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Investigation of sources to PFHxS in the environment

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CLIENT	Norwegian Environment Agency, Oslo Miljodirektoratet Grensesvingen 7 0661 Oslo Norway
PROJECT	Investigation of sources to PFHxS in the environment
CONSULTANT	Contact person for the tender BiPRO GmbH Alexander Potrykus Grauertstrasse 12 81545 Munich Germany APOT@ramboll.com
CONTACT	BiPRO GmbH
Telephone	+49-89-18979050
Telefax	+49-89-18979052
E-mail	APOT@ramboll.com
Website	http://www.bipro.de

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1 Background and objectives

Among the group of long-chain per- and polyfluoroalkyl substances (PFASs), perfluorohexane sulfonic acid (PFHxS), its salts and related substances have been subject to less attention than i.e. perfluorooctane sulfonic acid (PFOS) and PFOA. Similar to its C8 homologue, PFOS, PFHxS is extremely persistent and has long-range transport potential. Furthermore, PFHxS has higher bioaccumulation potential in humans than PFOS, with an elimination half-life of approximately 8.5 years. Based on the concern for hazardous properties and global presence of PFHxS (CAS 355-46-4), the Norwegian Environment Agency has nominated PFHxS, its salts and related substances to the Stockholm Convention on Persistent Organic Pollutants (SC) in May 2017. The nomination proposal specifically summarizes relevant evidence and address information requirements and screening criteria set in the Annex D of the SC for persistence, bioaccumulation, adverse effects and long-range transport¹.

Exposure to PFHxS, its salts and related substances have been reported in many parts of the world, both in wildlife and humans. Such exposure occurs through different routes, including drinking water supplied from groundwater. A comprehensive overview on the global production, use and releases of PFHxS, its salts, and related substances is still lacking. However, currently available information indicates that PFHxS and related substances may be present in certain industrial and consumer products such as fire-fighting foams, food contact papers, water-proofing agents, cleaning and polish products either for intentional uses (as surfactants or surface protection agents) or as unintentionally impurities from industrial production processes. In addition, perfluorohexane sulfonyl fluoride (PFHxSF; CAS 423-50-7) is the starting material for the production of PFHxS and the many PFHxS-related substances. PFHxSF is registered under the REACH C&L Inventory and produced at least in Italy and China.

The investigation of past and current production and uses in industrial and consumer products and production and use volumes can help identify possible paths to the environment and estimate the amounts of contaminants that can enter and may already have entered the environmental compartments. This information will be crucial for further evaluation of the risks posed by PFHxS and related substances.

The main objective of this project is to provide an overview of available information on global production and use of PFHxS, its salts, and related substances. The outcome of the project intends to support the nomination by Norway under the SC, in particular investigation of sources of PFHxS into the environment.

Therefore, the project aims to improve the information regarding the current production, import and export volumes, and use of PFHxS and related substances globally. Furthermore, quantitative information on the global production as well as import and export data will be summarized as far as possible with the aim to result in a better understanding of the current status of use of PFHxS and related substances. Both industrial applications and downstream uses in products and articles are part of the investigations. To the extent possible, the reporting will cover different regions of the world, i.e. North America, Europe, Africa, Asia, etc. In particular, the project intends to provide insight into the following main topics:

- 1) Global production (volume) of PFHxS and PFHxSF (including time trends).
- 2) Intentional use (application) of PFHxS (including salts) and PFHxS-related substances.
- 3) Occurrence of PFHxS (including salts) and PFHxS-related substances in substances and preparations (types of products, amounts)
- 4) Occurrence of PFHxS (including salts) and PFHxS-related substances in products/articles (types of products, amounts)

¹ For further information see proposal by Norway (UNEP/POPS/POPRC.13/4):
<http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx>

- 5) Downstream use/applications of PFHxSF in substances and preparations, including in products.

2 Identification of relevant substances

Perfluorohexane sulfonic acid (PFHxS), its salts and related substances belong to the group of per- and polyfluoroalkyl substances (PFAS) [1]. PFHxS, its salts and related substances are produced from the raw material PFHxSF, which may partially remain in products as an impurity due to incomplete reactions [2].

The chemical structures of PFHxS, an example of its salt (perfluorohexanesulfonate ammonium salt), a PFHxS-related substance (perfluorohexane sulfonamide) and PFHxSF, which all contain the moiety [C₆F₁₃SO₂], are illustrated in Figure 1, respectively.

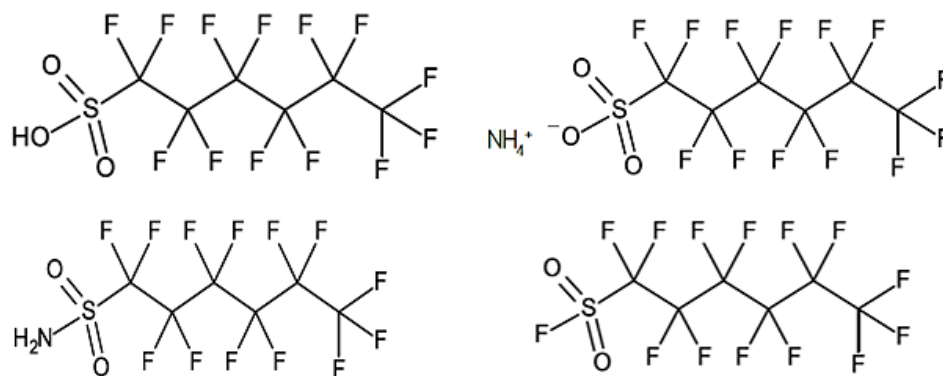


Figure 1: Chemical structures of PFHxS (top left), perfluorohexanesulfonate ammonium salt (top right), perfluorohexane sulfonamide (bottom left) and PFHxSF (bottom right) [1].

As the group of PFHxS, its salts and related substances comprises a large number of chemicals, a non-exhaustive list of substances covered by the survey has been compiled in close collaboration with the Norwegian Environment Agency and experts from ETH Zürich.

48 substances containing the fluorinated alkyl moiety [C₆F₁₃SO₂] identified by the Organisation for Economic Co-operation and Development (OECD) [3] served as a basis for the compilation of the list of relevant substances. This initial list was further expanded by adding substances that were identified by experts from ETH Zürich and by the Norwegian Environment Agency (e.g. in the ECHA database and SciFinder database) [4].

The final list, which includes in total 79 relevant substances, is shown in the Annex I (Annex I: List of Substances).

3 Evaluation of international market reports on PFHxS and PFHxSF

In order to fulfil the main objectives of the project, the work has been divided into three separate work packages (WP). In the first WP, available international market research reports on PFHxS and PFHxSF were acquired and evaluated. The studies were selected to preferably address all of the information needs indicated in Chapter 1 and to cover both the target substance PFHxS (CAS 355-46-4) as well as its starting material, PFHxSF (CAS 423-50-7), for production of PFHxS and PFHxS-related substances. Reading samples of the reports were obtained and carefully reviewed in advance and additional questions were posed to the providers of the relevant studies in order to assess the depth and quality of the information contained before purchase, as far as possible. The final decision on acquiring the market reports were made in close coordination with the Norwegian Environment Agency.

The acquired market research reports have been screened with respect to applicability to the main questions of this study. As far as possible, plausibility and reliability of available information and quantitative data were validated by for instance comparing it to the findings from other work packages (i.e. WP2 and WP3). In the following, the main information from the evaluated market research reports is presented.

▪ Information on Perfluorohexane sulphonyl fluoride (CAS 423-50-7)

Information from market research reports indicates that PFHxSF is consumed in different applications, in particular: textiles, surfactants and foams, packaging, electronics and semiconductors, industrial fluids, coatings, agrichemicals, and used as intermediate feedstock.

Based on available information and quantitative data on historic and present consumption, a steady increase of the global consumption of PFHxSF could be observed during the last 6-7 years in a range from about 400 - 700 Million US\$. Besides, a further increase in consumption is foreseen during the coming years, with an expected maximum value in a range of 700 - 900 Million US\$ (in 2020), followed by a slight decline (see Figure 2 displaying estimated ranges of PFHxSF world market during the time frame 2010 - 2023).

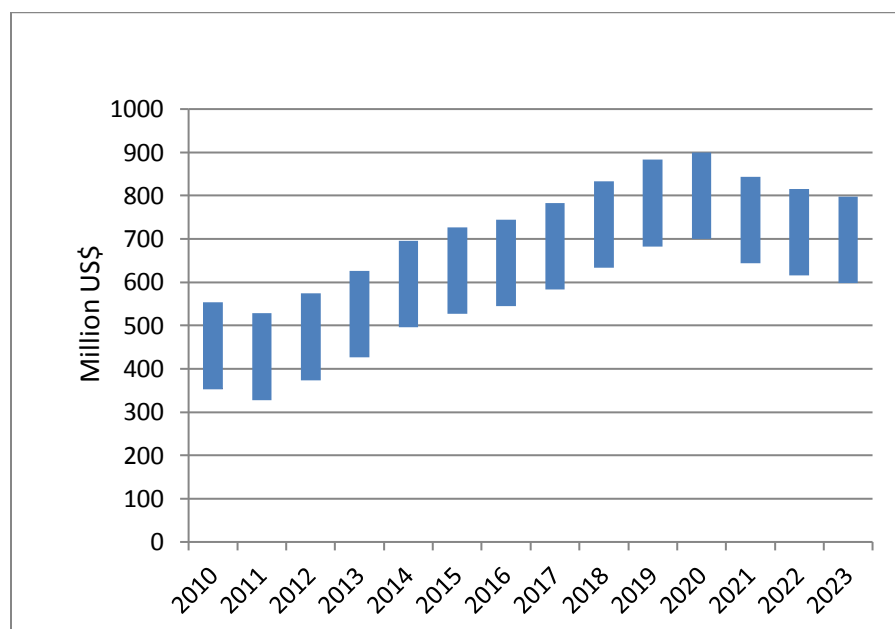


Figure 2: Estimated range of historic and forecast world market of PFHxSF

The maximum PFHxSF consumption is expected to be in the range of 100 Million US\$ (2019) in USA and Canada, 70-90 Million US\$ (2020) in Europe and more than 500 Million US\$ (2020) in Asia. Considering a current price for commercially available PFHxSF of around 2-10 US\$/g, around 10-60 tonnes PFHxSF are expected to be consumed in US and Canada, about 10-40 tonnes PFHxSF in Europe and between 60-300 tonnes in Asia, as a rough estimate. The historic and forecast markets of PFHxSF for the selected regions USA and Canada (Figure 5 and Figure 6), Europe (Figure 7 and Figure 8), and Asia (Figure 9 and Figure 10) are presented in the Annex (Annex II: Historic and forecast market of PFHxSF (diff. regions)).

The available information, also allows summarizing the present and expected future shares of PFHxSF used in different sectors globally (see Figure 3). The total present consumption of around 600-700 Million US\$ is divided into the following industries / sectors as follows:

Table 1: PFHxSF consumption shares in different sectors in the world market

Industries	Approximate shares in million US\$
Textiles	~65-70
Surfactants and Foams	~25-30
Packaging	~30-35
Electronics and Semiconductors	~55-60
Industrial Fluids	~15-20
Coating	~30-35
Agrichemicals	~25-30
Intermediate Feedstock	~250-300
Unspecified	~120-130
Total	~600-700

The predicted shares are almost identical compared to the present consumption (see Figure 3). The term “intermediate feedstock” has not been defined in the market research reports. It is, however assumed that it means that PFHxSF is used as raw material for manufacture or processing of products.

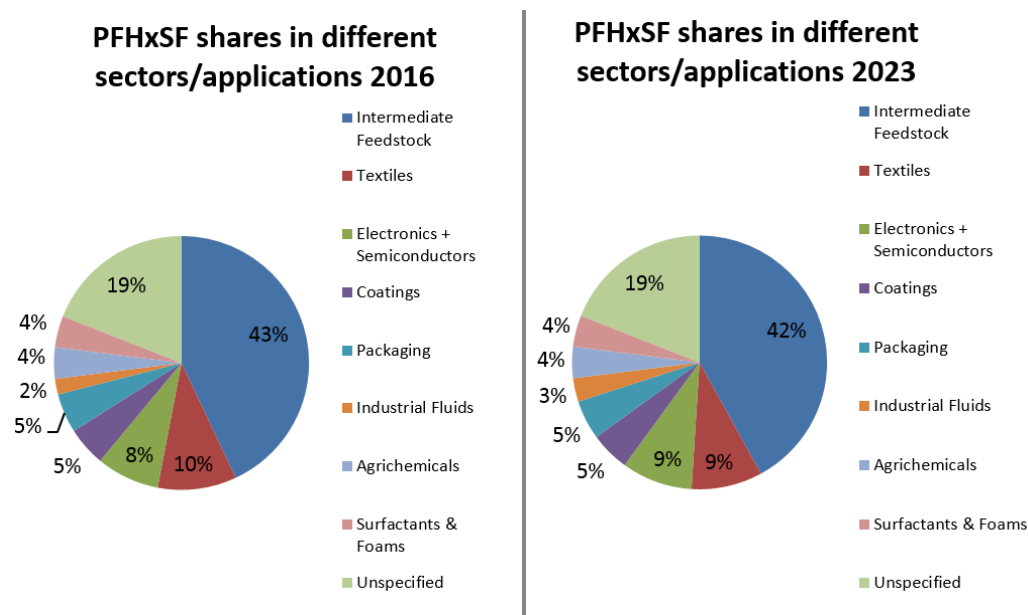


Figure 3: PFHxSF shares in different sectors / applications for the world market

Information on shares in different applications has been also identified for different regions and countries. However, for all regions and individual countries the same type of applications is indicated (shares show only slight variations). Figures for the shares in different applications are elaborated for the regions USA and Canada (Figure 6), Europe (Figure 8) and Asia (Figure 10) and are presented in Annex II: Historic and forecast market of PFHxSF (diff. regions).

