam for a specific liquid fire hazard, investigate whether other non-fluorinated techniques can achieve the required extinguishment and burn-back resistance;
- (c) Alternative techniques and agents must be evaluated well in advance of an emergency situation that requires urgent response;
- (d) Use training foams that do not contain fluorosurfactants for training purposes;
- (e) Use surrogate liquid test methods that do not contain fluorosurfactants for testing fixed system and vehicle foam proportioning systems;
- (f) Provide for containment, treatment, and proper disposal of foam solution – do not release directly to the environment. Develop firewater runoff collection plans for the use of fluorinated Class B foam.

83. In addition, the FFFC provides this information: The use of Class B foam is not recommended for Class A (wood) or Class C (electrical) hazards where there is minimal or no flammable liquid fire threat. If a flammable liquid threat exists, Class C applications must be de-energized since foam contains water that can conduct electricity. Examples of situations where Class B foams are not required include, but are not limited to, forest fires, residential and structural fires, computer rooms and telecommunications facilities, restaurants and commercial kitchens, and general facilities protection. In addition, Class B foams may not be necessary for small flammable liquid fire threats such as automobile fires without a significant fuel spill where a large water application rate or dry chemical extinguisher can be used.

84. Recognition of these facts led to the following COP-9 decision which states: “Also encourages Parties and others to use alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride where such alternatives are available, feasible and efficient, while considering that fluorine-based fire-fighting foams could have negative environmental, human health and socioeconomic impacts due to their persistency and mobility” (SC-9/5). The same recommendation was adopted for PFOA (decision SC-9/12).

2.3.1.2 Metal plating

85. During assessment of alternatives to PFOS several alternatives, including non-fluorinated chemical alternatives and technical solutions, were discussed (see Table 3 in UNEP/POPS/POPRC.14/INF/8).

86. Hard metal plating is used to protect metal components from wear and corrosion. Industrial rollers, hydraulic cylinders and crankshafts are examples of industrial applications of hard chromium electroplating. Through the electroplating process, a thin layer of chromium is deposited on the base metal or metal alloy surface of a workpiece where resistance and hardness are important attributes. In these applications the workpiece is submerged in a chromic acid (hexavalent chromium, Cr (VI)) bath. Fume suppressants are chemical agents added to the chromium bath to reduce the amount of chromium lost at the surface. Cr (VI) is a human carcinogen, and the fume (mist) suppressants reduce the occupational exposure and this lowers the risk of respiratory cancers. Chemical fume (mist) suppressants are surfactants that lower the surface tension of the plating solution and by controlling the surface tension, the process gas bubbles become smaller and rise more slowly than larger bubbles and mist is less likely to be emitted into the air and the droplets fall back into the plating bath.

87. It is not clear from the publicly available information on PFHxS how extensively the substance is used in metal plating. However, some patents (Dainippon, 1979, 1988; 3M, 1981; Hengxin, 2015) were identified for the use of PFHxS, its salts and various PFHxS-related compounds in metal plating as mist suppressants, suggesting that such use may have occurred (reviewed in Norwegian Environment Agency M-961/2018). It is likely that at least Hubei Hengxin in China has marketed the potassium salt of PFHxS for metal plating and PFHxSF as a raw material for various types of electroplating (decorative, etc) (Hengxin, 2019). It should be noted that the manufacturing (including importing) or processing of two salts of PFHxS (tridecafluorohexanesulfonic acid, compound with 2,2'-iminodiethanol (1:1); CAS No. 70225-16-0 and potassium *N*-ethyl-*N*-[(tridecafluorohexyl)sulphonyl]glycinate; CAS No. 67584-53-6) for use as a component of an etchant, including a surfactant or fume suppressant, used in the plating process to produce electronic devices shall not be considered a significant new use subject to reporting under the U.S. EPA Significant New Use Rule on perfluoroalkyl sulfonates and long-chain perfluoroalkyl carboxylate chemical substances (U.S. EPA, 2013). Furthermore, due to unintentional production of PFHxS during the ECF

process (Wang et al., 2017), it is likely that the PFOS-containing mist/fume suppressants used for metal plating contain unintentional amounts of PFHxS, its salts and/or PFHxS-related compounds.

Non-chemical alternative techniques

88. Some alternative technologies that omit the use of chemicals and prevent chromium (Cr) (VI) release during plating processes are available (Table 3 in UNEP/POPS/POPRC.14/INF/8). These include the use of PTFE-coated balls on top of the bath, and mesh or blanket covers for plating baths. However, the effectiveness of this approach relative to mist suppressants has been questioned (see section 2.5.3 in UNEP/POPS/POPRC.14/INF/8). There is also the use of control devices, such as Composite Mesh Pads (CMP) or Chromic Acid Fume Scrubber (<https://www.monroenvironmental.com/air-pollution-control/packed-bed-wet-scrubbers/>) to catch aerosols from chromium plating. According to the BAT/BEP Guidance for use of PFOS (UNEP2017b.) these techniques are considered alternatives to the use of PFOS-based control devices and it has been indicated that there are no factors limiting the accessibility of these control devices, and they are commercially available in Canada (UNEP/POPS/POPRC.12/INF/15/Rev.1.). The CMP system collects and transports chromium emissions through a mesh blanket-type pad where the chromium particles are condensed and collected, primarily through physical means. A CMP system typically consists of several mesh-pad stages. Early stages remove large particles, intermediate stages remove smaller particles and final stages remove microscopic particles. The CMP system is effective at removing droplets and eliminating the discharge of chromic acid mist. To our knowledge it is not known whether the use of CMP can lead to increased chromic acid wastes, and risks/costs arising from this. Additional alternative techniques available include chrome plating based on nanotechnologies (<http://www.greencoat.it/>), a 2-layer-system developed by Hauzer Techno Coating (<https://www.hauzertechnocoating.com/en/>) and the Hexagon system that builds on smart reservoirs that can hold onto anticorrosive chemicals that were previously incompatible with coatings (<https://www.hexigone.com/>). However, it is unclear whether these techniques can be used for hard metal plating as well as decorative metal plating.

