

Nordic Working Paper

Per- and polyfluoroalkylether substances: identity, production and use

Report prepared by Dr. Zhanyun Wang, Gretta Goldenman, Tugce Tugran, Alicia McNeil and Matthew Jones (Milieu Consulting)

This working paper was funded by the Nordic Council of Ministers. However, the content does not necessarily reflect the Nordic Council of Ministers' views, opinions, attitudes or recommendations

NA2020:901 ISSN 2311-0562 http://dx.doi.org/10.6027/NA2020-901

Nordic Council of Ministers Nordens Hus Ved Stranden 18 DK-1061 Copenhagen www.norden.org

Per- and polyfluoroalkylether substances: identity, production and use

Project Number 2019-007



January 2020

Report prepared by Dr. Zhanyun Wang, Gretta Goldenman, Tugce Tugran, Alicia McNeil and Matthew Jones (Milieu Consulting) for Nordic Working Group on Chemicals, Environment and Health, 2019

Contents

1	Abbre	eviations	8
2	Sumn	nary	9
3	Intro	luction	14
	3.1	Background	14
	3.2	Study objectives: to provide an overview of PFAEs on the EEA market	. 14
	3.3	Structure of the report	15
	3.4	Methods	16
	3.4.1	Database research based on CAS numbers	16
	3.4.2	Further internet search using CAS numbers	22
	3.4.3	Research regarding human and environmental exposure	. 22
	3.4.4	Interviews	26
4	Findir	ngs: Group 1: Perfluoropolyethers (PFPEs)	27
	4.1	Overview of the substances in Group 1	27
	4.1.1	Characteristics of Group 1 substances, including chemical structure	27
	4.1.2	Group 1 substances identified on the EEA market	29
	4.2	Group 1 substances used in mixtures	30
	4.3	Group 1 substances used in articles	33
	4.4	Key producers and suppliers	34
	4.5	Volumes of Group 1 substances	35
	4.5.1	Within the EEA	35
	4.5.2	Globally	37
	4.6	The potential for exposure	38
	4.6.1	Information from ECHA and SPIN	38
	4.6.2	Information from literature	39
	4.7	Key messages for Group 1 PFPE	40
5	Grou	2 2: PFAEs that are fluoropolymers	41
	5.1	Overview of the substances in Group 2	41
	5.1.1	Characteristics of Group 2 substances, including chemical structure	41
	5.1.2	Group 2 substances identified on the EEA market	43
	5.2	Group 2 substances used in mixtures	45
	5.3	Group 2 substances used in articles	45
	5.4	Key producers and suppliers	48
	5.5	Volumes of Group 2 substances	48
	5.5.1	Within the EEA	48
	5.5.2	Globally	48
	5.6	The potential for exposure	49
	5.6.1	Information from literature	49

	5.7	Key messages for Group 2 PFAEs	50
6	Grou	p 3: Perfluoroether non-polymers with unsaturated bonds	51
	6.1	Overview of the substances in Group 3	51
	6.1.1	Characteristics of Group 3 substances, including chemical structure	
	6.1.2	Group 3 substances identified on the EEA market	55
	6.2	Group 3 substances used in mixtures	56
	6.3	Group 3 substances used in articles	57
	6.4	Key producers and suppliers	58
	6.5	Volumes of Group 3 substances	58
	6.5.1	Within the EEA	58
	6.5.2	Globally	59
	6.6	The potential for exposure	59
	6.6.1	Information from ECHA	
	6.6.2	Information from literature	62
	6.7	Key messages for Group 3 PFAEs	62
7	Grou	p 4: Perfluoroether non-polymers with saturated bonds	63
	7.1	Overview of the substances in Group 4	63
	7.1.1	Characteristics of Group 4 substances, including chemical structure	63
	7.1.2	Group 4 substances identified on the EEA market	68
	7.2	Group 4 substances used in mixtures	69
	7.3	Group 4 substances used in articles	72
	7.4	Key producers and suppliers	74
	7.5	Volumes of Group 4 substances	75
	7.5.1	Within the EEA	75
	7.5.2	Globally	77
	7.6	The potential for exposure	
	7.6.1	Information from ECHA and SPIN	
	7.6.2	Information from the relevant literature	
	7.7	Key messages for Group 4 PFAEs	
8	Grou	p 5: Side-chain perfluoroether polymers	
	8.1	Overview of the substances in Group 5	
	8.1.1	Characteristics of Group 5 substances, including chemical structure	
	8.2	Group 5 substances used in mixtures	
	8.3	Group 5 substances used in articles	
	8.4	Key producers and suppliers	
	8.5	Volumes of Group 5 substances	
	8.5.1	Within the EEA	
	8.5.2	Globally	