▪ **Information related to Perfluorohexanesulfonic Acid (CAS 355-46-4)**

According to available data from market research reports, the production capacity of PFHxS remained constant at about 1,000 – 1,500 kg during the last five years (2011 – 2016). The actual production of PFHxS was at about 700 - 750 kg in 2012 and decreased to less than 700 kg in 2016. A further slight decrease in production of PFHxS is expected for 2017. Further, two key global PFHxS manufacturers (both from China) have been identified in market research reports, hereafter named Company X and Company Y (names of the companies are confidential) for the year 2016 with production market shares of almost 96 % and 5%, respectively. A summary of relevant information and quantitative data from those two companies is presented in the following.

Company X had a constant production capacity for PFHxS in a range between 900 - 1100 kg per year during the time period from 2012 to 2016. The actual annual production of PFHxS in this period was in average around 650 kg (min) and 690 (max). In 2017, a further decrease in production to the reported minimum volumes is expected. The price of PFHxS from Company X was in the range of less than 400 up to about 450 US\$ per kg.

The second Chinese PFHxS manufacturer (Company Y) had also a constant PFHxS production capacity of about 100 - 300 kg per year during the time-period from 2012 to 2016. The actual annual production of PFHxS was in the range of around 30 - 50 kg. The maximum price for 1 kg PFHxS was almost 650 USD (2014) and is expected to decrease about 100 USD for 2017 (550 USD).

In summary, according to information available from market research reports for PFHxS, there are two main producers with an accumulated annual production capacity between 1,000 – 1,500 kg and an actual global annual production of about 700 - 750 kg. It is, however, questionable that the indicated global capacity / production values are at such a low scale. This can possibly be explained by the fact that data from only two major producers has been presented in market reports and one would expect that the number of manufacturers are higher globally.

In addition, information and quantitative data on key countries' consumption has been identified. Around 620 - 640 kg of PFHxS was consumed in China, about 40 - 60 kg in Southeast Asia and about 10 - 30 kg in the rest of the world, leading to a total consumption in the range of 670 - 730 kg in 2016.

With regard to the application of PFHxS, information contained in market research reports covers application in firefighting foams and textile finishing which is a quite limited number of uses covered. The share in different applications (for 2016) is shown in Figure 4.

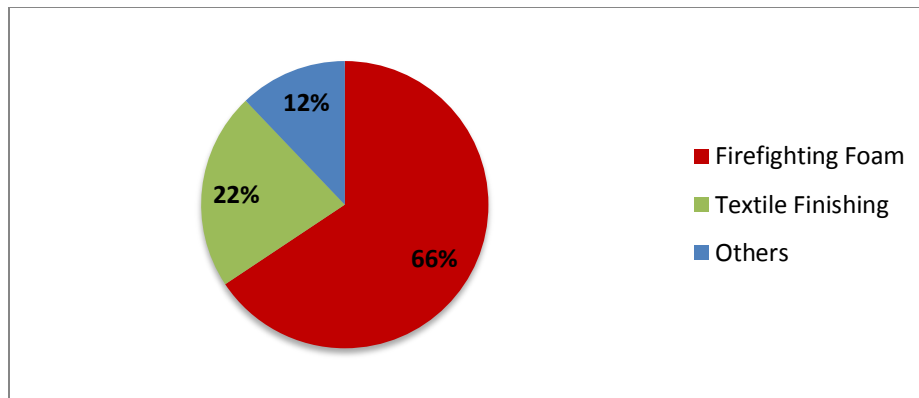


Figure 4: Global application of PFHxS in 2016

In summary, around 2/3 (~66%) of PFHxS was used in firefighting foams and the remaining 1/3 in textile finishing (~22%) and other applications (12%; application not further specified).

4 Evaluation of scientific publications and other sources

WP2: Collection and evaluation of peer-reviewed scientific articles and other information sources

In order to consider relevant information available beyond the market analysis reports, WP2 involved the collection and evaluation of relevant peer-reviewed scientific literature and other sources of information such as patents from major producers (e.g. Minnesota Mining and Manufacturing Co., USA (3M)), technical data sheets for products, and technical reports from other national and international regulatory institutions. The aim is to improve the basis of scientific information regarding PFHxS and related substances.

In a first step, an initial screening of available and possibly relevant peer-reviewed scientific literature and other relevant information sources was conducted. Based on the initial screening, the most relevant sources were prioritized in close coordination with the Norwegian Environment Agency. Data collection, screening, processing and analysis were conducted on the basis of a recently developed framework for a global emission inventory for perfluoroalkane sulfonic acids by Wang et al. [5]. The sections below provide an overview of the scientific information collected, and each offers a summary of the key information identified.

Sources and methods

Substantial efforts were made by the team to collect information from relevant, publicly available sources including:

- Peer-reviewed articles based on a Google scholar-search using keywords including “PFHxS”, “PFHS”, “PHxSF” and “PHSF”, and a SciFinder-search using CAS numbers listed in Annex I;
- Company websites;
- Technical reports by national and international agencies including previous OECD surveys;
- National inventories of existing and/or new chemicals using CAS numbers listed in Annex I;
- Information depositories by national agencies including over 4000 documents in the US EPA Administrative Record 226; and
- Patents based on searches in SciFinder using CAS numbers listed in Annex I.

Achieved results and overview of the status quo

In general, it was found that there is a lack of information on the production and uses of PFHxS and related substances in the public domain, particularly quantitative information. Despite this information scarcity, the following main findings were reached (with further detailed information presented later in the following sub-sections):

- PFHxS and related substances have been produced in large quantities in the past up until 2000–2002 when 3M made its global phase out of these substances. Most of this historical production was carried out by 3M and possibly by a Japanese manufacturer.
- After 3M’s phase-out, there has been ongoing large-scale industrial production of PFHxS and/or related substances by at least one manufacturer in Italy and by at least three manufacturers in China. There is no quantitative information regarding the current production and use of PFHxS and/or related substances in the public domain.

- A number of PFHxS and related substances can be identified in various national inventories of existing and/or new chemicals.
- Historical uses of PFHxS and related substances are primarily in the field of aqueous film-forming foams (AFFFs) for firefighting, metal plating mist suppressants, and aftermarket carpet protection. Current uses may further include textile surface treatments and within the manufacturing of semiconductors.
- Specific chemical information from industry sources was generally difficult to obtain, especially technical safety data sheets for previous and ongoing products that make use of PFHxS-related substances. However, for instance the US based tile manufacturer Fritztile, was found to provide technical data sheets for some of its floor care products listed as containing a PFHxS-related ingredient (i.e. CAS No. 67584-53-6).
- Among known uses, application of PFHxS and/or related substances in AFFFs is the most studied, with very limited information available on other uses.

OECD Surveys

The OECD developed a set of questionnaires to survey OECD member countries (and non-OECD member countries in the year 2009) on their production and use of perfluorooctane sulfonic acid (PFOS), perfluoroalkane sulfonic acids (PFSA), perfluorooctanoic acid (PFOA), perfluorocarboxylic acids (PFCAs), and their related substances (e.g. including salts, polymers, and precursors). The survey was conducted in the years 2004, 2006, and 2009, respectively. The responses received in each year were summarized in reports, and these reports were reviewed for any information relating to PFHxS or its related substances. Relevant findings for each survey year are provided below.

2004 Results

Results from the 2004 survey include reported manufacturing levels from Italy (i.e. Miteni) including PHxSF, PFHxS, and perfluorohexanesulfonamide (FHxSA) are provided in the table below [6]. The reported volumes are given only as upper bounds in year 2003 of <4000 kg PHxSF, <1500kg of PFHxS, and as 600 kg FHxSA. The uses for these produced volumes are described as industrial without any further description.

Chemical	Volume for 2003 calendar year [kg]	Known uses	Industrial and/or Consumer uses
PFHxSF (CAS No. 423-50-7)	<4,000	Unknown	Industrial
PFHxS•K, (CAS No. 3871-99-6)	<1,500	Unknown	Industrial
FHxSA (CAS No. 41997-13-1)	600	Unknown	Industrial

2006 Results

Results from the 2006 survey report that two C6 PFSA related substances existed at low concentrations of <0.05% in some undisclosed products. It also noted that "8 countries imported/manufactured products containing 29 [PFSA] related substances. Among these [PFSA] related substances, the compounds with perfluorinated carbon chains of C4, C5, C6 and C7 were in 6, 5, 6 and 6 products [,] respectively..." [7].

2009 Results

Results from the 2009 survey report that three C6 PFSA related substances were produced in 2008 (i.e., PFHxS (CAS No. 355-46-4), PFHxS-K (CAS No. 3871-99-6) and PFHxSF (CAS No. 423-50-7)), and they are described as being "used mainly as raw materials or precursors of production of PFAS-based products" [8].

US EPA Administrative Record 226

The United States Environmental Protection Agency's (US EPA) Administrative Record (AR) 226 contains thousands of documents, including many of those submitted by 3M before, during and following the phase-out of their production of products based on perfluorooctanesulfonyl fluoride (POSF)-based chemistry. Upon review of these documents, some key information was identified regarding PFHxS and related substances.

In a letter to the director of the EPA's Chemical Controls Division in July of 2000, 3M stated that they decided to "discontinue manufacture of products based on C-6 and C-10 homologs of POSF" [9]. Additional information has been presented to the US EPA but claimed as confidential business information and not publicly released.

According to an analysis report from the testing of four 3M fluorochemical products for residuals, higher levels of PFHxS impurities than PFOS impurities were found in some of the products (see table below), indicating that these samples were most likely treated with PFHxS-related compounds instead of PFOS-related compounds [10].

Sample Identification	PFHxS [ppm]	PFOS [ppm]
3M SG Carpet Protector Product	1900	610
3M SG Carpet Protector Treated Web	1900	470
3M T-7342*	330	180
3M T-7343**	270	190

* T-7342 – former post-production (aftermarket) application Scotchgard Brand carpet and upholstery protector containing FC-228, Lot NAMO, diluted 4:1 with tap water, 1.04% solids solutions; applied to skin as liquid on cotton gauze.

** T-7343 – former post-production (aftermarket) application Scotchgard Brand carpet and upholstery protector containing FC-228, Lot NAMO, diluted 4:1 with tap water, 1.04% solids solutions; applied to cotton gauze and dried prior to application to skin.

US EPA Inventory Updating Report (Database)

A US EPA database covering the historical inventory of national chemical import and production volumes is reported to contain information related to PFHxS-related substances. The table below shows these substances and their reported production or import volume ranges in the United States by year in pounds.

CAS Number	Chemical	1986 [1000 lbs]	1990 [1000 lbs]	1994 [1000 lbs]	1998 [1000 lbs]	2002 [1000 lbs]
423-50-7	PFHxSF	10 – 500	10 – 500	No Reports	10 – 500	No Reports
3871-99-6	PFHxS.	No Reports	10 – 500	No Reports	No Reports	No Reports
34455-03-3	EtFHxSE	10 – 500	10 – 500	10 – 500	10 – 500	No Reports
50598-28-2	FHxSA-derivative	No Reports	10 – 500	10 – 500	10 – 500	10 – 500

68555-75-9	MeFHxSE	10 – 500	10 – 500	10 – 500	10 – 500	No Reports
67584-57-0	MeFHxSE-acrylate	10 – 500	10 – 500	10 – 500	10 – 500	No Reports
38850-58-7	FHxSA-derivative	10 – 500	>500 – 1000	10 – 500	No Reports	No Reports
73772-32-4	FHxSA-derivative	No Reports	No Reports	No Reports	10 – 500	No Reports
68815-72-5	PFHxS-ester	10 – 500	10 – 500	10 – 500	10 – 500	No Reports

National Inventory Databases

Multiple countries have their own chemical registrations inventory or similar database. Many of these major national inventories were reviewed for containing PFHxS and related substances, including: the Australian Inventory of Chemical Substances (AICS), the Canadian Domestic Substance List (DSL), the Inventory of Existing Chemical Substances in China (IECSC), EU Pre-registered Substances, the Japanese Existing and New Chemical Substances Inventory (ENCS), Substances in Preparations in Nordic Countries (Nordic SPIN), the United States Toxic Substances Control Act Inventory (US TSCA; including substances listed under the Significant New Use Rule (S) or with a commenced pre-manufacture notice (P)). Table 2 below shows a list of identified PFHxS and related substances along with their CAS numbers and which of these of inventories/lists they appear on.

The identified presence of these chemicals within many of these inventories suggests that these chemicals are known to certain authorities, and that they have been, and may still be currently, imported to, produced in, or contained in products within these countries.

Table 2: PFHxS and related substances and their appearance on various national chemical inventories and lists. S = substances listed under the Significant New Use Rule; P = chemicals with a commenced pre-manufacture notice (P).

