PERFLUOROHEXANESULFONIC ACID & ITS SALTS

CANDIDATE PERSISTENT ORGANIC POLLUTANTS

Toxics Link
for a toxics-free world

The Stockholm Convention on Persistent Organic Pollutants (POPs) is an international environmental treaty that aims to eliminate or restrict the production and use of the chemicals designated as persistent organic pollutants (POPs).

The Persistent Organic Pollutants Review Committee (POPRC) is a subsidiary body of the Stockholm Convention established for reviewing chemicals proposed for listing in Annex A, Annex B, and/or Annex C. The POPRC reviews proposals submitted by Parties for listing new chemicals in accordance with Article 8 of the Convention.

The fifteenth meeting of the POPRC was held from 1st to 4th October 2019 in Rome, Italy.[1] to decide the fate of three chemicals-perfluorohexane sulfonic acid (PFHxS), Dechlorane Plus & Methoxychlor to be included in the list of POPs. However only perfluorohexane sulfonic acid (PFHxS) has been accepted as a POP to be listed in Annexure –A.

Outcome of the meeting:

The POPRC Committee after due evaluation adopted the risk management evaluation on perfluorohexane sulfonic acid (PFHxS), its salts and PFHxS-related compounds and proposed to list the chemicals in Annex –A that is complete elimination without specific exemptions.

The Committee also recommended for more comprehensive risk profile evaluation of Dechlorane Plus & Methoxychlor in the Annex E as both chemicals met the screening criteria in Annex D.

PERFLUOROHEXANESULFONIC ACID (PFHXS)

INTRODUCTION

Perfluorohexanesulfonic acid (C6F13SO2, PFHxS) is a chemical compound from the group of short-chain perfluorosurfactants. It is a perfluoro-alkane-sulfonic acid in which all thirteen hydrogen atoms attached to carbons have been replaced by fluorine.[2]

PFHxS was introduced as an alternative to PFOS. A number of chemicals are included in the group of PFHxS, its salts and PFHxS-related compounds including isomers. The Organization for Economic Co-operation and Development (OECD) has identified 72 PFHxS-related/precursor/polymer substances including PFHxS which contain the fluorinated alkyl moiety $C_6F_{13}SO_2$.

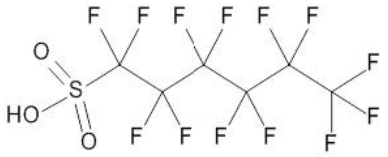
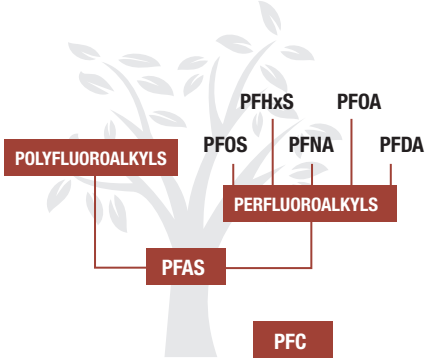


FIGURE 1
Tridecafluorohexane-1,1,2,2,3,3,4,4,5,5,6,6,6-Tridecafluorohexane-1- sulfonic acid



PFC: Perfluorinated compound
PFAS: Polyfluoro alkyl substances
PFDA: Perfluoro-decanoic acid
PFNA: Perfluoro-n-nonanoic acid
PFOA: Perfluoro-octanoic acid
PFOS: Perfluoro-octane-sulfonic acid
PFHxS: Perfluoro-hexane-sulfonic acid

https://www.wamc.org/post/senator-gillibrand-calls-faa-implement-law-regarding-pfas

PROCESS FOR LISTING A NEW CHEMICAL UNDER THE STOCKHOLM CONVENTION (ARTICLE 8)

1. A Party submits a proposal
2. The POPs Review Committee examines the proposal against Annex D screening criteria
3. If fulfilled, the POPs Review Committee prepares a risk profile based on Annex E information from Parties and observers
4. If adopted, the POPs Review Committee prepares a risk management evaluation based on Annex F information from Parties and observers
5. If adopted, the POPs Review Committee makes a recommendation on listing

PFHxS is very resistant to chemical, thermal and biological degradation due to their strong carbon-fluorine bonds which makes it persist in the environment.