	8.6	The potential for exposure
	8.7	Key messages for Group 5 PFAEs
9	Discu	ssion on findings and challenges
	9.1	A general lack of information on PFAEs as a group
	9.2	Gaps in regulatory frameworks contribute to this lack of information
	9.3	Impact of emerging technologies
10	Anne	xes
	10.1	Overview of Chemical Groups and the number of CAS numbers that appear in databases included in the study 102
	10.2	Overview of CAS numbers
	10.3	CAS numbers registered using process-based naming conventions
	10.4	Background information on ERCs Provided by REACH 10
	10.5	Exposure information from the SPIN database (Exposure toolbox) 102
	10.6	Substances found in Cape Fear River, North Carolina 108
	10.7	Glossary 110
	10.8	List of stakeholders contacted 11
	10.9	Bibliography 113
	10.9.	1 Reports, academic articles, newspaper articles, other documents
	10.9.	2 Databases and lists
	10.9.	3 Product pages and safety datasheets 119

LIST OF TABLES

trafluoroethylene	Table 1 Databases used, brief descriptions and limitations	
abble 3 The CAS numbers, chemical names, and molecular structures of the Group 1 substances. 28 abble 4 Overview of CAS numbers in Group 1 and appearance in databases. 29 bible 5 Registration status for selected CAS numbers. 29 bible 6 Perfluoropolyethers used in mixtures, identified via CAS number 31 bible 7 Derfluoropolyethers identified use in relation to articles. 33 bible 8 Estimated value of Group 1 substances imported into the US 35 bible 10 CAS numbers, the chemical names, and the structure for Group 2 substances. 42 bible 11 Overview of CAS numbers in Group 2 and appearance in databases. 43 bible 13 Trade name, family name, composition and manufacturer of PFAE co- and terpolymers of 44 trafluoropolymers used in mixtures, identified via CAS number. 44 bible 14 Fluoropolymers identified via cAS number 45 bible 15 Fluoropolymers identified via production between 1973 and 2015. 49 bible 14 Fluoropolymers identified via CAS numbers in Group 3 substances 52 bible 15 Proview of CAS numbers in Group 3 substances in the Europe-related databases. 55 bible 14 Proview of CAS numbers in Group 3 substances in the Europe-related databases. 55 bible 21 Prefluoropolymers with unsaturated bonds. 58 bible 22 Foritouro sta	Table 2 An example of how information is presented in the excel database	21
able 5 Registration status for selected CAS numbers .29 abble 6 Perfluoropolyethers used in mixtures, identified via CAS number .31 able 8 Estimated value of Group 1 substances imported into the US .33 able 8 Estimated value of Group 1 substances imported into the US .35 able 10 CAS numbers, the chemical names, and the structure for Group 2 substances .42 able 11 Overview of CAS numbers in Group 2 and appearance in databases .43 able 12 Registration status for selected CAS numbers .43 able 13 Trade name, family name, composition and manufacturer of PFAE co- and terpolymers of trafluorothylene .44 able 14 Fluoropolymers used in mixtures, identified via CAS number .45 able 15 Ropropolymers identified use in relation to articles .45 able 16 Roproted and estimated PFA production between 1973 and 2015 .49 able 17 The CAS numbers, chemical names, and chemical structure of Group 3 substances .52 able 21 Perfluoroether non-polymers with unsaturated bonds in mixtures .55 able 22 Tonnage bands of Group 3 substances registered under REACH .59 able 23 Conview of CAS numbers in Group 3 and appearance in databases. .52 able 24 Group 3 substances found in the Cape Fear River in North Carolina .62 bibe 24 Group 3 substances fou		
able 6 Perfluoropolyethers used in mixtures, identified via CAS number	Table 4 Overview of CAS numbers in Group 1 and appearance in databases	29
abble P Perfluoropolyethers identified use in relation to articles	Table 5 Registration status for selected CAS numbers	29
abble P Perfluoropolyethers identified use in relation to articles	Table 6 Perfluoropolyethers used in mixtures, identified via CAS number	31
able 9 Exposure information provided by SPIN database based on CAS numbers		