CAS No.	Chemical	AICS	Canada DSL	China IECSC	EU Pre-registered	Japan ENCS	Nordic SPIN	US TSCA Inventory
423-50-7	PFHxSF	✓		✓	✓			✓; S
355-46-4	PFHxS				✓			✓; S
3871-99-6	PFHxS, K	✓	✓	✓	✓	✓	✓	✓; S
55120-77-9	PFHxS, Li			✓		✓		✓; P, S
68259-08-5	PFHxS, NH ₃	✓	✓	✓	✓			✓; S
41997-13-1	FHxSA							
68259-15-4	MeFHxSA		✓	✓	✓			✓; S
68555-75-9	MeFHxSE	✓	✓	✓	✓		✓	✓; S
34455-03-3	EtFHxSE	✓	✓	✓	✓		✓	✓; S
85665-64-1	PrFHxSE				✓			
50598-28-2	FHxSA-deriv.			✓	✓			✓; S
68957-61-9	FHxSA-deriv.	✓	✓		✓			✓; S
68957-32-4	EtFHxSE-deriv.				✓			✓; S
67584-53-6	EtFHxSE-deriv.	✓	✓	✓	✓	✓	✓	✓; S
68555-70-4	EtFHxSE-deriv.				✓			✓; S
68298-09-9	FHxSA-deriv.							✓; S
68957-58-4	FHxSA-deriv.	✓	✓	✓	✓	✓	✓	✓; S
52166-82-2	FHxSA-deriv.	✓	✓	✓	✓	✓	✓	✓; S
85665-66-3	PrFHxSE-deriv.				✓			
66008-72-8	MeFHxSA-deriv.		✓		✓			✓; S
68227-98-5	MeFHxSE-acrylate				✓			✓; S
67584-57-0	MeFHxSE-acrylate			✓	✓		✓	✓; S
67584-61-6	MeFHxSE-acrylate			✓	✓		✓	✓; S

CAS No.	Chemical	AICS	Canada DSL	China IECSC	EU Pre-registered	Japan ENCS	Nordic SPIN	US TSCA Inventory
38850-52-1	FHxSE-deriv.				✓			✓; S
1893-52-3	EtFHxSE-acrylate	✓		✓	✓			✓; S
38850-60-1	FHxSA-deriv.				✓			✓; S
80621-17-6	FHxSA-deriv.			✓	✓	✓		
67906-70-1	EtFHxSE-acrylate			✓	✓			✓; S
38850-58-7	FHxSA-deriv.	✓	✓	✓	✓		✓	✓; S
73772-32-4	FHxSE-deriv.	✓		✓	✓			✓; S
81190-38-7	FHxSE-deriv.	✓		✓	✓			✓; S
67939-92-8	EtFHxSE-deriv.				✓			✓; S
68815-72-5	PFHxS-ester	✓	✓	✓	✓		✓	✓; S
68555-90-8	MeFHxSE-acrylate polymer mixtures	✓	✓	✓				✓; S
56372-23-7	EtFHxSE-driv. polyethoxylates	✓	✓	✓	✓		✓	✓; S
30295-56-8	FHxSA-deriv.			✓				
70900-36-6	MeFHxSA-deriv.				✓			
70776-36-2	MeFHxSE-acrylate polymer mixtures	✓	✓	✓				✓; S
68298-74-8	EtFHxSE-deriv.				✓			
68877-32-7	EtFHxSE-acrylate polymer mixtures		✓					✓; S
68586-14-1	MeFHxSE-acrylate polymer mixtures	✓	✓	✓	✓			✓; S
68555-92-0	MeFHxSE-acrylate polymer mixtures	✓	✓	✓	✓			✓; S
68555-91-9	EtFHxSE-acrylate polymer mixtures	✓	✓	✓				✓; S

Peer-reviewed Articles

A search of peer-reviewed scientific literature resulted in a limited set of additional information regarding PFHxS and related substances. The information found below stems from various publications found to contain relevant information across different aspects, with a primary focus on helping to identify uses qualitatively:

Production and Use

- Olsen et al. reports that “3M produced PFHS [perfluorohexanesulfonate] as a building block for compounds incorporated in fire-fighting foams and specific post-market carpet treatment applications” [11].
- One study by Yang et al. identified the synthesis of N-propyl-N-hydroxyethyl perfluorohexyl sulphonamide, which is described as “a novel fluorocarbon surfactant” synthesised using perfluorohexyl sulphonyl fluoride (PFHxSF) as the raw material. When applied to cotton, the product is reported to have had “excellent water, oil and stain repellency, as well as good washing durability” [12].
- A set of previously sold AFFF formulations were sampled and tested by Place et al., with a focus on AFFFs that were designed for use by the US military [13], producing some of the following main findings:

- All of the sampled AFFFs produced by 3M were found to contain C6-C8 PFASs. The study notes that "this is consistent with the frequent detection of perfluoroalkyl sulfonates found in AFFF-impacted groundwater."
- The six sampled 3M AFFFs were noted to be "comprised of zwitterionic C4–C6 perfluoroalkyl sulfonamides containing carboxylic acid and tertiary amine functionalities." They note that this is "consistent with patent information and Material Safety Data Sheets (MSDS) that list "amphoteric fluoroalkylamide derivatives".
- Zwitterionic compounds (a molecule with two or more functional groups) were found only in the 3M AFFFs manufactured in 1993, 1998, and 2001 but not in those from 1988 or 1989. They explain that "the 3M AFFFs were recertified in 1992, but the addition of zwitterionic fluorochemicals to 3M AFFFs is not well documented. AFFF formulation recertification would occur if there were changes to military specifications or if the AFFF formulation itself was significantly changed (i.e., a change in chemical components)."
- From the AFFFs analyzed, "no C8-based homologues of the zwitterionic class or the corresponding impurities were identified."
- D'Agostino et al. later identified "twelve novel and ten infrequently reported PFAS classes" in AFFF concentrates and commercial fluorinated surfactant concentrates comprising a total of 103 compounds with fluorinated chain lengths from C3 to C15 [14].
- Barzen-Hanson et al. most recently analyzed the contents of sampled AFFFs from US military bases and commercial products produced previously by 3M and DuPont. They also analyzed groundwater samples from firefighting training areas of thirteen US military bases taken between 2011 and 2015. Published results include the identification of "forty classes of novel anionic, zwitterionic, and cationic PFASs" as well as that "an additional 17 previously reported classes were observed for the first time in AFFF and/or AFFF-impacted groundwater" [15].

Human Exposure

- Rotander et al. investigated 149 firefighters working at training facilities in Australia that use AFFFs. Measurements of PFOS and PFHxS in their serum found that they were "positively associated with years of jobs with AFFF contact." They also note that "the highest levels of PFOS and PFHxS were one order of magnitude higher compared to the general population in Australia and Canada ... " [16].
- Jin et al. found that the "serum concentration of PFHxS was statistically higher in firefighters" than PFOS and PFOA, and that PFOS and PFOA "were also found higher in firefighters, though not statistically significant" [17]. Both studies suggest that occupational firefighting can create a risk of exposure of firefighters specifically to PFHxS.
- A recent study by Siebenaler et al. investigated the serum concentrations of perfluoroalkyl acids of a set of thirty-seven adults in the United States. The results show that PFHxS levels in serum were associated with some behaviors such as vacuuming less often and consuming more microwaveable foods [18].

Environmental Exposure

A study measuring the groundwater concentrations of PFASs from five military bases in the United States by Backe et al. found that "PFHxS occurs at concentrations greater than or similar to those of PFOS", however they note that "in all 3M AFFF formulations tested, the abundance of PFHxS is lower

than PFOS (Table 3)." These PFHxS levels are thought to possibly "arise from the degradation of the newly-identified telomer- and electrofluorination-based PFAS for which the C6 is the most abundant homolog" [19]. Raw results from the study describing the measured concentrations in 3M AFFFs are reproduced in the table below as taken from the supporting information (Table S6).

Table 3: Concentrations (mg/L) of newly-identified and legacy perfluorinated chemicals in 3M aqueous film forming foam formulations manufactured in 1989-2001

	1989 mg/L	1993a mg/L	1993b mg/L	1998 mg/L	2001 mg/L
PFBSaAm ^a	9	120 ± 2.0	180	140	110
PFPeSaAm ^a	8	140 ± 1.8	180	140	110
PFHxSaAm ^a	189	660 ± 8.1	850	743	690
PFHpSaAm	ND	12 ± 0.40	15	30	24
PFOSaAm	9.9	62 ± 1.1	75	67	37
PFBSaAmA ^a	ND	140 ± 3.1	120	110	150
PFPeSaAmA ^a	4	200 ± 6.3	170	140	130
PFHxSaAmA ^a	ND	930 ± 13	850	850	960
PFHpSaAmA	ND	17 ± 0.16	17	34	44
PFOSaAmA ^a	ND	72 ± 0.81	58	53	65
PFBS	380	220 ± 2.0	160	210	250
PFPeS	210	120 ± 1.5	80	90	120
PFHxS	1700	910 ± 14	760	850	900
PFHpS	410	120 ± 2.0	120	93	140
PFOS	15000	8000	9300	6700	7900
PFNS	160	53 ± 0.97	56	9	27
PFDS	102	51 ± 0.34	52	11	27

Patents

A search for patents using the CAS numbers identified in Annex I related to the development or production of PFHxS and related substances was completed with SciFinder and Google Patents. The patents found represent a wide array of applications, fluorinated chemistries, and were granted throughout the past decades.

A table with each of the patents found is provided (Annex III: Patents involving PFHxS and related substances) and contains information on the application, patent holder, year granted, and chemical description. Upon review of these patents, some specific observations and general conclusions can be drawn regarding the uses of PFHxS and related substances:

- Granted patents were found for PFHxS-related substances from as early as 1972 to as recent as 2015.
- Most patents found are related to use as surfactants in AFFFs and in mist inhibitors for metal plating.
- The most recent patents found date to 2012 and 2015. One of which is a fog inhibitor in metal plating intended as an alternative to conventional PFOS-based inhibitors. The other two are described as a surfactant and as an acrylate monomer, both with unclear intentions for use.

5 Results and outcome of stakeholder consultation

The main intention of WP3 was to bridge remaining data gaps from WP1 and WP2 with information from industry stakeholders (e.g. producers and users). In the first step, relevant industry stakeholders were identified and directly addressed. For the identification of relevant industry stakeholders, the following sources were used:

- a) Contacts from previous projects (BiPRO and ETH Zürich); during previous PFAS related projects, the project team gained extensive insights in relevant industries which produce and use per- and polyfluorinated substances in their production. In this context, members of the project team had been in close contact with various individual companies and associations within e.g. the paper, textile, fire-fighting foam and building materials sectors.
- b) Contacts identified during review of various literature sources (incl. producers and users mentioned in scientific articles and internet databases such as PubChem, ChemSpider, Safety Data Sheet (SDS) and ECHA homepage, etc.)
- c) Contacts identified during the evaluation of available market research reports
- d) Contacts identified through a targeted internet research (search CAS No, substance names)

One aspect that was relevant for the selection of the stakeholders was the distribution of potential users to different industry sectors as mentioned in a). The named industries have been known to use fluorinated substances for their manufacture of industrial and consumer products and were therefore considered and consulted for the elaboration of use volumes and contamination paths.

As a first step, relevant industry stakeholders were contacted via telephone. In case the respective stakeholders agreed to participate, an initial e-mail including background information, all relevant questions and a letter of appointment by the Norwegian Environment Agency was forwarded. Moreover, a date for a telephone appointment was proposed, allowing the respective stakeholder to coordinate within their company and prepare the answers. Finally, specific questions have been clarified via telephone during the agreed appointment. During the telephone calls, notes were taken electronically, and after the telephone call, the collected information was summarized and sent to the respective interview partner for final validation. In a few cases, follow up e-mails were sent to selected stakeholders (i.e. former producers) with additional questions on historic production.

In total 56 stakeholders have been addressed (via telephone calls or via e-mail). Both, possible producers and potential users (from various industrial sectors including e.g. paper, textile, and fire-fighting foams, etc.) were consulted. The complete list of contacted stakeholders is included in Annex IV which also provides an overview of the received feedback.

In summary, responses were received from 30 companies. Four companies directly replied that they do not want to participate. Most of the contacted stakeholders, however, indicated that they are either not producing or using any of the substances investigated. Only one respondent (who wants to remain anonymous) indicated a past use of PFHxS of 25-30 t/a (in paper food packaging). Due to the particular importance of the company 3M as former producers, additional follow up questions specifically related to their past production were asked, however, without success. Further, the company Miteni from Italy is considered as the main current producer of PFHxSF and related substances in Europe, and was therefore repeatedly contacted (also by an Italian native speaker) and has further received the questionnaire translated in Italian. Despite all efforts, it has not been successful. In addition, several potential Chinese producers were contacted during the consultation period. The Chinese companies were contacted by a Chinese native speaker (directly via phone calls and/or emails containing related questions in Chinese. No relevant quantitative information could be obtained from Chinese companies.

6 Conclusion

The collection and evaluation of relevant peer-reviewed scientific literature was completed, in addition to the review of other sources of information such as patents from major producers (e.g. 3M), technical data sheets for products, technical reports and inventories from other national and international regulatory institutions. Further, market research reports were acquired and evaluated, and selected companies (potential producers and users) were directly consulted.

Across all evaluated sources of information as well as from consultation of stakeholders, it was found that there is in general a lack of available information on the quantitative production levels and descriptions of product specific uses of PFHxS and related substances. Review of the information found to be available led to the following specific conclusions and general observations.