Chemical alternatives

89. Poulsen et al. (2011) have demonstrated that it is possible to use PFOS-free mist suppressants for non-decorative hard chromium plating (Cr VI) in closed loop systems. The fluorinated alternative Fumetrol® 21 from Atotech, which is based on 1*H*,1*H*,2*H*,2*H*-perfluorooctane sulfonic acid (6:2 fluorotelomer sulfonic acid; CAS No. 27619-97-2) reduces the Cr (VI) emission. This alternative polyfluoroalkyl chemical will ultimately degrade to a mixture of perfluorocarboxylic acids that have alkyl chains with no more than six perfluorinated carbon atoms. Attempts to use Cr (III) also for hard chromium plating are also ongoing for development of an environmentally friendly alternative to hexavalent chromium in chrome plating (<https://www.pfonline.com/blog/post/nucor-invests-in-environmentally-friendly-chrome-plating>). Fluorine free alternatives such as alkylsulfonate and olea amine are also available (ECHA, 2019c).

2.3.1.3 Textiles including leather and upholstery

90. Finishing agents based on PFASs are widely used in textiles to achieve water, oil and dirt repellency of the material, while at the same time maintaining breath-ability. According to Hubei Hengxin, the PFHxS-related compound [*N*-methyl-perfluorohexane-1-sulfonamide] ethyl acrylate (CAS No. 67584-57-0) is used in oil repellent- and water-repellent products for leather and textiles (Hengxin, 2019). The use of PFASs in textile production accounts for about 50% of global use of PFASs (Danish EPA, 2015). According to a study performed by the Danish Government (Danish EPA, 2015) five alternative non-fluorinated chemical groups are mentioned in the report; (1) paraffins, (2) stearic acid-melamine, (3) silicone, (4) dendrimers and (5) nano-materials. The report concluded that non-fluorinated alternatives, which provide durable water repellence are available, but that non-fluorinated chemical alternatives for oil and dirt repellence are limited (Danish EPA, 2015). A range of fluorocarbon-free, water-repellent finishing agents for textiles include commercial products such as BIONIC-FINISH®ECO and RUCO-DRY® ECO marketed by Rudolf Chemie Ltd., Geretsried/Germany; Purtext® WR, Purtext® WA, Purtext® AP marketed by the Freudenberg Group, Weinheim/Germany; and ecorepel® marketed by SchoellerTechnologies AG, Sevelen/Switzerland. Also, textile and carpet surface treatment applications based on acrylate, methacrylate and adipate are available (UNEP/POPS/POPRC.13/7/Add.2).

91. A consumer study investigating the variation in functionality between long-chain (C₈) PFAS repellent chemistry, shorter-chain (C₆) PFAS repellent chemistry, and non-fluorinated repellent chemistry within outdoor apparel fabrics aimed to report a novel comparison of currently commercially available repellent fabrics for outdoor apparel as well as an assessment on their repellent functionality both for water and oil resistance (Hill et al., 2017). For outdoor apparel consumers, non-fluorinated chemistry can currently meet the water repellence requirements. The authors propose that the use of PFAS chemistry for outdoor apparel is therefore over-engineering, providing oil repellence that is more than the consumer requires. In a different study, side-chain fluorinated polymers (SFPs) and non-fluorinated water-repellent agents based on polydimethylsiloxanes or hydrocarbons showed excellent water repellence and durability in some cases while short-chain SFPs were the more robust of the alternatives compared to long-chain SFPs in terms of water repellence (Schellenberger et al., 2018). A strong decline in oil repellence and

durability with perfluoroalkyl chain length was shown for SFPs. Non-fluorinated alternatives were unable to repel oil, which might limit their potential for substitution in textile applications that require repellence towards non-polar liquids, such as medical textiles in surgical gowns and drapes, in operating rooms, doctor and nurse apparel and for laboratory personnel that are required to be protected from blood and body fluids as carriers for infections and viruses. (Schellenberger et al., 2018). This is in line with information provided in the assessment of alternatives to PFOS that was updated in 2018 (UNEP/POPS/POPRC.14/INF/8). However, in the same study it was shown experimentally that some fluorine-free and even biodegradable durable water repellents could provide some degree of stain repellence (Schellenberger et al., 2018).

2.3.1.4 Polishing agents and cleaning/washing agents including coatings, impregnation/proofing (for protection from damp, fungus, etc.)

92. Some products are available through internet search however there is little information on the content- and identity of chemicals in these products. For example, 'Impregno' stone impregnator is a fluorine-free, waterproof/dirt repellent (<https://impregno.de/>).

93. There is not much publicly available information on the use of PFHxS in cleaning-, washing- and/or polishing products. One PFHxS-related compound (CAS No. 67584-53-6, [*N*-Ethyl-*N*-(tridecafluorohexyl) sulfonyl]glycine, potassium salt) was reportedly used in polishing agents and cleaning/washing agents at least between 2000 and 2015 in Denmark, Norway and Sweden (SPIN, 2018).

94. One PFHxS-related compound (CAS No. 67584-61-6, 2-[Methyl[(tridecafluorohexyl) sulfonyl]amino]ethyl methacrylate) was reportedly used in impregnation/proofing for protection from damp, fungus, etc. at least in four products between 2003 and 2009 in Denmark (SPIN, 2018). Furthermore, the same PFHxS-related compound (CAS No. 67584-61-6) was also found registered in the same use category in Norway in 2011.

95. The FluoroCouncil has reported (see UNEP/POPS/POPRC.14/INF/8) that many global suppliers are offering "non-fluorinated" alternatives, including:

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

2.3.1.5 Manufacturing of electronics and semiconductors

96. Several studies have reported release and emission of PFHxS from the semiconductor industry (reviewed in the risk profile for PFHxS; UNEP/POPS/POPRC.14/6/Add.1) indicating that PFOS has been substituted by PFHxS in this application. Investigations revealed that PFHxS was the main PFAS constituent in the final waste effluent from a semiconductor fabrication plant in Taiwan province of China (Lin et al., 2009). This information is further strengthened by published information that indicates that PFHxS is used in the semiconductor industry. PFHxS (133.3 ng/L), together with PFOS (128.7 ng/L), was one of the primary contaminants at a semiconductor fabrication plant waste water effluent site. Both PFASs are present in the effluent in similar amounts showing that PFHxS is a primary substance in this process (Lin et al., 2010). PFAS (e.g. PFOS or PFHxS) does not remain in the semiconductors but in the case where PFASs is not removed from the waste water before it is released, it will follow the waste water and be released into the environment.