PFHxS AS A CANDIDATE POP: STOCKHOLM CONVENTION

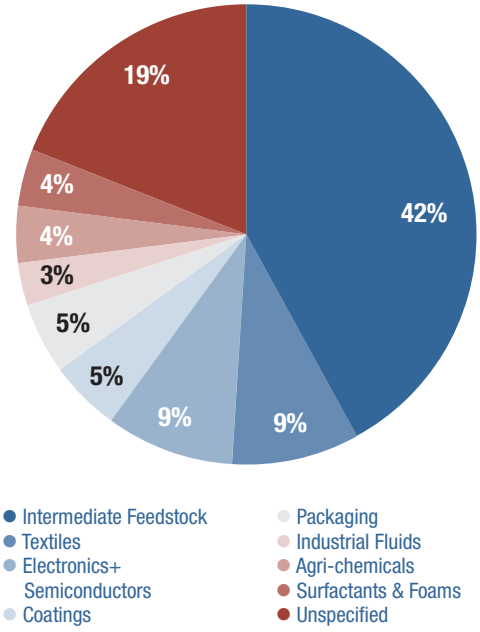
PFHxS was added to annexure –D in the POPRC meeting held in 2017; however in this meeting, the committee members unanimously agreed for the chemical to be included in Annexure –A. The chemical has the following characteristics to be qualified as a candidate POP[3].

- **Potential for long-range transport:** PFHxS can undergo atmospheric long-range transport due to persistence in air and water
- **Extreme environmental persistence:** In comparison to PFOS or PFOA, PFHxS is more water-soluble, more environmentally mobile, less absorbable to soils and sediments
- **Widespread distribution:** Its occurrence in abiotic & biotic matrices has been reported in remote locations
- **Long biological/bio-elimination half-lives:** PFHxS has a half-life of approximately eight years. The estimated serum elimination half-life of PFHxS in humans varies from 5.3 to 14.7 years.[4]
- **Established links to specific diseases** or pathological conditions.

APPLICATIONS

PFHxS, its salts and PFHxS-related compounds have intentionally been used in the following applications:[5]

- AFFFs for firefighting
- Metal plating
- Coating in carpets, textiles, leather and upholstery
- Polishing agents and cleaning/washing agents
- Coatings, impregnation/proofing (for protection from damp, fungus, etc)
- Wthin the manufacturing of electronics and semiconductors
- Pesticides and insecticide bait (SULFLURAMID)
- Flame retardants
- Making & printing inks and sealants



PFHxS is found in Arctic air, sediment, snow, ice, soil, sediment and biota (including humans) and in Antarctic biota and snow

Application	Alternative available	Types of alternative
Fire-fighting foam	Yes	Non-fluorinated firefighting foams, polyorganosiloxane
Metal plating	Yes	Hard chromium electroplating, Composite Mesh Pads (CMP) or Chromic Acid Fume Scrubber
Textiles	Yes	Alternatives to provide durable water repellence: 1) paraffins, 2) stearic acid-melamine, 3) silicone, 4) dendrimers and 5) nano-material.
Polishing, cleaning- and Coating, impregnation/ proofing washing agents	Yes	(a) paraffin-metal salt formulations; (b) Hydrophobic modified polyurethanes or dendrimers (c) Polyorganosiloxane-based products; (d) Resin-based repellents consisting of fatty modified melamine resins
Electronic and semiconductors	Yes	amyl acetate; anisole; n-butyl acetate; ethyl lactate; methyl-3-methoxypropionate and propylene glycol methyl ether acetate.
Paper and packaging	Yes	High-density papers, bio-wax, Polylactic Acid

ROUTES OF HUMAN EXPOSURE

The potential route of exposure includes inhalation, and dermal contact with compounds at workplaces where it is produced or used. The exposure also occurs through the use of consumer products, eating contaminated food, or drinking contaminated water. PFHxS can be present in food crops, in packaged food items, or in the fish people catch and eat.[6]

HEALTH IMPACT

Like other perfluoro alkyl chemicals, PFHxS & its salts also have adverse effect on human beings. The long elimination half-lives in blood might indicate that PFHxS accumulates directly in the blood or that the substance circulates between other tissues/ organs and blood or both.