Summary of main information and concerns related to available market research reports

- A steady increase of the global consumption of PFHxSF could be observed during the last 6-7 years in a range from 400-700 Million US\$. Besides, a further increasing trend is foreseen in the coming years, with an expected maximum value in the range of 700 - 900 Million US\$ (in 2020).
- PFHxSF is consumed in different applications with following approximate shares, i.e. textiles (~65-70 Million US\$), surfactants and foams (~25-30 Million US\$), packaging (~30 -35 Million US\$), electronics and semiconductors (~55-60 Million US\$), industrial fluids (~15-20 Million US\$), coatings (~30 -35 Million US\$), agrichemicals (~25-30 Million US\$), use as intermediate feedstock (~250-300 Million US\$) and other unspecified applications (~120-130 Million US\$).
- The reported PFHxSF share/distribution in the different applications are almost identical (with only slight variations i.e. $\pm 1-2\%$) in all regions and individual countries covered.
- The maximum PFHxSF consumption is expected to be in the range of 100 Million US\$ (2019) in USA and Canada, 70-90 Million US\$ (2020) in Europe and more than 500 Million US\$ (2020) in Asia. Considering a current price for commercially available PFHxSF of around 2-10 US\$/g, 10-60 tonnes PFHxSF are expected to be consumed in US and Canada, about 10-40 tonnes PFHxSF in Europe and between 60-300 tonnes in Asia, as a rough estimate.
- According to available data from market research reports, the global production capacity of PFHxS remained constant at about 1,000 – 1,500 kg during the period between 2011 – 2016, while the actual production was about 700 - 750 kg in 2012 with a decrease to less than 700 kg in 2016. A further slight decrease in production of PFHxS was reported for 2017.
- Two key global PFHxS manufacturers (both from China) have been identified with production market shares of almost 96% and about 5%, respectively.
- In addition, information and quantitative data on key countries' consumption has been reported. Around 620-640 kg of PFHxS was consumed in China, about 40-60 kg in Southeast Asia and about 10-30 kg in the rest of the world in 2016.
- Available information covers applications of PFHxS in firefighting foams and textile finishing. About 66% of PFHxS was used in firefighting foams and the remaining 22% in textile finishing and other applications (i.e. 12%) respectively in 2016.

In the following some of the major concerns regarding available market research reports are summarized. The scientific quality and reliability of data contained in market research reports is questionable. The evaluated reports lack a description of the applied methodology to collect and evaluate data. The market research reports either only provide a link to the provider's website describing the general methodological approach used for all market research reports of that provider, or no explanations related to the applied

methodology are provided at all. Further, neither of the reports includes any reference (e.g. scientific literature sources) which makes it difficult to validate the contained information. Information on methods applied for forecasts is also lacking. Several important technical terms used in the reports are not explained. In addition, some specific concerns occurred that need to be addressed.

PFHxSF cannot be directly used in any application, but is used as a parent compound for different derivatives to be used in various applications. Without further information, it is not possible to draw any conclusions on the application of PFHxS or any of the PFHxS related compounds from available market reports on PFHxSF (CAS 423-50-7) as it is not clear how much of the “intermediate feedstock” is used to synthesize the target substance PFHxS or other related compounds.

The reports additionally fail to explain as to why the PFHxSF market is expected to decrease after 2020. Regulatory actions, such as restrictions, or the application of (shorter-chain) alternatives for specific uses might be possible explanations; however, this is not obvious from the available information. Furthermore, there is no further information/explanations available to support the reason for the similar application pattern globally. One explanation for the global situation is that it may possibly have been projected to other regions of the world.

With regard to PFHxS, the highlighted low global production capacity and actual production can possibly be explained by the fact that data from only two major producers from China have been identified and included in the market report. The figures related to consumption, support the main concern that the market report for PFHxS has overlooked the main producers on a global scale, and consequently presents only a small fraction of the actual production of PFHxS. This is further assumed, since no explanation and information on the consumption figures in different regions and countries is given. Furthermore, the number of identified applications in this market report is low and limited to firefighting foams and textile finishing only, and one would expect a higher number of applications for this substance. It is also unclear how much direct use of PFHxS in the various applications is ongoing. Most likely, there is unknown use of PFHxS-related substances in consumer products worldwide but this downstream use is not revealed in the market report on PFHxS. However, in the market report on PFHxSF it is stated that as much as 42-43% of the PFHxSF produced is used as “intermediate feedstocks” which can be understood as “used as raw material for production of PFHxS related compounds” that is further used in consumer products.

Conclusions related to evaluation of peer-reviewed scientific literature and other sources

Across all sources, it was found that there is in general a lack of information on the quantitative production levels and regarding descriptions of product specific uses of PFHxS and related substances in the public domain. Review of the information found to be available led to the following specific conclusions and general observations.

- PFHxS and related substances have been produced in large quantities in the past until 2000–2002 (when 3M made its global phase out of these substances), mostly by 3M and possibly a Japanese manufacturer at least.
- After 3M’s phase-out, there is still ongoing large-scale industrial production of PFHxS and/or related substances by at least one manufacturer in Italy and three manufacturers in China. There is no quantitative information regarding the current production and use of PFHxS and/or related substances in the public domain.
- Significant product information or technical data sheets from manufacturers were generally difficult to obtain on company websites or product catalogues. However, for instance the US based tile manufacturer Fritztile, was found to provide technical data sheets for some of its floor care products listed as containing a PHxSF-based ingredient (i.e. CAS No. 67584-53-6).

- A number of PFHxS and related substances were identified to be included within various national inventories of existing and/or new chemicals. This suggests that these chemicals are known to some regulatory authorities and highlights that they have been, and may still be currently, imported to, produced in, or contained in products within these countries.
- The documents from 3M as well as the retrieved patent applications show that historical uses of PFHxS and related substances are mainly in the field of aqueous film-forming foams (AFFFs) for firefighting, metal plating mist suppressants, and aftermarket carpet protection. Current uses may further include textile surface treatments as well as the semiconductor industry.
- Among known uses within the scientific literature, the uses of PFHxS and/or related substances in AFFFs are the most studied and cover investigations that have discovered a wide range of PFAS formulations that have been used as well as significant human and environmental exposure. This research has heavily focused on use and exposure within North America, and very limited information was found in the literature in relation to other uses.

Conclusions related to stakeholder consultation

In summary, responses were received from 30 companies. Four companies directly replied that they do not want to participate. Most of the contacted stakeholders, however, indicated that they are either not producing or using any of the substances investigated. So far only one respondent (who wants to remain anonymous) indicated a past use of PFHxS of 25-30 tons/annually (use in paper food packaging). Another respondent from Germany indicated a current demand for fluorinated products between 150 – 300 kg/year for improving the wetting of water-based adhesives, coatings, etc. on the substrate (no further information was supplied on the exact chemicals used).

Due to the particular importance of the company 3M as former producers, additional questions specifically related to their past production were asked, however, without success. It was only indicated that there is currently no known manufacture or use of PFHxS or related substances by 3M. There was no reply on questions on past production.

Further, the company Miteni (Italy) is considered as the main current producer of PFHxSF and related substances in Europe. According to their web page Miteni currently manufactures 3 different PFHxSF and related substances (RM70 CAS No. 423-50-7, RM75 3871-99-6, and RM570 CAS No. 41997-13-1) and was therefore repeatedly contacted (also by an Italian native speaker) and has received the questionnaire translated in Italian. All efforts have not been successful and no information could be obtained from Miteni.

In addition, several potential Chinese producers and users, among them also companies supposed to be major global producers, were contacted during the consultation period. The Chinese companies were contacted by a Chinese native speaker (directly via phone calls and/or emails containing related questions in Chinese), but no relevant quantitative information could be obtained from the Chinese companies. In addition, companies identified in market research reports (Company X and Company Y) considered as major producers of PFHxS worldwide, have been contacted. Company Y replied that they do not supply any of the substances from Annex I: List of Substances), which represents a clear contradiction with the data given in the respective market research report. Company X was repeatedly contacted and agreed to participate in the survey. An e-mail text in Chinese with survey questions has been forwarded. However, no further information was provided by Company X. In summary, most of the Chinese Companies have not replied to the inquiry. From the contacted Chinese companies, four companies indicated that they do not produce or use PFHxS and related chemicals. At least in two cases this is definitely not consistent with what is presented on their website where one company indicates manufacture of products containing PFHxS substances and one company indicates use of PFHxS as textile finishing agent.

Finally, during consultation of Chinese companies, the project team received information that a similar project is currently done by the Chinese Ministry of Environment. Possibly, information from China will be made available in the near future for further international discussions on PFHxS and PFHxS related substances.

7 Scientific References

- [1] UNEP/POPS/POPRC.13/4, Proposal to list perfluorohexane sulfonic acid (CAS No: 355-46-4, PFHxS), its salts and PFHxS-related compounds in Annexes A, B and/or C to the Stockholm Convention on Persistent Organic Pollutants (2017).
- [2] X. Li, L.W. Yeung, S. Taniyasu, M. Li, H. Zhang, D. Liu, P.K. Lam, N. Yamashita, J. Dai, Perfluorooctanesulfonate and related fluorochemicals in the Amur tiger (*Panthera tigris altaica*) from China, *Environ. Sci. Technol.* 42 (2008) 7078-7083.
- [3] Lists of PFOS, PFAS, PFOA, PFCA, related compounds and chemicals that may degrade to PFCA. ENV/JM/MONO(2006)15 (as revised in 2007).
- [4] Norwegian Environmental Agency. Potential PFBS and PFHxS Precursors. Literature study and theoretical assessment of abiotic degradation pathways leading to PFBS and PFHxS. Report M 792 (2017).
- [5] Z. Wang, J.M. Boucher, M. Scheringer, I.T. Cousins, K. Hungerbuehler, Toward a comprehensive global emission inventory of C4–C10 perfluoroalkane sulfonic acids (PFSA)s and related precursors: focus on the life cycle of C 8 -based products and ongoing industrial transition, *Environ. Sci. Technol.* (2017). doi:10.1021/acs.est.6b06191.
- [6] OECD, Results of Survey on Production and Use of PFOS, PFAS and PFOA, Related Substances and Products/ Mixtures Containing these Substances (2004), (2004).
- [7] OECD, Results of the 2006 Survey on Production and Use of PFOS, PFAS, PFOA, PFCA, their Related Substances and Products/Mixtures Containing these Substances, (2006). [http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?doclanguage=en&cote=env/jm/mono\(2006\)36](http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?doclanguage=en&cote=env/jm/mono(2006)36).
- [8] OECD, Outcome of the 2009 Survey on the Production and Use of PFOS, PFAS, PFOA, PFCA, their Related Substances and Products/Mixtures Containing these Substances, (2009). [http://www.oecd.org/officialdocuments/displaydocumentpdf?cote=env/jm/mono\(2010\)46&doclanguage=en](http://www.oecd.org/officialdocuments/displaydocumentpdf?cote=env/jm/mono(2010)46&doclanguage=en).
- [9] 3M, Voluntary use and exposure information profile: perfluorooctanoic acid and salts (AR226-0595), US EPA Administrative Record 226, 2000. file:///Users/Jerry/Documents/Library.papers3/Reports/2000/3M/2000 3M-7.pdf.
- [10] Fraunhofer Institute of Toxicology and Experimental Medicine (ITEM), Final report: 28-day repeated dermal contact study of 3M test articles in sprague-dawley rats. (226-1874a), US EPA Administrative Record 226, 2004. file:///Users/Jerry/Documents/Library.papers3/Reports/2004/Fraunhofer Institute of Toxicology and Experimental Medicine (ITEM)/2004 Fraunhofer Institute of Toxicology and Experimental Medicine (ITEM).pdf.
- [11] G.W. Olsen, H.Y. Huang, K.J. Helzlsouer, K.J. Hansen, J.L. Butenhoff, J.H. Mandel, Historical comparison of perfluorooctanesulfonate, perfluorooctanoate, and other fluorochemicals in human blood, *Environ. Health Perspect.* 113 (2005) 539–545. doi:10.1289/ehp.7544.
- [12] Y. Yang, J. Shen, L. Zhang, X. Li, Preparation of a novel water and oil-repellent fabric finishing agent containing a short perfluoroalkyl chain and its application in textiles, *Mater. Res. Innov.* 19 (2015) S8-401-S8-404. doi:10.1179/1432891715Z.0000000001708.