97. There is no other available information on what specific processes in the manufacture of electronics and semiconductors that PFHxS is used and it is therefore necessary to review all the information available on alternatives to PFOS within the manufacture of electronics and semiconductors. According to the guidance on alternatives to PFOS (UNEP/POPS/POPRC.9/INF/11/Rev.1) small amounts of PFOS-based compounds are required during the following critical photolithography applications in manufacturing semiconductor chips:

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

98. PFHxS, like PFOS, can be used as a surfactant in the manufacture of compound semiconductors and rinsed out during the subsequent washing treatment.

99. Several non-fluorinated chemical alternatives were identified during the assessment of alternatives to PFOS (UNEP/POPS/POPRC.14/INF/8/Add.1). The following alternatives were classified as potentially not to have POP-characteristics; amyl acetate, anisole, *n*-butyl acetate, ethyl lactate, methyl-3-methoxypropionate and propylene glycol methyl ether acetate. The scientific literature indicates that it should be possible to develop a PFOS-free photo-resist system (Ayothi et al., 2006). Also, some patents describe fluorine-free photoresist compositions as

alternatives to PFOS/PFAS use (see UNEP/POPS/POPRC.12/INF/15/Rev.1). In 2010, IBM announced a fluorine-free photo-acid generator as part of their PFAS phase-out and IBM notes that the fluorine-free process meets performance requirements for both dry immersion exposures (<https://www.spiedigitallibrary.org/conference-proceedings-of-spie/7639/1/Design-synthesis-and-characterization-of-fluorine-free-PAGs-for-193/10.1117/12.846600.short>) and Fuji describes photo-resists that are “PFOS & PFAS free” for use in the semiconductor industry (https://www.fujifilmusa.com/products/semiconductor_materials/photoresists/krf/index.html#features).

2.3.2 Other uses

100. In addition to the above-mentioned applications, other potential use categories may include pesticides, flame retardants, paper, and in the oil industry as well as cook wear. Furthermore, information from various sources indicates that PFHxS was detected in food contact material, sealants, adhesives, architectural foam, and coatings as well as in some applications in buildings and construction (See Table 1.9 in UNEP/POPS/POPRC.14/INF/4).

101. The Imaging and Printing Association Europe (I&P Europe), which includes all the major manufacturers of photographic products (photo-imaging industry and photographic industry) within the European Union, provided notification that their members are not using PFHxS, its salts or PFHxS-related compounds (I&P Europe, Annex F information).

2.4 Summary of information on impacts on society of implementing possible control measures

102. A positive impact on human health and the environment can be expected from a global reduction or elimination of PFHxS, its salts and PFHxS-related compounds. It is important to consider the specific characteristics of PFHxS when assessing the human health and the environmental impacts of restrictions. These substances are considered POPs and therefore have defined properties related to the potential for PFHxS to persist in the environment. Therefore, due to its persistency in the environment, and as a result of its long-range transport, PFHxS is present in the environment on a global scale, including in remote areas where emissions are negligible. In addition, PFHxS has the potential to accumulate in living organisms, which, along with its toxicological properties, may lead to adverse effects on human health and the environment arising from the potential for long-term exposure. PFHxS also has the longest half-life in human serum ever reported for any PFAS. Therefore, the risk management of these substances is driven by scientific data and precautionary action in accordance with Article 8, paragraph 9 of the Stockholm Convention.

2.4.1 Health, including public, environmental and occupational health

103. The elimination of production, use, export, and import of PFHxS and PFHxS-related compounds through a listing in Annex A without exemptions would positively impact human health and the environment by decreasing and ultimately eliminating emissions. As outlined in the risk profile, PFHxS has widely contaminated the environment including humans and wildlife (UNEP/POPS/POPRC.14/6/Add.1). A broad range of impacts have been observed in humans and animals as a result of PFHxS exposure. These can include negative effects on liver function, lipid and lipoprotein metabolism, endocrine disruption, alterations in serum cholesterol, lipoproteins, triglycerides, and alkaline phosphatase, effects on reproduction, and may affect the developing brain and immune system. Effect on the antibody response to vaccination is demonstrated in some epidemiology studies. It is found in blood, umbilical cord blood and breast milk (UNEP/POPS/POPRC.14/6/Add.1). PFHxS has a very long half-life time in humans (Olsen et al., 2007) and is passed from one generation to the next via placental transfer and breast milk (Winkens et al., 2017).

104. Drinking water has been identified as an important source of human exposure, and in areas with contaminated drinking water, increasing trends are observed in human blood levels of PFHxS (Li et al., 2018). Due to the widespread use of PFASs in AFFFs and historical, and in some countries, continuing practice of training in the open field in combination with the persistency of PFASs, drinking water sources have been contaminated in many countries on all continents (Gobelius et al., 2018; Banzhaf et al., 2017; Mak et al., 2009; Kabore et al., 2018; Zafeiraki et al., 2015; Boiteux et al., 2012; Ericson et al., 2009, see Table 1.6 in UNEP/POPS/POPRC.14/INF/4 for details). In a 2014 investigation, it was estimated that the drinking water for 3.6 million people was affected by PFASs, including PFHxS, out of the approximately 10 million inhabitants of Sweden (Banzhaf et al., 2017). In the period 2010 to 2015, PFHxS was detected in drinking water in 23 U.S. States among 134 water utilities serving 5.5 million people (EWG's Tap Water Database). PFHxS was detected in 55 U.S. public water sources out of 4,920 with levels >minimum reporting level (MRL= 0.03 µg/L), and 207 samples out of 36,971 contained PFHxS (U.S. EPA, 2017).

105. To protect their inhabitants, limit values for some PFASs in drinking water have been set in many countries (see section 1.5). In 2014, the Swedish Chemicals Agency and the Swedish Food and Drug Administration initiated a national PFAS network for authorities, researchers, county administrative boards, municipalities and water producers. The network focuses on addressing the problem of PFASs in drinking water and discusses solutions to remove the substances from the soil and in drinking water, but also for more initiatives including research on perfluorinated

substances. The network is a platform for communicating contacts and supporting various actors in the country (KemI, 2014).