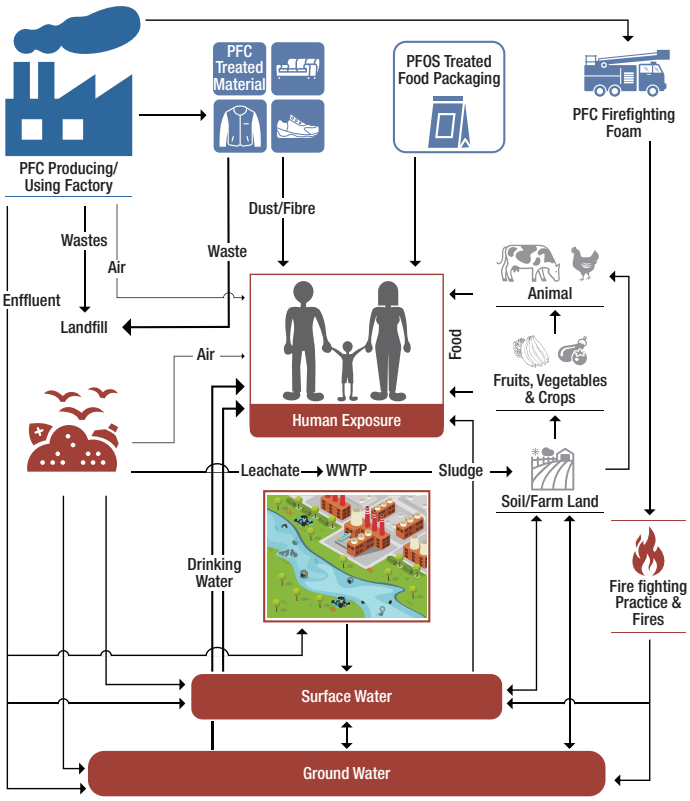
Once in the body, PFHxS and its salts adversely affects various organs and processes including liver, thyroid, nervous system, endocrine system and lipid protein metabolism.[i]

Adverse Effect

Epidemiological studies in human	Experimental studies in rodents
Endocrine-disrupting effects on the thyroid hormone	adverse effects to the liver
potential for immunotoxic effects in children	effects on serum level of chlosterol, lipoproteins, fatty acids
increased serum level of chloestrol, lipoproteins, triglycerides	thyroid organ toxicity
asthama in children	liver steatosis
immunosuppressive potential	neurotoxic
	delayed metamorphosis in frog

PFHxS IN ENVIRONMENT

PFHxS is water soluble and transported through water to remote areas. PFHxS has been detected from soil, water and a variety of biota from remote areas as well such as Greenland Sea, Alaska, the Northern Baltic Sea, the Arctic and Antarctica showing that it is persistent and does not undergo any abiotic or biotic degradation under normal environmental conditions.[7,8]



Detailed research studies by The European Chemical Agency (ECHA) suggest that PFHxS has bio-magnification potential.[9]

Many studies have detected PFHxS in effluents from waste water treatment plants (WWTPs) and industries. Contamination with PFHxS is especially apparent in the vicinity of fire-fighting training areas as a result of the historical (and ongoing) use of PFHxS-containing foams.