- [13] B.J. Place, J.A. Field, Identification of Novel Fluorochemicals in Aqueous Film- Forming Foams (AFFF) Used by the US Military, *Environ. Sci. Technol.* 46 (2012) 7120–7127. doi:10.1021/es301465n.Identification.
- [14] L.A. D’Agostino, S.A. Mabury, Identification of novel fluorinated surfactants in aqueous film forming foams and commercial surfactant concentrates, *Environ. Sci. Technol.* 48 (2014) 121–129. doi:10.1021/es403729e.
- [15] K.A. Barzen-Hanson, S.C. Roberts, S.J. Choyke, K. Oetjen, A. McAlees, N. Riddell, R. McCrindle, P.L. Ferguson, C.P. Higgins, J.A. Field, Discovery of 40 classes of per- and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater, *Environ. Sci. Technol.* (2017) acs.est.6b05843. doi:10.1021/acs.est.6b05843.
- [16] A. Rotander, L.-M.L. Toms, L. Aylward, M. Kay, J.F. Mueller, Elevated levels of PFOS and PFHxS in firefighters exposed to aqueous film forming foam (AFFF), *Environ. Int.* 82 (2015) 28–34. doi:10.1016/j.envint.2015.05.005.
- [17] C. Jin, Y. Sun, A. Islam, Y. Qian, A. Ducatman, Perfluoroalkyl Acids Including Perfluorooctane Sulfonate and Perfluorohexane Sulfonate in Firefighters, *J. Occup. Environ. Med.* 53 (2011) 324–328. doi:10.1097/JOM.0b013e31820d1314.
- [18] R. Siebenaler, R. Cameron, C.M. Butt, K. Hoffman, C.P. Higgins, H.M. Stapleton, Serum perfluoroalkyl acids (PFAAs) and associations with behavioral attributes, *Chemosphere.* 184 (2017) 687–693. doi:10.1016/j.chemosphere.2017.06.023.
- [19] W.J. Backe, T.C. Day, J.A. Field, Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from U.S. military bases by nonaqueous large-volume injection HPLC-MS/MS, *Environ. Sci. Technol.* 47 (2013) 5226–5234. doi:10.1021/es3034999.

Annex I: List of Substances

PFHxS, its salts and related substances including the raw material PFHxSF - List of substances covered by the survey		
No	CAS No.	Name
1	355-46-4	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-; Perfluorohexane-1-sulphonic acid = PFHxS
2	423-50-7	1-Hexanesulfonyl fluoride, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-; Perfluorohexanesulfonyl fluoride = PFHxSF
3	55591-23-6	1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulphonyl chloride
4	67584-48-9	N-allyltridecafluorohexanesulphonamide
5	67939-61-1	4-[methyl[(tridecafluorohexyl)sulphonyl]amino]butyl methacrylate
6	67969-65-7	N-ethyltridecafluoro-N-[2-(phosphonooxy)ethyl]hexanesulphonamide
7	68239-74-7	Precursor for PFHxS: Tridecafluoro-N-(4-hydroxybutyl)-N-methylhexanesulphonamide
8	68299-21-8	Sodium [(((tridecafluorohexyl)sulphonyl)amino)methyl]benzenesulphonate
9	68891-98-5	Diaquatetrachloro[μ-[N-ethyl-N-[(tridecafluorohexyl)sulphonyl]glycinato-O1:O1']]-μ-hydroxybis(propan-2-ol)dichromium
10	68957-53-9	Ethyl N-ethyl-N-[(tridecafluorohexyl)sulphonyl]glycinate
11	70225-16-0	Tridecafluorohexanesulphonic acid, compound with 2,2'-iminodiethanol (1:1)
12	70248-52-1	Bis[trimethyl-3-[(tridecafluorohexyl)sulphonyl]amino]propylammonium] sulphate
13	73772-33-5	N-[3-(Dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonamide acetate (1:1)
14	73772-34-6	N-[3-(Dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-{2-[2-(2-hydroxyethoxy)ethoxy]ethyl}-1-hexanesulfonamide
15	82382-12-5	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, sodiumsalt
16	68555-70-4	Sodium N-ethyl-N-[(tridecafluorohexyl)sulphonyl]glycinate
17	3871-99-6	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, potassium salt (1:1)
18	55120-77-9	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, lithium salt (1:1)
19	68259-08-5	1-Hexanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, ammonium salt (1:1)
20	41997-13-1	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
21	1270179-82-2	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N,N-dimethyl-
22	68259-15-4	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-methyl-
23	1427176-17-7	1-Hexanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-methyl-
24	1270179-93-5	1-Hexanesulfonamide, N,N-diethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-

25	68555-75-9	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-(2-hydroxyethyl)-N-methyl-
26	34455-03-3	1-Hexanesulfonamide, N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-(2-hydroxyethyl)-
27	85665-64-1	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-(2-hydroxyethyl)-N-propyl-
28	76848-59-4	Benzene, 1-chloro-4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-
29	50598-28-2	1-Hexanesulfonamide, N-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
30	68957-61-9	1-Hexanesulfonamide, N-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-, hydrochloride (1:1)
31	1427176-20-2	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N,N-bis(2-methoxyethyl)-
32	68957-32-4	Glycine, N-ethyl-N-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-
33	68298-09-9	1-Hexanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-N-(phenylmethyl)-
34	254889-10-6	Pyridinium, 1-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, inner salt
35	67584-53-6	Glycine, N-ethyl-N-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, potassium salt (1:1)
36	68957-58-4	1-Propanaminium, N,N,N-trimethyl-3-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, iodide (1:1)
37	52166-82-2	1-Propanaminium, N,N,N-trimethyl-3-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, chloride (1:1)
38	85665-66-3	Glycine, N-propyl-N-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, potassium salt (1:1)
39	68227-98-5	2-Propenoic acid, 4-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]butyl ester
40	67584-57-0	2-Propenoic acid, 2-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester
41	67584-61-6	2-Propenoic acid, 2-methyl-, 2-[methyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester
42	38850-52-1	1-Propanaminium, 3-[(carboxymethyl)[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-N,N,N-trimethyl-, inner salt
42	1893-52-3	2-Propenoic acid, 2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester
44	38850-60-1	1-Propanesulfonic acid, 3-[3-(dimethylamino)propyl][(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-
45	80621-17-6	1-Propanesulfonic acid, 3-[methyl[3-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]propyl]amino]-, sodium salt (1:1)

46	67906-70-1	2-Propenoic acid, 2-methyl-, 2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]ethyl ester
47	38850-58-7	1-Propanaminium, N-(2-hydroxyethyl)-N,N-dimethyl-3-[(3-sulfopropyl)[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-, inner salt
48	73772-32-4	1-Propanesulfonic acid, 3-[[3-(dimethylamino)propyl][(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-2-hydroxy-, sodium salt (1:1)
49	81190-38-7	1-Propanaminium, N-(2-hydroxyethyl)-3-[(2-hydroxy-3-sulfopropyl)[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino]-N,N-dimethyl-, hydroxide, sodium salt (1:1:1)
50	67939-92-8	1-Hexanesulfonamide, N,N'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
51	93416-31-0	Isoxazolidine, 4-(4-methoxyphenyl)-2-methyl-5-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-
52	76848-68-5	1H-Benzimidazolium, 1,3-diethyl-2-methyl-5-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-, 4-methylbenzenesulfonate (1:1)
53	68815-72-5	Benzoic acid, 2,3,4,5-tetrachloro-6-[[[3-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]oxy]phenyl]amino]carbonyl]-, potassium salt (1:1)
54	56372-23-7	Poly(oxy-1,2-ethanediyl), $\hat{1}\pm$ -[2-[ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-Poly(oxy-1,2-ethanediyl), α -(2-(ethyl[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]amino)ethyl)-omega-hydroxy-
55	111393-39-6	1-Hexanesulfonyl bromide, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
56	89863-64-9	2,4-Pentanedione, 3-[1-(2-furanyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
57	89863-63-8	2,4-Pentanedione, 3-[1-(2-thienyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
58	89863-56-9	Furan, 2-[1-(nitromethyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
59	89863-55-8	Thiophene, 2-[1-(nitromethyl)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
60	89863-50-3	Benzene, 1-methyl-4-[1-(phenylthio)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
61	89863-49-0	Furan, 2-[1-(phenylthio)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
62	89863-48-9	Thiophene, 2-[1-(phenylthio)-2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethyl]-
63	680187-86-4	Hexane, 1-(ethenylsulfonyl)-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
64	86525-52-2	Benzene, 1-methoxy-4-[2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethenyl]-
65	86525-51-1	Benzene, 1-methyl-4-[2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethenyl]-
66	86525-48-6	Furan, 2-[2-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]ethenyl]-

67	86525-43-1	Thiophene, 2-[2-[(tridecafluorohexyl)sulfonyl]ethenyl]-
68	171561-95-8	Benzene, 1-nitro-4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-
69	149652-30-2	Benzene, 1-fluoro-4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-
70	147029-28-5	Benzenamine, 4-[(1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexyl)sulfonyl]-
71	30295-56-8	1-Hexanesulfonamide, N-[3-(dimethyloxidoamino)propyl]- 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-
72	70900-36-6	2-Propenoic acid, 2-methyl-, 2-[[[2-methyl-5-[[4- [methyl[(tridecafluorohexyl)sulfonyl]amino] butoxy]carbonyl]amino]phenyl]amino]carbonyl]oxy]propyl ester
73	70776-36-2	Polymer based on 67584-57-0
74	68298-74-8	2-Propenoic acid, 2-methyl-, 2-[[[5-[[2-[ethyl [(tridecafluorohexyl)sulfonyl]amino]ethoxy]carbonyl]amino]-2- methylphenyl]amino]carbonyl] oxy]propyl ester
75	68555-90-8	Polymer based on 67584-57-0
76	68877-32-7	Polymer based on 67906-70-1
77	68586-14-1	Polymer based on 67584-57-0
78	68555-92-0	Polymer based on 67584-61-6
79	68555-91-9	Polymer based on 67906-70-1

Annex II: Historic and forecast market of PFHxSF (diff. regions)

USA and Canada Market

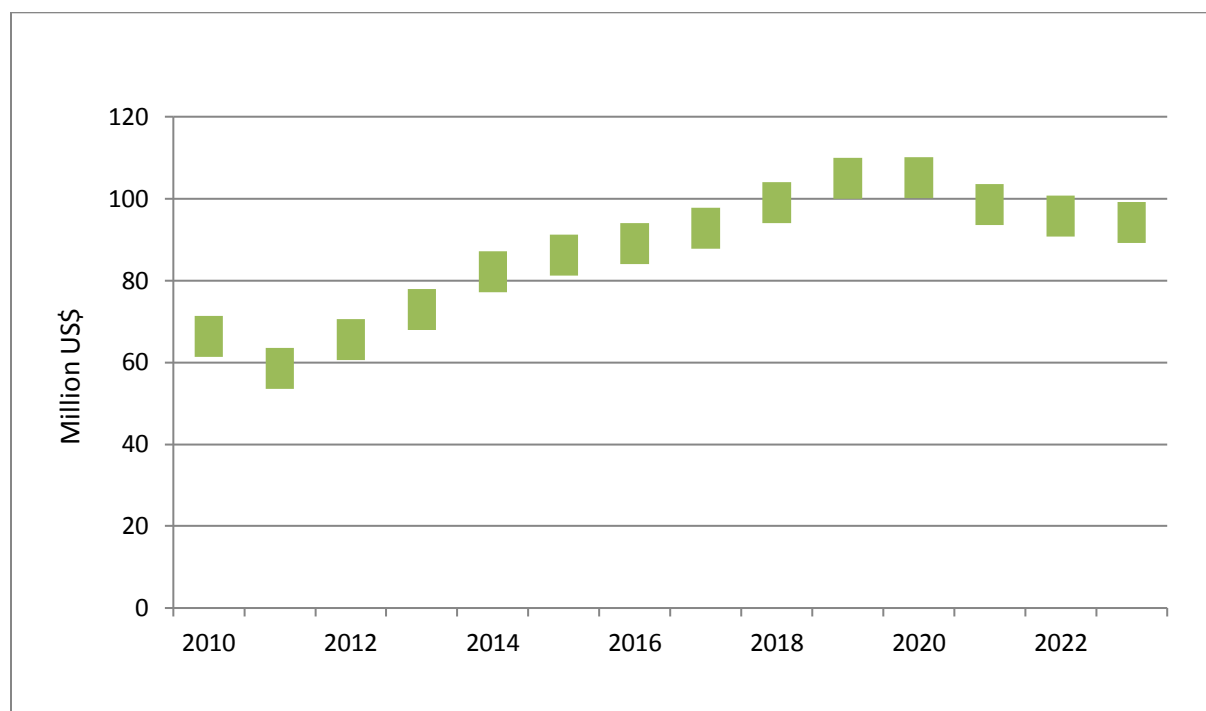


Figure 5: Estimated range of historic and forecast market of PFHxSF in USA and Canada