106. Traditional water treatment techniques such as ferric or alum coagulation, granular/micro-/ultrafiltration, aeration, oxidation (i.e., permanganate, ultraviolet/hydrogen peroxide), and disinfection (i.e., ozonation, chlorine dioxide, chlorination, and chloramination) are mostly ineffective in removing PFASs (Boone et al., 2019). The water treatment methods for disinfection such as chlorination and ozone treatment have been shown to degrade precursors from a group of four zwitterionic/cationic polyfluoroalkyl amide and sulfonamides to PFOA and PFOS (Xiao et al., 2018). Increased levels of individual PFASs have also been observed in efflux compared to influx in WWTP. PFHxA, PFOA, PFHxS, and PFOS had a net mass increase in efflux compared to influx in all WWTPs, with mean increases of 83%, 28%, 37% and 58%, respectively (Eriksson et al., 2017). The load of precursors and intermediates in influent water and sludge combined with net mass increase of persistent PFCAs and PFSAs in effluents from WWTPs included in the study support the hypothesis that degradation of precursor compounds is a significant contributor to PFASs contamination of the environment (Eriksson et al., 2017).

107. Some techniques have proven efficient in removing PFASs from water although at high cost, see section 2.4.4. These techniques could also be used on WWTP effluents to reduce emissions to the environment. PFHxS had greater than 95% removal by nanofiltration in deionized water when artificial groundwater and a fouling layer were present on the filtration membrane, which more accurately represents a real-world scenario. Micro- or ultrafiltration coupled with reverse osmosis has been shown to remove targeted PFASs, including PFHxS. Although less effective on several other short-chained PFAS compounds, ion exchange resin can effectively remove >97% of PFHxS (reviewed in Arvaniti and Stasinakis, 2015). Anion exchange (AE) and granular activated carbon (GAC) treatment preferentially removed longer-chain PFASs and the PFSAs compared to the PFCAs, and reverse osmosis demonstrated significant removal for all the PFASs, including the smallest PFASs. such as perfluorobutanoic acid (Appleman et al., 2014). Furthermore, both GAC and AE have been shown to have a higher removal efficiency of linear compared to branched PFSAs, indicating that designers and operators of AE and GAC treatment processes must take into consideration the selective nature of PFAS removal and associated desorption of short-chain PFCAs during co-removal of multiple PFASs (McCleaf et al., 2017).

108. Dust is an important source of exposure, especially for occupational exposure, but also for toddlers, which due to their hand to mouth behaviour they have an elevated exposure to dust. At a Chinese fluorochemical manufacturing plant for PFOS-related compounds, indoor dust (67.3%) and diet (31.6%) were found to be the largest sources to human PFHxS exposure (Gao et al., 2015). Serum concentrations of PFHxS were in the range 12.8–10,546 ng/mL, and indoor dust levels ranged from n.d. to 257,201 ng/g (mean=15,726) (Gao et al., 2015). In another study from a fluorochemical manufacturing plant in the same district, serum concentrations of PFHxS in family members of occupational workers were in the range 4.33–3,164 ng/mL, dust in residences connected to the plant had PFHxS in the range 0.44–708 ng/g, both significantly higher than for ordinary residents in the plant area. In addition, PFHxS in the diet ranged from 0.067–0.448 ng/g ww and PFHxS in drinking water ranged from n.d. to 3.2 ng/L (Fu et al., 2015). Air ventilation, personal protective equipment (PPE) and strict procedures for changing protective-clothing in different zones could reduce the exposure.

109. Firefighters would benefit from a ban of PFHxS, its salts and PFHxS-related compounds. In firefighters, serum levels of PFHxS were in the range of 49–326 ng/mL serum, whereas the control group ranged from 0.2–22 ng/mL serum (Rotander et al., 2015a). Levels of PFOS and PFHxS were strongly correlated and the highest levels of PFOS and PFHxS were one order of magnitude higher compared to the general population in Australia and Canada. Study participants who had worked ten years or less had levels of PFOS (and PFHxS) that were similar to or only slightly above those of the general population. This coincides with the phase out of 3M AFFF from all training facilities in 2003 and use of fluorine-free foam after 2010 and suggests that the exposures to PFOS and PFHxS in AFFF have declined in recent years (Rotander et al., 2015b).

2.4.2 Agriculture, including aquaculture and forestry

110. A phaseout of PFHxS, its salts and PFHxS-related compounds would be beneficial for agriculture and reduce the risk of direct and indirect exposure to humans and the environment. Research suggests that the spread of PFASs in agricultural soils is mainly a result of irrigation with contaminated water, the use of polluted sewage sludges or industrial wastes as soil conditioners (Ghisi et al., 2019). PFASs (including PFHxS) are absorbed by plants to different extents according to their concentrations, chain lengths, functional group, plant species and variety, growth media (hydroponics vs. soil), and soil and biosolid characteristics (reviewed in Ghisi et al., 2019). Use of biosolids (treated sludge from WWTP) to fertilise soil can increase levels of PFASs in crops. PFHxS and PFHxS-related compounds have been detected in sludge and effluents from WWTPs (Table 1.5, UNEP/POPS/POPRC.14/INF/4). Uptake in plants of PFHxS from PFAS-spiked soil, has been observed (Wen et al., 2014). Furthermore, plants have been shown to biotransform precursors e.g. wheat has been shown to biotransform PFOSA to PFOS, PFHxS and PFBS (Zhao et al., 2018).

111. As reviewed in the risk profile, studies have reported the presence of PFHxS in food items (EFSA, 2012; Gebbink et al., 2015; Noorlander et al., 2011, Food Standards Australia New Zealand, 2016; Table 1.7 in UNEP/POPS/POPRC.14/INF/4). PFHxS and other PFAS have been detected in fruits and vegetables from Europe (Herzke et al., 2013 and D'Hollander et al., 2015). In Australia, environmental samples mainly from contaminated sites found highest mean upper bound PFHxS in cattle meat, rabbit meat and eggs (Food Standards Australia New Zealand, 2016). Other foods with high concentrations were crustaceans, fish liver and sheep meat (Food Standards Australia New Zealand, 2016). Studies on wheatgrass grown on soil contaminated with AFFF showed that PFHxS was bioavailable and bioaccumulated (Bräunig et al., 2019).