Compilation of research studies on half-life for PFHxS in humans

Reference	Setting	Subjects	Initial Level (ng/ml, serum) (median)	Half-life years
Olsen *et al*	Retired fluorochemical workers, followed 5 years; Repeated samplings with batch wise analysis	22 men, 2 women, Age: 55-75	193	7.1
Brede *et al*	Drinking water exposure; follow up 2 years after installation of charcoal filters	20 children, 22 mothers, 23 men	2.0	Relative reduction 2006-08 (30% in women, 14% in men)
Worley *et al*	Drinking water exposure, emanating from contaminated sewage sludge applied to agricultural fields; follow up after 6 years	First sample: 63 men, 90 women; Last sample: 22 men, 23 women	6.4	15.5

PFHxS has also been detected in the liver of Arctic polar bears, in the Atlantic Ocean, and in Antarctic fur seals.[10]

PRODUCTION

DuPont was the parent company producing PFHxS as a replacement to PFOAs. After the famous legal verdict against DuPont on PFOAs, 3M the sister concern of DuPont was producing PFHxS, its salts and PFHxS-related compounds. However, restriction was imposed on this chemical and gradually the production of this chemical was phased out since 2002[11].

Presently only two key global PFHxS manufacturers are there (both from China). Italian company Miteni has stopped manufacturing since 2013 but still selling PFHxS as a product on its website.[12]

In addition, PFHxSF may be unintentionally produced as a byproduct from the Electro Chemical Fluorination (ECF) of octanesulfonyl fluoride or chloride, the process to produce perfluorooctane sulfonyl fluoride (POSF).

The Norwegian Environment Agency has appointed BiPRO for investigation of the sources of PFHxS in the environment and its global production details. As per BiPRO report (2018) the total consumption of PFHxS & its salts was in the range of 670 - 730 kg in 2016.[13]

India depends on import for its requirements of PFHxS and its salts.

Worldwide pattern of PFHxS consumption

- **70-90m US$ in Europe**
- **100 m US$ in USA & Canada**
- **> 500m US$ in Asia**

REGULATIONS

The chemical has been identified as toxic and steps have been taken to restrict the use of the chemical in various products. Further, there are also stringent regulations in place on the presence of the chemical in drinking water and food products

In 2017, The European Union had identified PFHxS and its salts as Substances of Very High Concern (SVHC) and it has been added to REACH SVH list. Therefore, due authorization from The European Chemical Agency is required to place the chemical in the market.[14]

The Swedish National Food Agency has recently introduced a conservative "limit of action threshold" of 90 ng /L for the sum of seven PFASs (PFBS, **PFHxS**, PFOS, PFPeA, PFHxA, PFHpA, and PFOA) for drinking water.[15]

Guideline values for PFHxS

Country/ Agency	Guideline
Australia	PFOS + PFHxS should not exceed 0.07ppb in drinking water[16]
Germany	guidance value for PFHxS in drinking water of 0.1 µg/L[17]
Minnesota Department of Health	0.047 ppb for PFHxS in groundwater[18]
Few US State departments	0.01 to 0.09 ppb for PFHxS in drinking water[19]
Environmental Working Group of US	0.1ppb in drinking water[20]
Republic of Korea	The preliminary limit value for drinking water is 0.48 mg/L
Canada	Drinking Water Screening Value of 0.6 µg/L for PFHxS[21]
Denmark	limit value is 0.1 µg/L drinking water (for the presence of all the 12 PFASs including PFHxS)[22]
India	**No guidelines**

INDIAN CONTEXT

There are few research studies on presence of PFHxS in the environment and human health but they are not representative of the detailed situation and impact of PFHxS and its salts in India.

In India, there is no regulation or restriction on the use of PFHxS and its salts.

- Sharma *et al* (2016) have reported 81ppt PFHxS in tap water collected from Goa, Coimbatore, and Chennai.
- A 2010 study measured PFHxS along with other PFAS in the livers of pigs living on a large-scale municipal waste dump site in Perungudi near Chennai. Female pigs contained substantially higher levels of PFA chemicals.
- Lin *et al* (2008) found significant PFAS levels for PFOS, PFOA, PFHxS, and PFBS in women from Chidambaram, Kolkata, and Chennai. 36% samples showed positive concentration of PFHxS level in breast milk samples.

ENDNOTES

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2 http://www.ebi.ac.uk/chebi/searchId.do?chebiId=CHEBI:132448

3 https://ipen.org › files › pfhxs_socio economic_impact_final_oct.2019.pdf

4 https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5749314/

5 http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-PUB-factsheet-PFHxS-201907.English.pdf

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