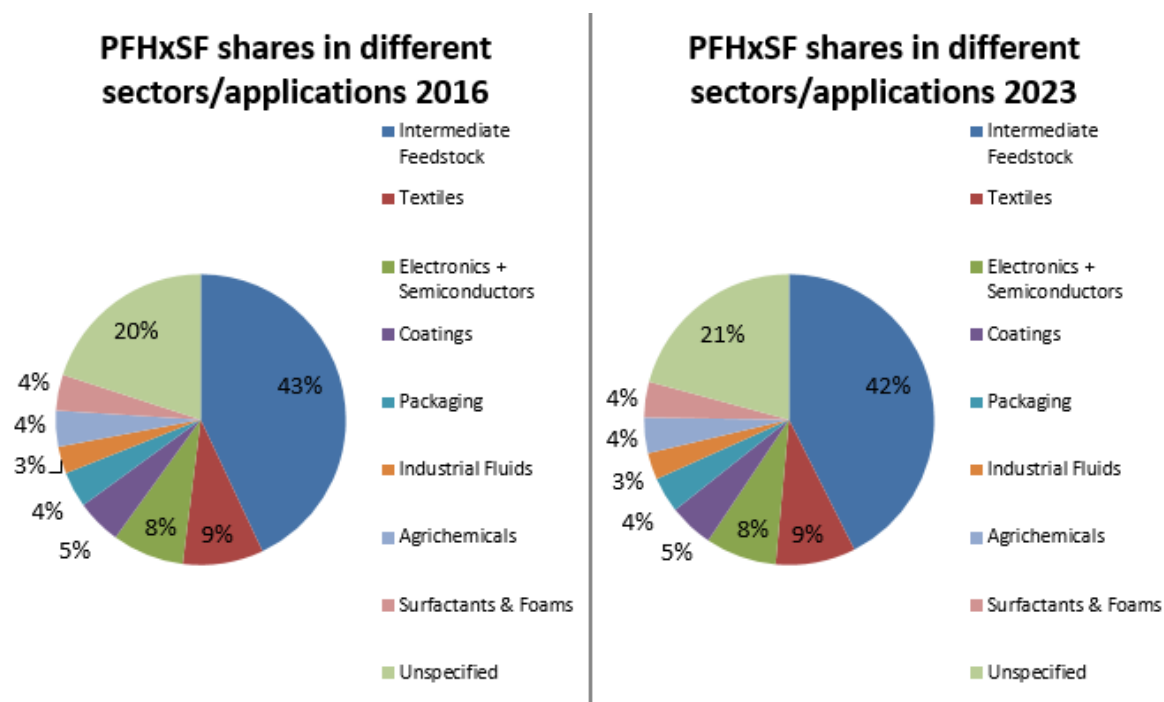


Figure 6: PFHxSF shares in different sectors / applications within USA and Canada in 2016 and 2023

Europe Market

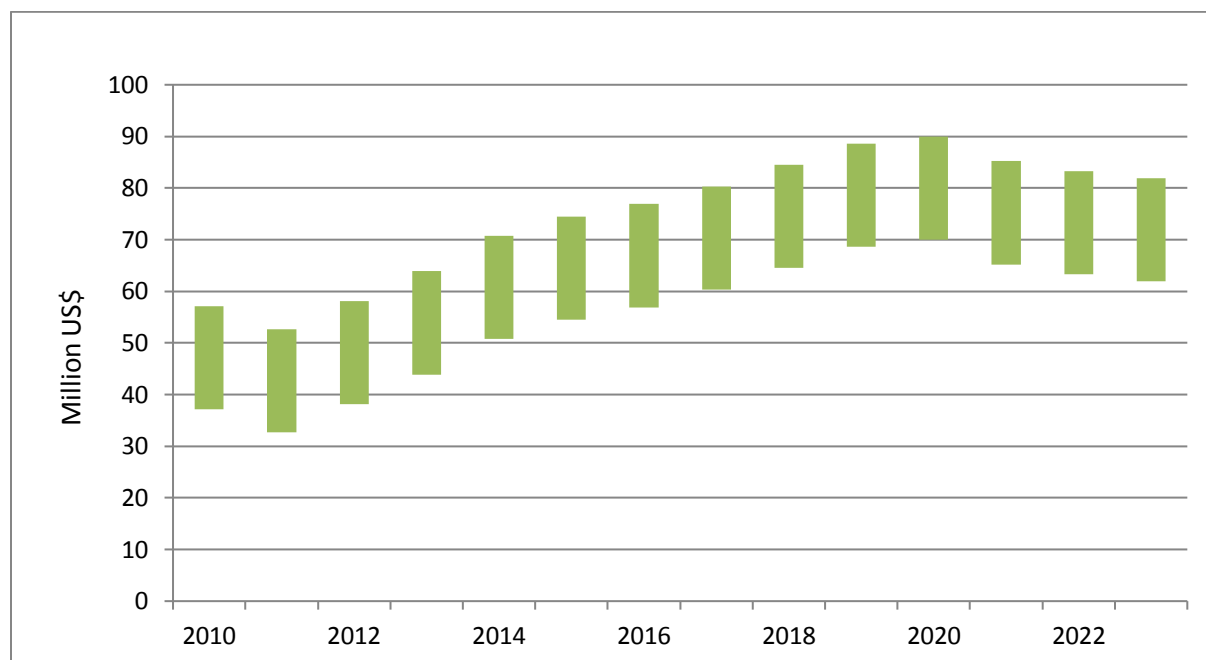


Figure 7: Estimated range of historic and forecast market of PFHxSF in Europe

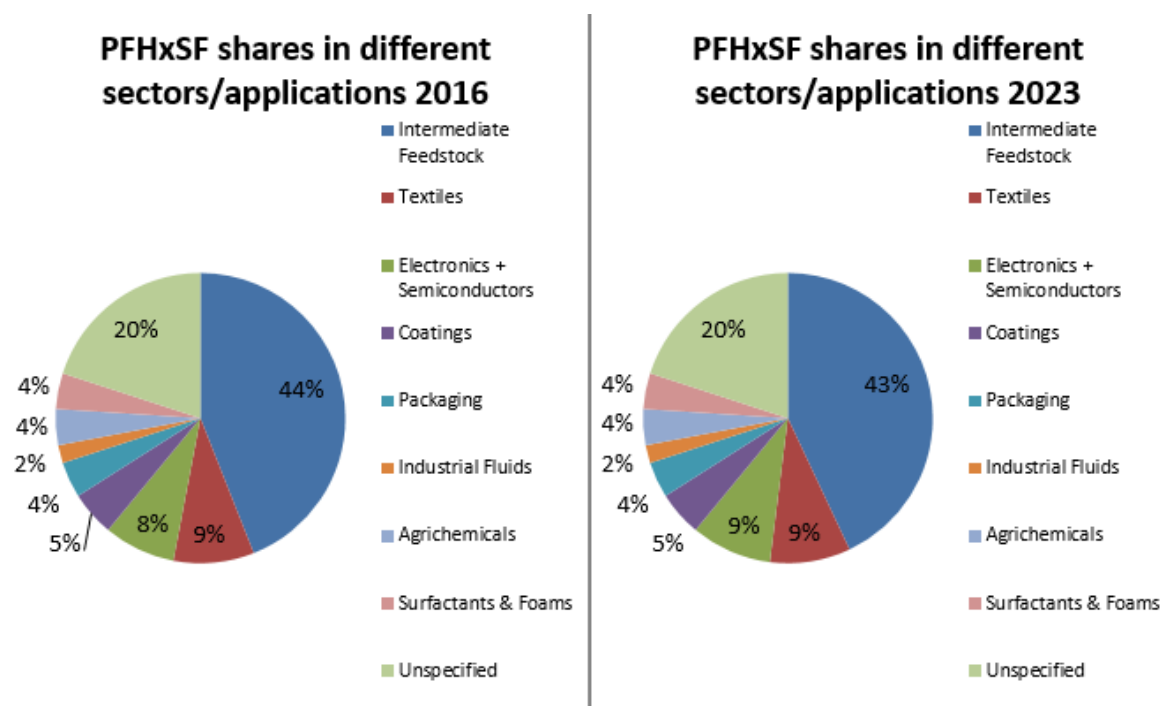


Figure 8: PFHxSF shares in different sectors / applications within Europe in 2016 and 2023

Asia Market

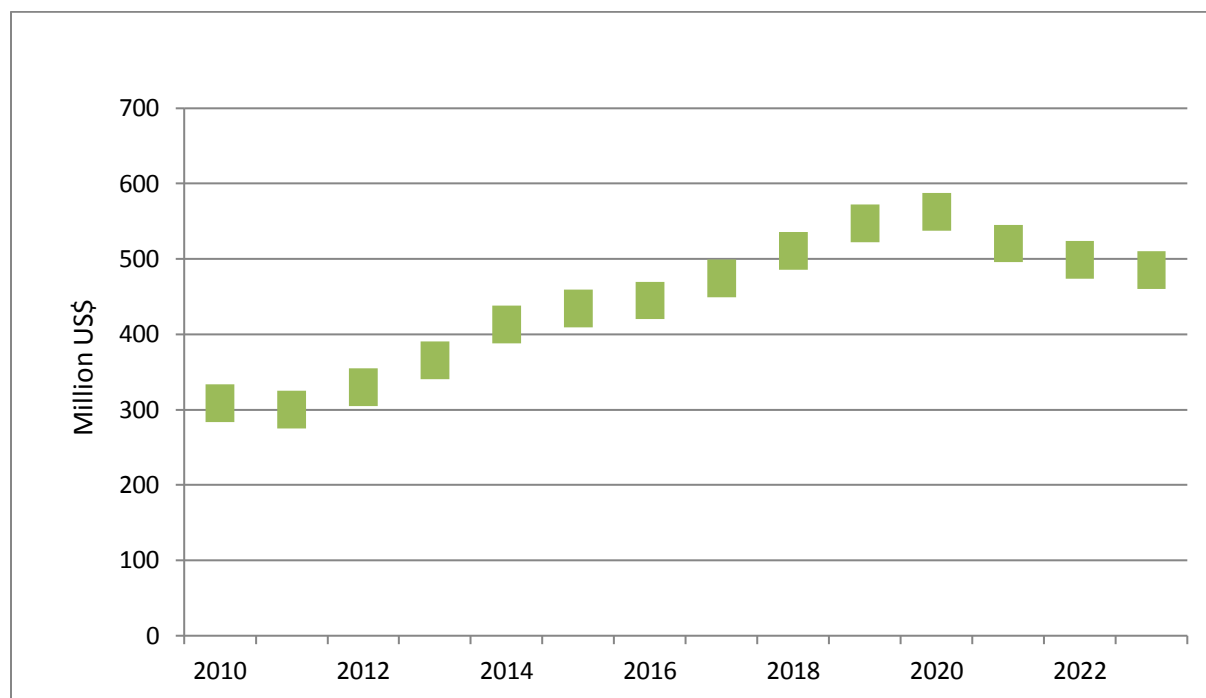


Figure 9: Estimated range of historic and forecast market of PFHxSF in Asia

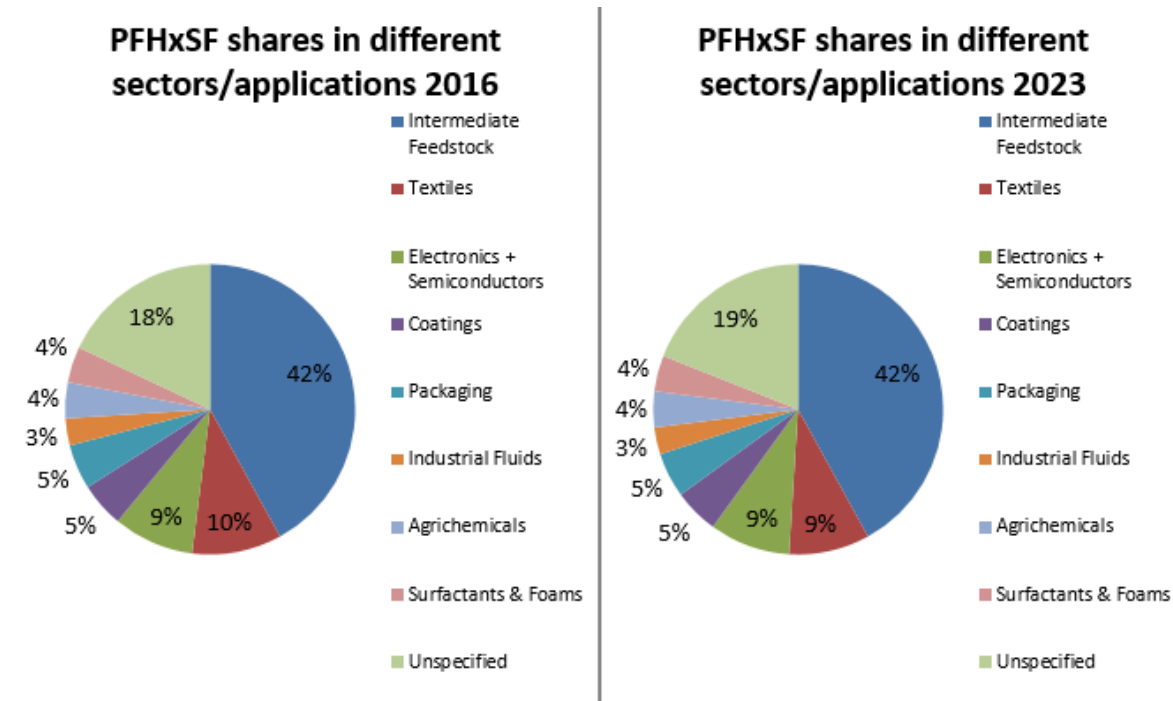
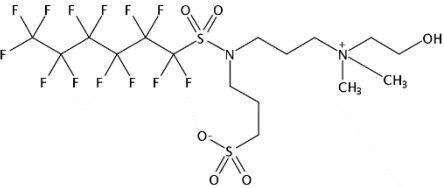
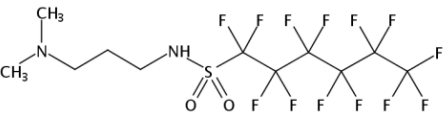
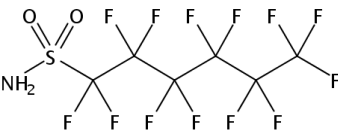
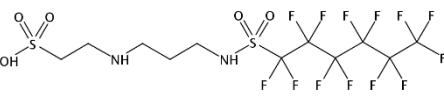
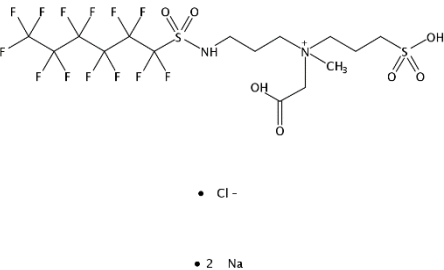
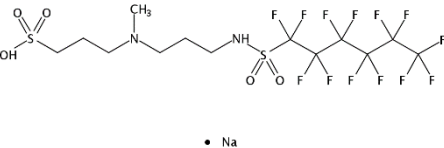
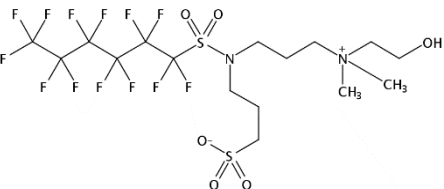