112. Due to the use of PFHxS and other PFASs in several industrial- and household applications the substances are regularly detected in WWTP effluents and landfill leachates (Hamid et al., 2018; Arvaniti and Stasinakis, 2015, see Table 1.5 in UNEP/POPS/POPRC.14/INF/4). In a study by Allred (et al., 2014), several PFHxS precursors (FHxSAA, MeFHxSAA, EtFHxSAA) were detected in leachates from landfills indicating that these PFHxS precursors and/or their parent compounds were likely used in a variety of applications since the landfills had received residential and commercial waste, construction and demolition waste, biosolids from waste water treatment plants as well as non-hazardous industrial waste. Air emission of PFHxS from landfills and WWTPs as well as accumulation in leaves around landfills have been reported (Ahrens et al., 2011; Tian et al., 2018).

113. PFHxS has been detected in many aquatic species (see Table 1 in UNEP/POPS/POPRC.14/INF/4). A phaseout of PFHxS, its salts and PFHxS-related compounds would also be beneficial for aquaculture, especially in areas where aquatic species are an important food source and where fish product consumption was shown to be a pathway for exposure to PFHxS for residents. High PFASs and PFHxS serum levels were observed in fishery employees located in Tangxun Lake and in the aquatic diet of residents to Baiyangdian Lake, adjacent to fluorochemical plants (Zhou et al., 2014; Cui et al., 2018).

2.4.3 Economic aspects and social costs

Prohibition on use

114. Based on present knowledge, PFHxS, its salts and PFHxS-related compounds are or may have been used in many of the same use categories as PFOS, its salts and related compounds. No request for exemptions for any application has been raised for PFHxS, its salts and PFHxS-related compounds. Furthermore, expected volumes of existing stocks should be minimal, and PFHxS as an unintentional byproduct in PFOS products would be eliminated due to phase-out of PFOS. Based on current knowledge it therefore it is considered that industry may substitute any current uses of PFHxS, its salts and PFHxS-related compounds without significant socioeconomic costs (RPA, 2019). Several countries have already introduced some regulation of long-chained PFAS which include PFHxS (see section 1.5).

115. Enforcement costs may be shared with the costs of enforcing other restrictions on PFASs, e.g. to target the occurrence of PFOS, PFOA, C₉-C₁₄ PFCA and PFHxS and related compounds in articles at the same time. Methods specified by the European Committee for Standardization (CEN) for PFOS could be used to detect ionic forms of PFHxS and its salts (see section 1.1. for more information about analytical methods and challenges). Thus, the enforcement costs specific to PFHxS should be small in magnitude. However, some cost for capacity building may be anticipated. There will also be some difficulties in enforcement due to the low levels of PFHxS (as for other PFASs) in products. Development of analytical methods that can clearly distinguish between substances that are covered by the listing and those that are not covered will be important (similar issues were discussed in RAC/SEAC in the case of the PFCAs C₉-C₁₄, and the PFOA restriction proposal under REACH (ECHA, 2018, 2015)).

116. A study by Oosterhuis et al., (2017) sought to provide information that could be used to develop a benchmark for assessing the proportionality of measures to control PFOA, PFOS and other POP-like substances. It looked at the cost-effectiveness estimates for regulatory measures that have been applied or considered. The available evidence suggests that in the past, regulatory measures costing less than 1,000 €/kg substance use or emission reduction have usually not been rejected, whereas for measures with costs above 50,000 €/kg substance such a rejection is likely. However, it was not possible to link the decision on whether measures were rejected or not to any proportionality benchmark since explicit statements on 'disproportional costs' are scarcely made.

117. A study using the limited data available for PFHxS, its salts and PFHxS-related substances indicates that costs related to disposing of AFFF containing PFHxS as the main fluoro-active ingredient is likely to be proportionate (RPA, 2019).

Control of discharge and emissions

118. Health costs (estimated at 2.8–4.6 million euros for the Nordic countries) and clean-up costs (estimated at 46 million to 11 billion euros for the Nordic countries) are high in areas receiving PFASs contaminated water or containing contaminated soil (NCM, 2019). In the view of IPEN, lifetime costs for using AFFF far outweigh those of fluorine-free foams just because of the legal and financial liabilities of using a fluorochemical based foam (IPEN,

2018). For example, the Australian government announced AUD 73.1 million (USD 50.7 million) in 2018 to support those affected by PFAS contamination, of which AUD 55.2 million (USD 38.3 million) will be spent across five years to give people access to safe drinking water. The government has spent more than AUD 100 million (USD 69.4 million) on PFAS investigation, management and remediation activities. Some of the measures taken have addressed the human impacts of the contamination, e.g., public outreach, help-lines, counselling services, and a voluntary blood-testing program and associated epidemiological study for affected communities.

119. PFHxS has the longest half-life in humans amongst the PFASs with known values and is found in most environmental and biota samples analysed (see UNEP/POPS/POPRC.14/INF/8). Monetary valuation of human health and environment impacts caused by PFHxS is lacking because a quantitative cause and effect relationship between PFHxS levels and different health endpoints has not yet been defined and would furthermore be difficult to separate from that for other PFASs, such as PFOS, with similar effects. However, the socioeconomic analysis in the study from the Nordic Council finds that the costs of inaction are substantial, with annual health-related costs estimated to 2.8–4.6 billion euros for the Nordic countries³ and 52–84 billion euros for all European Economic Area (EEA) countries. Overall non-health costs are estimated at 46 million–11 billion euros for the Nordic countries (NCM, 2019). The report is based on monetising a few selected health endpoints linked to PFAS exposure covering kidney cancer, all-cause mortality and hypertension. Effects on children such as low birth weight and infection (days with fever due to effects on immune system) have not been monetised. The report also monetised the non-health costs covering treatment of drinking water resources and remediation of contaminated soil. The costs related to PFAS contamination of drinking water for two case examples have been estimated to be 1 million euros per year for charcoal filtering of water in Uppsala and to be 3 million euro for a new water supply in Ronneby, which is a small city where approximately 5000 households were immediately affected when high levels of PFASs were discovered in 2013 (KemI, 2016). In addition, it is a social cost that exposure to PFASs including PFHxS via drinking water causes increased health problems as well as anxiety in affected populations.