Figure 10: PFHxSF shares in different sectors / applications within Asia in 2016 and 2023

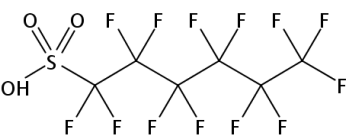
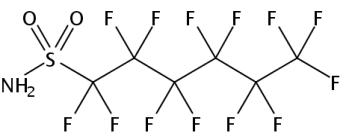
Annex III: Patents involving PFHxS and related substances

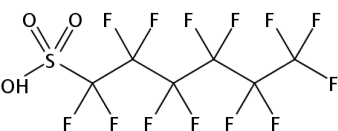
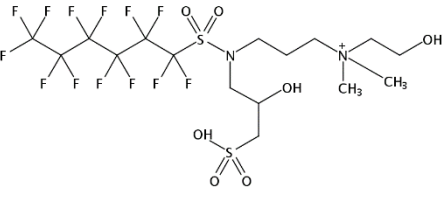
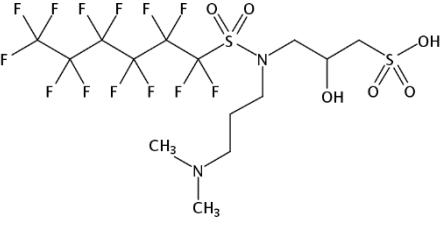
Patent Number	Year	Assignee	Descriptive Note(s)	Chemical Abstract Service (CAS) Number(s) Included for PFHxS Related Chemical(s) / Chemical Structure
<i>Aqueous Film-Forming Foams</i>				
DE 2165057	1972	Minnesota Mining and Manufacturing Co. USA (3M)	Product Description: Branched ampholytic surfactant suitable for the manufacture of aqueous film-forming concentrates and fire fighting foams. C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ N+Me ₃ Cl ⁻ was treated with NaOMe in iso-PrOH to give C ₆ F ₁₃ SO ₂ N-(CH ₂) ₃ N+Me ₃ which, when treated with ClCH ₂ CO ₂ H and NaOMe in a solution of MeOH and iso-PrOH gave C _n F _{2n} +1RN[(CH ₂) _γ R ₁](CH ₂) ₃ N+R ₂ ³ (n = 6, γ = 1, R = SO ₂ , R ₁ = CO ₂ ⁻ , R ₂ = Me).	 38850-58-7
DE 2315326	1973	Minnesota Mining and Manufacturing Co. USA (3M)	Product Description: A fire from 454 liters of aviation gasoline burning over a 37 m ² area was extinguished in 60 sec by 16 liters of a solution composed of: C ₆ F ₁₃ SO ₂ N(C ₃ H ₆ SO ₃ ⁻)C ₃ H ₆ N+Me ₂ CH ₂ OH 2.7, C ₈ F ₁₇ SO ₂ NHCH ₂ C ₆ H ₄ SO ₃ Na 1.8, C ₈ H ₁₇ C ₆ H ₄ (OCH ₂ CH ₂) ₃ OH 2.8, Bu(OCH ₂ CH ₂) ₂ OH 30, and H ₂ O 62.7 weight %.	 50598-28-2
JP 58038571	1983	Dainippon Ink and Chemicals, Inc., Japan; Kamura Physical and Chemical Research Institute	Product Description: A foam fire extinguisher containing polyethylene glycol [CAS: 25322-68-3] 10, C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ NH(CH ₂) ₂ SO ₃ Na [CAS: 80621-18-7] 3, C ₆ F ₁₃ SO ₂ NH ₂ [CAS: 86402-38-2] 2, C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ N+(CH ₃)(CH ₂ CO ₂ Na)(CH ₂) ₃ SO ₃ N a Cl ⁻ [CAS: 41997-13-1] 2, Butyl Carbitol [CAS: 112-34-5] 20, and water 63% foamed to a 7.1-fold volume and had high fire-extinguishing power.	 41997-13-1  • Na

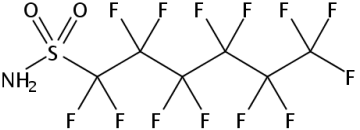
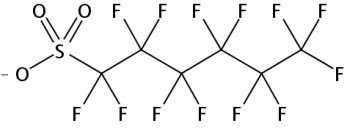
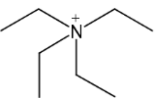
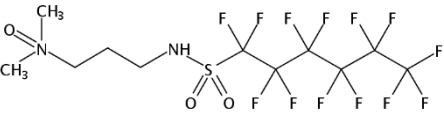
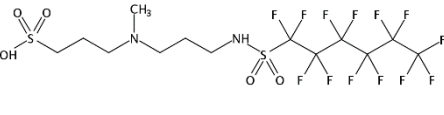
				<p>80621-18-7</p>  <p>• Cl⁻</p> <p>• 2 Na⁺</p> <p>86402-38-2</p>
JP 58050971	1983	Dainippon Ink and Chemicals, Inc., Japan	Product Description: A fire extinguisher (pH 7.4) containing C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ N(Me)CH ₂ CH ₂ CH ₂ SO ₃ Na [CAS: 80621-17-6] 5, hydroxypropyl Me siloxane sulfate polyethoxylated quaternary ammonium salt, Butyl Carbitol [CAS: 112-34-5], polyethylene glycol [CAS: 25322-68-3], and ion-exchanged water was diluted with water and used to extinguish fires.	 <p>• Na⁺</p> <p>80621-17-6</p>
JP 60099272	1985	Dainippon Ink and Chemicals, Inc., Japan	Product Description: A fire extinguisher containing C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ NMe(CH ₂) ₃ SO ₃ Na [CAS: 80621-17-6] (F-system surfactant) 0.09, H ₂ N(CH ₂)IO(CH ₂ CH ₂ O) _n (CH ₂) _m NH ₂ (l = m = 3, mol. wt. ~6000) [CAS: 34901-14-9] 0.09, polyethylene glycol 0.8, Butyl Carbitol 1, and water 98.02% was packed into a 3 L vessel and used for fire extinguishing.	
JP 61191369	1986	Dainippon Ink and Chemicals, Inc., Japan	Product Description: An aqueous solution containing Butyl Carbitol 20, polyethylene glycol 10, C ₆ F ₁₃ SO ₂ NHCH ₂ CH ₂ OH 2, C ₈ H ₁₇ (C ₆ H ₄)O(CH ₂ CH ₂ O) ₅ H 10, and C ₅ F ₁₁ CH ₂ CH ₂ SO ₂ NH(CH ₂) ₆ NH(CH ₂)SO ₃ Li 2% was diluted with water and used for fire extinguishing.	

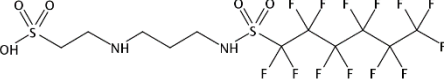
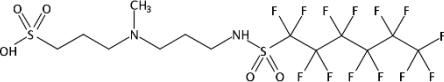
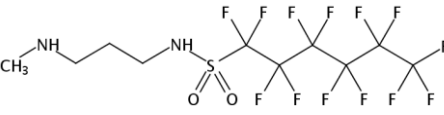
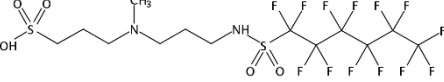
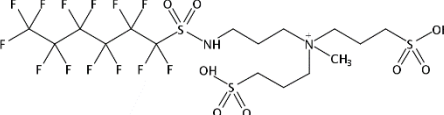
US 5085786	1992	Minnesota Mining and Manufacturing Co., USA (3M)	<p>Product Description: An improved aqueous film-forming foamable concentrate which is particularly useful for extinguishing flammable liquid fires. The preferred formulation contains (a) fluoroaliphatic amphoteric surfactant, preferably a fluorinated aminocarboxylate having a C4 to C10 perfluoroaliphatic group, (b) fluoroaliphatic anionic surfactant, preferably a C4 to C10 perfluoroalkane sulfonate, and (C) short chain (C6 to C10) alkyl ether sulfate hydrocarbon surfactant. Representative fluoroaliphatic amphoteric surfactants for the formulations of the invention include, among others: C6 F13 SO2 N[CH2 CH(OH)CH2 SO3 -]C3 H6 N+ (CH3)2 C2 H4 OH.</p>	 <p>38850-58-7</p>
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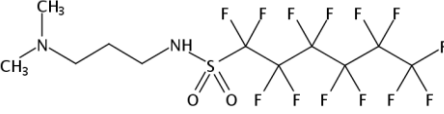
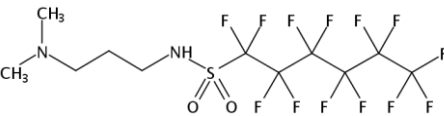
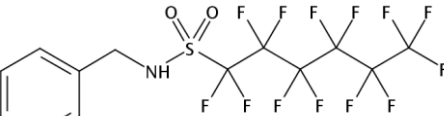
Surface Coating

JP 58213057	1983	Dainippon Ink and Chemicals, Inc., Japan; Kawamura Physical and Chemical Research Institute	<p>Product Description: A 0.01% methanolic solution of a 70:30 mixture of C6F13SO3K [CAS: 3871-99-6] and C6F13SO2NH2 [CAS: 41997-13-1] was coated on glass and dried for 3 minutes to give a smooth-surfaced coating with a decane contact angle of 82°. The same solution was coated on steel and dried for 3 minutes to give a coating with a salt water resistance >5 h.</p>	 <p>• K</p> <p>3871-99-6</p>  <p>41997-13-1</p>
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<i>Fog Inhibitor in Metal-Plating</i>				
JP 54076443	1979	Dainippon Ink and Chemicals, Inc., Japan	Product Description: The formation of metal-containing mists in the air above plating baths due to vigorous gas evolution at the electrodes is eliminated by the addition of K or triethylammonium perfluoroalkanesulfonate surfactant mixtures, which cause formation of a viscous foam on the bath surface and prevent the metallic mist from escaping.	 <p>• K</p> <p>3871-99-6</p>
GB 2077765	1981	Minnesota Mining and Manufacturing Co., USA (3M)	Product Description: Fluroaliphatic surfactant added to methal electrowinning baths in order to supress mists. Reaction product of RSO2NHC3H6N(CH3)2 (where R is mainly C6F13-) and C4H9OC2H4OH to produce mainly [C6F13SO2N(CH2CHOHCH2SO3Na)C3H6N+(CH3)2C2H4OH]OH-.	 <p>• Na</p> <p>• OH-</p> <p>81190-38-7</p>  <p>• Na</p> <p>73772-32-4</p>

JP 63208561	1988	Dainippon Ink and Chemicals, Inc., Japan	Product Description: C ₆ F ₁₃ SO ₂ NH ₂ , prepared by sulfonamidation of C ₆ F ₁₃ SO ₂ F, was mixed with dioxane and ClCH ₂ CH(OH)CH ₂ OH at 60° and then the resulting mixture was stirred with dropwise addition of aqueous NaOH at 80°. The reaction mixture was kept overnight to give (dihydroxypropyl)sulfonamide I (R ₁ = C ₆ F ₁₃ , B = SO ₂ , R = CH ₂ CH(OH)CH ₂ OH) (II).	 41997-13-1
CN 104611733	2015	Hubei Hengxin Chemical Co.	Product Description: Presentation of a novel chromium-free PFOS fog inhibitor, with the aim to being an alternative for conventional chromium-based PFOS fog inhibitor. Manufactured using perfluorohexanesulfonyl fluoride, triethylamine and Me triethoxy silane in inert solvent.	 108427-53-8  66-40-0
<i>Synthesis of PFHxSF, PFHxS, and related substances</i>				
DE 2008531	1970	Minnesota Mining and Manufacturing Co. USA (3M)	Product Description: The H ₂ O-soluble surface-active title compounds F ₃ C(CF ₂) _n X(CH ₂) ₂ N(O)Me ₂ (I, X = SO ₂ NHCH ₂ , CONHCH ₂ , CH ₂) with a high tendency to deposit on solid surfaces and useful as foaming and oil-repellent agents, and in the extinguishing of burning liquids.	 30295-56-8
JP 56128750	1981	Dainippon Ink and Chemicals, Inc., Japan; Kawamura Physical and Chemical Research Institute	Product Description: Preparation of fluorine containing amino sulfonate surfactants such as C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ NMe(CH ₂) ₃ SO ₃ Na (I) [CAS: 80621-17-6] and C ₆ F ₁₃ SO ₂ NH(CH ₂) ₃ NH(CH ₂) ₂ SO ₃ Na [CAS: 80621-18-7].	 80621-17-6