120. Due to the extensive use of AFFF, one of the biggest sources of PFASs (especially PFOS) to the environment is the dispersal from contaminated soils. As PFHxS is often present in PFOS based AFFF, it has therefore spread in environments around fire-fighting training sites. In Norway and many other countries, airports and their vicinity are especially burdened with contamination from PFASs, as there are obligations to regularly test and practice fire-fighting. In Norway, 50 airports have been investigated, and PFOS, as well as PFHxS and other PFASs has been identified at a majority of the sites, with amounts ranging from low concentrations and small remaining amounts in the soils, to heavily contaminated sites with dispersals to nearby lakes and fjords. Remediation is ongoing at several airports but the exact costs for this remediation are still uncertain. The activated charcoal (AC) filters that are suggested to be used, are known to easily get clogged if the water contains material, such as humic substances. Depending on the frequency of replacing the filters, the costs for this remediation solution could be up to NOK 50 million (USD 6.5 million) at one site (Evenes airport) over thirty years. The installation of the water pump- and treatment system is estimated to be NOK 14 million (USD 1.8 million). One of the highest uncertainties for cost estimates is the time-frame for PFOS to be washed out of the soil to such an extent that the water in a stream does not have a negative impact on the receiving lake, nor the fjord (Alling et al., 2017). If remediation action is done properly this could secure drinking water resources and wildlife and fishing resources in surface waterbodies such as lakes and inland water. However, monitoring of water, sediments and biota has to be undertaken to assess the improvement achieved through the remediation action taken.

Waste management and stockpiles

121. As mentioned earlier, in Boucher et al (2019), the highest estimated emission sources of PFHxS are from use and disposal. A schematic overview of the fate of PFHxSF-based products during use and disposal are given in the Supplementary of this publication (Boucher et al., 2019 S2.1.3). The overview shows possible routes in the waste streams that can result in emissions of PFHxS to the environment (Figure S6). These include emission through waste water (gases, effluent and sludge), and through solid wastes (landfill, land treatment).

122. In accordance with paragraph 1 (d) (ii) of Article 6, if PFHxS is listed under the Stockholm Convention, PFHxS-containing products should be disposed of in such a way that their POP content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of POPs or otherwise disposed of in an environmentally sound manner. Special waste management and disposal related to PFHxS could be costly. Due to the legacy use as impregnates for textiles, this waste stream could be affected. Furthermore, the widespread use in several product categories would have an impact on household waste, waste from electronic and electrical equipment (WEEE) and end-of-life vehicles (ELV) as well. Capacity of high-temperature incineration could be an issue. For developing countries, UNIDO has recommended a variety of effective non-combustion techniques, including methods suitable for PFAS destruction such as gas phase chemical reduction and ball milling (UNIDO, 2007). The updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs) under the Basel Convention lists Gas Phase Chemical Reduction as capable of destroying all POPs (UNEP/CHW.14/7. Tab 4). Electrochemical oxidation has been demonstrated to destroy C₄–C₈ PFAAs (AECOM, 2018). In addition, cement kiln co-incineration can be used for high temperature incineration

and this is often present in most countries. However, the products of pyrolysis or combustion, the temperatures at which these will occur, and the extent of destruction are not well characterized (U.S. Air Force (2017). Costs related to waste management is not known. The technical guidelines on PFOS (use, inventory and waste) are highly applicable for PFHxS containing waste as well (UNEP, 2017 a,b; 2015).

123. The POPRC previously developed a series of recommendations to manage the PFOS waste stream. Decision POPRC-6/2 outlines a series of risk reduction measures in a short-term, medium-term and long-term framework. Since the use patterns of PFHxS, its salts and PFHxS-related compounds are similar to PFOS these recommendations are largely applicable to PFHxS. They include "To use best available technique and best environmental practice destruction technologies for wastes containing PFOS in current production and industrial uses of PFOS. No landfilling of these wastes should be permitted, unless leachate containing PFOS is properly treated. To ensure safe storage when destruction technologies are not readily available. To launch urgent investigations into landfills where waste from PFOS producers or from PFOS industrial users (paper, carpet, textile, chromium plating and other industries having used PFOS) are deposited. Drinking water from reservoirs and wells in the vicinity of these landfills and also around the PFOS production and user areas should be analysed".

124. Detailed recommendations are also developed to reduce risk from use, existing stocks, recycling of articles, consumer products deposited in municipal landfills, and releases from contaminated sites (decision POPRC-6/2).

2.4.4 Movement towards sustainable development

125. Elimination of PFHxS is consistent with sustainable development plans that seek to reduce emissions of toxic chemicals and that links chemical safety with sustainable development and poverty reduction. Environmentally sound management of chemicals and all wastes throughout their life cycle is addressed in UN Resolution 70/1 and is part of the sustainable development goals under the 2030 Agenda for sustainable development. Perfluorinated chemicals and the transition to safer alternatives are recognized under SAICM as an issue of concern. The Overarching Policy Strategy (OPS) of SAICM also states that "chemicals or chemical uses that pose an unreasonable and otherwise unmanageable risk to human health and the environment based on a science-based risk assessment and taking into account the costs and benefits as well as the availability of safer substitutes and their efficacy, are no longer produced or used for such uses." The OPS further suggests that POPs could be among those groups of chemicals prioritized for an assessment to support the transition to safer alternatives.

2.5 Other considerations

126. Listing PFHxS in Annex A without exemptions will involve the need for control measures to be communicated and therefore should be effective and suitable, including for countries that have limited chemical regulatory infrastructure. Information on alternatives is readily available and can be communicated as needed. With regard to environmental monitoring and biomonitoring, PFHxS can be added to existing programmes for monitoring other POPs, particularly PFOS and PFOA.

2.5.1 Access to information and public education

127. Several Parties, observers and NGOs have information and public education concerning PFAS on their webpages. e.g.:

- (a) OECD; Portal on per and poly fluorinated chemicals. <http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/>;
- (b) ECHA: European Chemical Agency. <https://echa.europa.eu/>; (search using CAS No.)
- (c) ATSDR; Agency for Toxic Substances & disease registry. <https://www.atsdr.cdc.gov/pfas/index.html>;
- (d) Australia: <https://www.pfas.gov.au/>,
<http://www.defence.gov.au/Environment/PFAS/Publications/Default.asp>,
<http://www.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-hbgv.htm>;
- (e) Miljø- og Fødevarerministeriet Denmark: <https://mst.dk/>;
- (f) Swedish Environmental Protection Agency: <http://www.swedishepa.se/Global-links/Search/?query=PFAS>;
- (g) Norwegian Environment Agency; <http://www.environment.no/>;
- (h) Information related to initiatives under the Canadian Environmental protection Act, 1999: <https://www.canada.ca/en/environment-climate-change/services/canadian-environmental-protection-act-registry/general-information/fact-sheets.html>;

- (i) Information on the assessment and management of substances in Canada: <https://www.canada.ca/en/environment-climate-change/services/canadian-environmental-protection-act-registry/general-information/fact-sheets/management-process.html>;
- (j) The State of Alaska: Division of Spill Prevention and Response. Contaminated sites: <https://dec.alaska.gov/spar/csp/pfas-contaminants>;
- (k) Access to data generated by FluoroCouncil members: <https://fluorocouncil.com/health-environment/scientific-studies/>;
- (l) German Environment Agency: <https://www.umweltbundesamt.de/>;
- (m) Swedish Chemicals Agency: <https://www.kemi.se/en/chemical-substances-and-materials/highly-fluorinated-substances>;
- (n) National Food Agency, Sweden: <https://www.livsmedelsverket.se/en/food-and-content/oonskade-amnen/miljogifter/pfas-in-drinking-water-fish-risk-management>;
- (o) Queensland Government Australia: Environmental Management of Firefighting Foam-Operational Policy: <https://www.qld.gov.au/environment/pollution/management/disasters/investigation-pfas/operational-policy>;
- (p) U.S. EPA PFAS website: <https://www.epa.gov/pfas>.

2.5.2 Status of control and monitoring capacity

128. PFHxS is included in several ongoing monitoring programs.
129. Canada is monitoring for PFHxS in air and/or precipitation as one of the substances under the Global Atmospheric Passive Sampling (GAPS) network (monitored in air since 2009), the Northern Contaminants Program (NCP) in the Arctic (monitored in air since 2006) and the Great Lakes Basin (GLB) Monitoring and Surveillance under the Chemicals Management Plan (CMP) (monitored in precipitation and air since 2006 and 2019, respectively).
130. Monitoring in human blood, specifically blood plasma, is done in the framework of the German Environmental Surveys (GerES) and the German Environmental Specimen Bank (ESB). Time trend data on PFHxS is available concerning the years 1982–2010 (Schröter-Kermani, 2013). A project is in progress which will add the years 2013–2019 to the time trend analysis (Germany Annex F information). In the U.S., PFHxS is included in the NHANES biomonitoring survey (https://www.cdc.gov/biomonitoring/PFAS_FactSheet.html). PFASs, including PFHxS, are included in the Swedish Environmental Surveillance Program (Naturvårdsverket) and the Swedish health related monitoring program (Karolinska Institutet). PFHxS and other perfluorinated compounds are also monitored in humans in Canada, for example under the NCP in the Arctic, Canadian Health Measures Survey (CHMS) and Canadian Maternal-Infant Research on Environmental Chemicals (MIREC). Under the CHMS, PFHxS has been monitored in the general Canadian population in 2007–2009 and 2009–2011, 2016–2017, and 2018–2019 (Government of Canada, 2013; Haines et al., 2017). The Korean National Environmental Health Survey (KoNEHS) started monitoring five kinds of PFASs including PFHxS from 2018 (Republic of Korea, Annex F information).
131. The European Joint Programme HBM4EU, coordinated by the German Environment Agency, has identified per- and polyfluorinated substances as priority substances and will compile EU-wide data on exposure and effect until 2021. Within the European Human Biomonitoring Initiative HBM4EU, PFHxS will be measured in blood serum of European teenagers aged 12–19 years from all parts of Europe (Schoeters et al., 2018).
132. Norway has annual monitoring of air, freshwater, marine and terrestrial biota that includes PFHxS (<http://www.miljodirektoratet.no/no/Tema/Miljoovervakning/Naturovervakning/Giftfritt-miljo/>).
133. PFASs including PFHxS monitoring information is available from Europe, North America and Asia. To follow the effectiveness of potential actions, PFHxS should be added to the existing global POP monitoring programmes.

3. Synthesis of information

3.1 Summary of risk profile information

134. At its fourteenth meeting in 2018, the POPs Review Committee adopted the risk profile and concluded that PFHxS, its salts and PFHxS-related compounds are likely, as a result of their long-range environmental transport, to lead to significant adverse human health and environmental effects such that global action is warranted.
135. PFHxS, its salts and PFHxS-related compounds have been used as surfactants, water- and stain- protective coatings for carpets, paper, leather and textiles and in fire-fighting foams among other applications, often as a replacement for PFOS. PFHxS has been unintentionally produced during the ECF processes used in production of other PFAS substances, e.g. PFOS. Information about current global manufacture of PFHxS, its salts and

PFHxS-related compounds is limited. Historical production was mainly carried out by 3M. A few producers located in China have been identified, however, quantitative production data are not publicly available.

136. PFHxS is extremely persistent in the environment. Numerous studies have reported elevated levels of PFHxS in soil, water and a variety of biota. Based on a read-across approach from the conclusions applied to the persistence of perfluorobutane sulfonic acid (PFBS), PFOS and PFOA, it can be concluded that PFHxS is not degradable under natural conditions and is very persistent in water, soil and sediment. Furthermore, the PFHxS ion is relatively water-soluble and it binds to proteins in target organisms. Based on the identified protein-binding associated with bioaccumulation, standard BCF/BAF in aquatic organisms are less meaningful descriptors for bioaccumulation for PFASs including PFHxS. However, biomagnification does occur, with biomagnification factors (BMFs) and trophic magnification factors (TMFs) >1 (BMF range 1.4–48 and TMF range 0.1–4.3) available for PFHxS. The estimated serum elimination half-life of PFHxS in humans is higher than other PFASs with an average of 8.5 years (range 2.2–27 years).

137. PFHxS is found very widely spread throughout the environment and in biota globally. Studies have reported exposure in remote areas that can be attributed to long-range environmental transport. PFHxS is detected in water, snow, air and biota (including humans) at remote locations. The main mechanism of transport to remote regions like the Arctic is presently most likely through ocean currents. However, transport of PFHxS and PFHxS-related compounds via the atmosphere cannot be excluded since PFHxS has been measured in snow, rainwater and air as well as in lichen. It is likely that both PFHxS and PFHxS-related compounds are transported through air to remote regions and that PFHxS-related compounds degrade to PFHxS locally.