				 <p>• Na</p> <p>80621-18-7</p>
JP 58026850	1983	Dainippon Ink and Chemicals, Inc., Japan	Product Description: Preparation of the fluoroalkyl surfactant C6F13SO2NHCH2CH2CH2NMeCH2CH2CH2SO3Na [CAS: 80621-17-6].	 <p>• Na</p> <p>80621-17-6</p>  <p>85520-91-8</p>
JP 58179300	1983	Dainippon Ink and Chemicals, Inc., Japan; Kawamura Physical and Chemical Research Institute	Product Description: Preparation of fluorine-containing sulfobetaine-type amphoteric surfactants C8F17SO2NHCH2CH(OH)CH2N+Me[CH2CH(OH)CH2SO3Na]2 Cl- (I) [CAS: 89294-71-3] and C6F13SO2NHCH2CH2CH2N+Me(CH2CH2CH2SO3Na)2 I- [CAS: 89294-72-4].	 <p>• Na</p> <p>80621-17-6</p>  <p>• I -</p> <p>• 2 Na</p> <p>89294-72-4</p>

WO 9210470	1992	Minnesota Mining and Manufacturing Co., USA (3M)	Product Description: Surfactants useful for preparing aqueous film-forming foams for extinguishing burning liquid hydrocarbons and other flammable liquids. Reacting $\text{H}_2\text{N}(\text{CH}_2)_3\text{NMe}_2$ with $\text{CF}_3(\text{CF}_2)_5\text{SO}_2\text{F}$ gave $\text{CF}_3(\text{CF}_2)_5\text{SO}_2\text{NH}(\text{CH}_2)_3\text{NMe}_2$ which reacted with $\text{H}_2\text{C}:\text{CHCO}_2\text{H}$ to give $\text{CF}_3(\text{CF}_2)_5\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{CO}_2-)(\text{CH}_2)_3\text{N}+\text{Me}_2\text{H}$.	 50598-28-2
CN 102731348	2012	Hubei Hengxin Chemical Co., Ltd.	Product Description: [bis(perfluoroalkyl)sulfonamido]ethyl acrylate monomers and their preparation method. Involving formulas containing C1-C6 perfluoroalkyl. The prepared compounds are characterized with low surface energy, good water resistance and oil resistance, and degradability.	—
CN 105017097	2015	Wuhan Chemical Industry Research Institute Co., Ltd., Peoples. Republic of China	Product Description: A method for preparation of a surfactant of N-carboxyethyl-N-3-dimethylaminopropyl-perfluoro hexyl sulfonamide.	 50598-28-2
<i>Others</i>				
DE 3231403	1983	Dainippon Ink Chemical Industry Co.	Product Description: Separation and recovery of metal salts from aqueous solutions.	 68298-09-09

JP 57101302	1982	Mitsubishi Metal Corp., Japan; Tohoku Fertilizer Co., Ltd.	Product Description: Antistatic and heat-resistant rubbers containing C6F13SO3Li (I) [CAS: 55120-77-9].	<p>The chemical structure shows a perfluorinated chain with six carbon atoms. The first carbon is part of a sulfonate group, bonded to a sulfur atom which is double-bonded to two oxygen atoms and single-bonded to a hydroxyl group. The remaining five carbons are part of a chain where each carbon is bonded to two fluorine atoms, except for the terminal carbon which is bonded to one fluorine atom. The chain is shown in a zig-zag conformation.</p> <p>• Li</p> <p>55120-77-9</p>
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Annex IV: List of Contacted Stakeholders

No	Name	Substance	Potential User / Producer	Industry	Country	Source (stakeholder identified)	Answer received
1	3M	Fluorinated derivatives	Former producer	Chemicals	Belgium	Proposed by project team (Previous projects)	It was indicated that there is no known manufacture or use of PFHxS or related substances by 3M; There was no reply on follow up questions on past production.
2	Akzo Nobel Europe	Possible use PFHxS	User	Construction materials	Netherlands	Proposed by project team (Previous projects)	No response received
3	Archroma (prev Clariant)	They have fluorine free water repellent Nuva® N for textile but they have fluorochemicals & Cartaseal® barrier additives in the paper business	User	Paper, Textile (water-repellent)	Switzerland	Proposed by project team (Previous projects)	No response received
4	Arkema	Fluorinated chemicals	Producer	Chemicals	France	Proposed by project team (Previous projects)	No response received
5	BASF CH	Possible use PFHxS	User	Paper	Switzerland	Proposed by project team (Previous projects)	It was indicated that they do not use any fluorinated substances in their paper industry sector and thus cannot provide any additional data.
6	BASF SE	Possible use PFHxS	User	Construction materials	Sweden	Previous projects	It was indicated that BASF does not take part in surveys at all.
7	Bernd Schwegmann GmbH	Fluorosurfactants /Wetting additives free of PFOS und PFOA	User	Construction materials	Germany	Proposed by project team (Previous projects)	It was indicated that they are user (but no producer) of fluorinated products, but they do not use products covered by this survey (CAS number of used products not listed).
8	Bio-ex s.a.s.	Fluorine and fluorine free products	User	Fire-fighting foam	France	Proposed by project team (Previous projects)	No response received
9	Brillux	Possible use PFHxS	User	Construction materials	Germany	Proposed by project team (Previous projects)	It was indicated that they have not used fluorinated substances in the past nor do they use them now.

10	Caparol Farben Lacke	Possible use PFHxS	User	Construction materials	Germany	Proposed by project team (Previous projects)	It was indicated that the company is specialised on paints for the end user and that they don't use fluorinated substances at all in their production process.
11	CHT R. Beitlich	Seems to use fluorinated free, waterproofing (fluorine-free) silicones	User	Paper, textiles	Germany	Proposed by project team (Previous projects)	It was indicated that fluorinated chemicals play a minor role in the company and that they cannot provide any data related to the query.
12	Dandong Gilkuhn Co., Ltd.	Perfluorohexanesulfonic potassium salt	Producer	Chemicals	China	Web search	No response received
13	Daikin	PFA	Producer	Chemicals	Belgium	Proposed by project team (Previous projects)	No response received
14	Dainippon Ink and Chemicals Inc.	Fluoropolymers	Producer	Chemicals	Japan	Scientific literature	No response received
15	Dr. Sthamer	Fluorine and fluorine free products	User	Fire-fighting foam	Germany, UK	Proposed by project team (Previous projects)	No response received
16	Eimermacher	Possible use PFHxS	User	Textile	Germany	Proposed by project team (Previous projects)	No response received
17	Exfluor	Possible use PFHxS	Producer	Chemicals	USA	Proposed by project team (Previous projects)	No response received
18	Fenix Outdoor Fjällräven	Possible use PFHxS	User	Textile	Sweden	Proposed by project team (Previous projects)	No response received
19	Company Y	PFHxS	Producer	Chemicals	China	Market research reports	It was indicated that they do not supply the subject products and cannot answer the questions related to PFHxS.
20	Fritz Tile	Possible use of PFHxS related compound	User	Construction materials	USA	Web search	No response received
21	Fubao Group	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	The manager agreed to participate and a follow up email in Chinese with survey questions has been sent. No response received

22	Grünperga Papier	Possible use PFHxS	User	Paper	Germany	Proposed by project team (Previous projects)	It was indicated that none of their raw and auxiliary materials contain PFHxS and related substances. Further, current suppliers state that they have not used PFHxS for the manufacture of their products in the past and that PFHxS has never played a role in paper coating for food packaging.
23	Halo Polymer	PTFE and other fluorinated products	Producer	Chemicals	Russia	Proposed by project team (Previous projects)	The company does not produce PFHxS.
24	Hubei Hengxin Chemical	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	An email in Chinese with survey questions has been sent to the Sales Department, but the email got returned. Company has been contacted again. No response received
25	Hubei Nopon	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	It was indicated that they do not use PFHxS related chemicals in their electrolyte products.
26	Hunan Heaven		Producer	Chemicals	China	Web search	No response received
27	Julius Schulte Trebsen	Possible use PFHxS	User	Paper	Germany	Proposed by project team (Previous projects)	No response received
28	Kono Chem. Limited	PFHxSF	Producer	Chemicals	China	Web search	No response received
29	Lanxess Deutschland GmbH	Possible use PFHxS	User	Textile	Germany	Proposed by project team (Previous projects)	It was indicated that they do not use or produce any covered substances. Further, a reconstruction of past uses is very difficult and unlikely.
30	Lindenfarb Textilvered-lung	Possible use PFHxS	User	Textile	Germany	Proposed by project team (Previous projects)	It was indicated that they use C6 fluorocarbons which they purchase from different producers. There is a contact in the textile association and the initial e-mail will be forwarded. Further, they are in contact with producers of fluorinated substances and might be able to help in getting information on tonnages of production and/or use.
31	Lithofin AG	Possible use PFHxS	User	Construction materials	Germany	Proposed by project team (Previous projects)	Do not want to participate
32	Merck KGaA	possible use PFHxS	User	Construction materials, semiconductors	Germany	Proposed by project team (Previous projects)	The company does not use any C6 or C8 substances at all.

33	Metsä tissue	n/a	User	Paper	Finland	Proposed by project team (Previous projects)	No response received
34	Miteni	Fluorinated derivatives, fluorinated building blocks	Producer	Building blocks	Italy	Proposed by project team (Previous projects)	Company has been contacted several times. No response received
35	Möller-Chemie	Possible use PFHxS	User	Construction materials	Germany	Proposed by project team (Previous projects)	No response received
36	Omnova Solutions	Possible use PFHxS	User	Textile (repellent), Fluoro surfactants	Worldwide	Proposed by project team (Previous projects)	No response received
37	Company from the paper sector	Possible use PFHxS	User	Paper (food packing water repellent)	Germany	Proposed by project team (Previous projects)	They have checked all CAS numbers provided in the excel file none of the substances is included in the used fluorocarbon resins Past use volumes of PFHxS: approx. 25-30 t/a
38	Purtex	Possible use PFHxS	User	Textile	Czech Republic	Proposed by project team (Previous projects)	They don't produce textiles, they purchase the textiles from Belgium and Germany and they don't use any chemicals for textile treatment;
39	Rudolf GmbH	Seems to have products free of PFOS and PFOA	User	Textile (water repellent), construction chemicals	Germany	Proposed by project team (Previous projects)	Do not want to participate
40	Rühl AG	Fluorine free products	User	Fire-fighting foam	Germany	Proposed by project team (Previous projects)	No response received
41	SCA Hygiene Products	Possible use PFHxS	User	Paper (packing)	Sweden	Proposed by project team (Previous projects)	SCA does not produce or use any of the substances that asked in this survey.
42	Schmitz-Werke GmbH	Possible use PFHxS	User	Textile	Germany	Proposed by project team (Previous projects)	No participation due to data privacy.
43	Shanghai Worldyang Chemical Co. Ltd.	Fluoro products	Producer	Chemicals	China	Web search	No response received
44	Shaowu Huaxin Chemical Co., Ltd	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	They don't produce the products covered by the survey, their main products includes: Anhydrous Hydrogen Fluoride, Ammonium Bifluoride

							(Ammonium Fluoride), and Electronic Hydrofluoric Acid.
45	Solberg Scandinavian AS	Fluoro surfactant and fluoropolymer-free firefighting foam, PFOS-free synthetic firefighting foam	User	Fire-fighting foam	Norway	Proposed by project team (Previous projects)	They do not use PFHxS or related substances.
46	Solvay	Fluorinated derivatives elemental fluorine, inorganic fluorides, organic intermediates and a large choice of fluorinated specialties	Producer	Synthesis of active pharmaceutical and agro-chemical ingredients, brazing of aluminum heat exchangers (Nocolok®) and for electronic applications	Belgium	Proposed by project team (Previous projects)	None of the covered substances are used by the company. No reference to any product that is covered by the survey is listed in their catalogue.
47	Company X	PFHxS	Producer	Chemicals	China	Market research reports	The company agreed to participate. A follow up email in Chinese with survey questions has been forwarded. No response received
48	Texindex	PFHxS or precursors	Potential user	Waterproofing agent for textiles	China	Scientific publication Ma et al. 2017	No response received
49	Tyco fire protection	Possible use PFHxS	User	Fire-fighting foam (fire protection products)	Germany	Proposed by project team (Previous projects)	No response received
50	W.L Gore & associates GmbH	Possible use PFHxS	User	Textile, semiconductors and electronics	United Kingdom	Proposed by project team (Previous projects)	No response received
51	Whitford Europe	Possible use PFHxS	User	Textile	United Kingdom	Proposed by project team (Previous projects)	They state that none of the chemicals are declared in their SDS.
52	Wuhan Chemical Industry Institute Co., Ltd	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	The company stopped producing organofluorine products for more than one year.
53	Wuhan Defu Economic Development Co., Ltd	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	The chief engineer answered the phone. He agreed to take a look at the survey materials and provide information that is available. A follow up email in Chinese with survey questions has been sent. No response received

54	Wuhan Yangtze river fluorine technology	PHxSF and its derivatives	Producer	Chemicals	China	Proposed by project team (Previous projects)	The company does not manufacture or use the PFHxS related products (this is not consistent with what shown on their website), but agreed to take a look at the survey materials. A follow up email in Chinese with survey questions has been sent. No response received
55	ZK71	PFHxS or precursors	Potential user	Waterproofing agent for textiles	China	Scientific publication Ma et al. 2017	No response received
56	Zjartschem (China)	Perfluoro Hexanoyl Fluoride	Import export of chemicals		China	Proposed by project team (Previous projects)	No response received