138. Humans are exposed to PFHxS mainly through intake of food and drinking water but also through the indoor environment through dust or consumer products containing PFHxS or its precursors. Following PFOS and PFOA, PFHxS is the most frequently detected PFAS in blood-based samples from the general population worldwide. PFHxS is present in the umbilical cord blood and breast milk. Breast milk may be an important source of exposure for breast-fed infants since it is documented that PFHxS is excreted via lactation. Contamination of drinking water can result in highly increased PFHxS serum levels due to the long elimination-time in humans. Use of drinking water for food preparation can add to the background levels present in foods.

139. In rodents, various effects on the liver have been observed from PFHxS exposure. Effects on liver lipid and lipoprotein metabolism and altered serum cholesterol, triglycerides and lipoproteins have been observed in both rodents and humans. Neurotoxic and neurodevelopmental effects have been observed in controlled laboratory experiments in mice and rats, and some studies indicate association between behavioural inhibition in children and certain PFASs (including PFHxS) exposure prenatally and in childhood. Effects on the thyroid hormone system have been reported in rats, but studies indicate that PFHxS also might affect thyroid system in birds, polar bears and humans too. Furthermore, several epidemiology studies indicate that the naive and developing immune system might be vulnerable to certain PFASs and PFHxS exposure.

140. Recent data from polar bear studies at Svalbard (Norway) revealed increasing levels of PFHxS in plasma. PFASs, including PFHxS, contribute to the multiple-stressor effects observed in polar bears from Svalbard indicating a risk for adverse effects in wildlife. Combined exposure of PFASs with other POPs have unknown consequences and may cause increased toxicity for heavily stressed species.

3.2 Summary of risk management evaluation information

141. Restricting or prohibiting PFHxS, its salts and PFHxS-related compounds would positively impact human health and the environment by decreasing emissions and subsequently human and environmental exposures.

142. PFHxS, its salts and PFHxS-related compounds are synthetic substances with no known natural occurrence. C₆, C₈ and C₁₀ perfluoroalkanesulfonic acids (PFASs) were mainly produced by 3M from 1958 in the U.S. and from 1971 in Belgium, up to 2002. Reported production of PFHxS by 3M in the U.S. from 1958 to 1997 was approximately 228 metric tons per year. After phaseout of production from 3M, production continued at one manufacturer in Italy that advertised PFHxS and its precursors until it filed for bankruptcy in November 2018. However, main production and use has moved to Asia and increased since 2002, with at least some manufacturers in China. PFHxS is and has been unintentionally produced during the electrochemical fluorination (ECF) processes of producing other PFASs. PFOSF-based products may contain up to 10 % PFHxS as unintentional impurities if not removed to increase purity.

143. Use of PFHxS, its salts and PFHxS-related compounds are as far as we know overlapping with use categories for PFOS- and sometimes PFOA-compounds, and in many applications PFHxS or PFHxS-related compounds could have been used as replacements for PFOS and sometimes PFOA. Intentional use, in at least the following applications: (1) AFFFs for fire-fighting; (2) metal plating; (3) textiles, leather and upholstery; (4) polishing agents and cleaning/washing agents; (5) coatings, impregnation/proofing (for protection from damp, fungus etc.); and (6) within the manufacturing of electronics and semiconductors, have been identified. Other potential use categories may include pesticides, flame retardants, paper and packaging, in the oil industry, and hydraulic fluids. In addition, PFHxS, its salts and related compounds have been used in certain PFASs containing consumer products.

144. The regular assessment of alternatives to PFOS under the Stockholm Convention has revealed that alternatives are available for all potential applications which could also be relevant for PFHxS, its salts and related compounds. Alternatives include both fluorinated and non-fluorinated substances as well as alternative (non-chemical) technical solutions. Information on availability, accessibility and price of alternatives, as well as information on regulatory measures and use in different countries, reveal that the socioeconomic costs of implementing a ban on the use of PFHxS are considered small and are outweighed by the benefits of an elimination/ regulation. High costs are estimated for remediation of contaminated sites, such as old and current fire-fighting foam training sites and airports, landfills for industrial waste, and hazardous waste, as well as for the removal of PFASs, including PFHxS, from drinking water and water sources affected by PFHxS (and other PFASs) contamination. Implementation of control measures for PFHxS, its salts and PFHxS related compounds would contribute to avoiding such future costs.

145. Emissions of PFHxS to the environment occur at all its life cycle stages but are assumed to be highest during service life and in the waste disposal phase. PFHxS is very widely present in environmental compartments such as surface water, deep-sea water, drinking water, waste-water treatment plants (WWTPs) and leachates from landfills, sediment, groundwater, soils, the atmosphere, dust, as well as biota (including wildlife), and humans globally. Efficient control measures for the handling of waste will be essential to reduce environmental levels. According to Article 6 of the Convention, waste shall be disposed of in such a way that the POP content is destroyed or irreversibly transformed so that it does not exhibit the characteristics of POPs, or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option, or the POP content is low. The limited knowledge about current use of PFHxS, its salts and PFHxS-related compounds, and the fact that standardized analytical methods to detect and quantify individual PFHxS-related compounds are at present lacking, makes it difficult to identify these compounds in chemical products and chemical mixtures. The lack of information on the content of these compounds in consumer articles/products will make it difficult to separate these products in the waste stream and during waste treatment. For newer products to be placed on the market it should be possible for the importer to request this information, but for products already placed on the market this task is more difficult. However, this situation is not unique to PFHxS, its salts and PFHxS-related compounds but relevant for other regulated PFASs as well.

3.3 Suggested risk management measures

146. No exemptions have been requested. There is at present no information available that PFHxS is unintentionally produced from incineration, suggesting that a listing in Annex C is not required. Therefore, the suggested control measure to achieve “Prohibition or restriction of production, use, import and export” is listing PFHxS, its salts and PFHxS-related compounds in Annex A of the Convention, without exemptions.

4. Concluding statement

147. Having decided that perfluorohexane sulfonic acid (CAS No. 355-46-4, PFHxS), its salts and PFHxS-related compounds are likely as a result of their long-range environmental transport to lead to significant adverse human health and/or environmental effects such that global action is warranted; having prepared a risk management evaluation and considering the management options and noting the information on the availability of alternatives; the POPs Review Committee recommends, in accordance with paragraph 9 of Article 8 of the Convention, the Conference of the Parties to the Stockholm Convention consider listing and specifying the related control measures for perfluorohexane sulfonic acid (CAS No. 355-46-4, PFHxS), its salts and PFHxS-related compounds in Annex A without specific exemptions.

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