able 10 CAS numbers, the chemical names, and the structure for Group 2 substances.	Table 8 Estimated value of Group 1 substances imported into the US	35
able 11 Overview of CAS numbers in Group 2 and appearance in databases	Table 9 Exposure information provided by SPIN database based on CAS numbers	39
able 12 Registration status for selected CAS numbers	Table 10 CAS numbers, the chemical names, and the structure for Group 2 substances	42
able 13 Trade name, family name, composition and manufacturer of PFAE co- and terpolymers of trafluoroethylene.	Table 11 Overview of CAS numbers in Group 2 and appearance in databases	43
trafluoroethylene	Table 12 Registration status for selected CAS numbers	43
able 14 Fluoropolymers used in mixtures, identified via CAS number	Table 13 Trade name, family name, composition and manufacturer of PFAE co- and terpolymers of	
able 15 Fluoropolymers identified use in relation to articles		
able 16 Reported and estimated PFA production between 1973 and 2015		
able 17 The CAS numbers, chemical names, and chemical structure of Group 3 substances		
able 18 Overview of CAS numbers in Group 3 and appearance in databases		
able 19 The registration status of Group 3 substances in the Europe-related databases. .55 able 20 The use of perfluoroether non-polymers with unsaturated bonds in mixtures .56 able 21 Perfluoroether non-polymers with unsaturated bonds. .58 able 22 Tonnage bands of Group 3 substancers registered under REACH .59 able 23 Environmental release categories (ERCs) associated with life-cycle stages of the substances .61 able 24 Group 3 substances found in the Cape Fear River in North Carolina .62 able 25 Overview of CAS numbers in Group 4 and appearance in databases .68 able 26 Overview of CAS numbers in Group 4 and appearance in databases .68 able 29 Perfluoroether non-polymers with saturated bonds use in mixtures .70 able 29 Perfluoroether non-polymers, identified use in relation to articles .73 able 30 Tonnage bands of Group 4 substances registered under REACH .76 able 31 Industrial uses of GALDEN LMW at industrial sites .78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances .80 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 .83 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands .86 able 36 Results of measurements on different water med	Table 17 The CAS numbers, chemical names, and chemical structure of Group 3 substances	52
able 20 The use of perfluoroether non-polymers with unsaturated bonds in mixtures	Table 18 Overview of CAS numbers in Group 3 and appearance in databases	55
able 21 Perfluoroether non-polymers with unsaturated bonds. 58 able 22 Tonnage bands of Group 3 substancers registered under REACH. 59 able 23 Environmental release categories (ERCs) associated with life-cycle stages of the substances 61 able 24 Group 3 substances found in the Cape Fear River in North Carolina 62 able 25 CAS numbers, the chemical names, and the structure for Group 4 substances. 64 able 26 Overview of CAS numbers in Group 4 and appearance in databases. 68 able 27 Registration status for selected CAS numbers. 68 able 28 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 29 Perfluoroether non-polymers, identified use in relation to articles 73 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 36 Results of measurements on soil carried out in 2018 at different locations in the Netherlands. 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the Netherlands. 86 able 37 Results of measurements on different wate	Table 19 The registration status of Group 3 substances in the Europe-related databases	55
able 22 Tonnage bands of Group 3 substancers registered under REACH 59 able 23 Environmental release categories (ERCs) associated with life-cycle stages of the substances 61 able 24 Group 3 substances found in the Cape Fear River in North Carolina 62 able 25 CAS numbers, the chemical names, and the structure for Group 4 substances 64 able 26 Overview of CAS numbers in Group 4 and appearance in databases 68 able 27 Registration status for selected CAS numbers 68 able 29 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the NEtherlands 86 able 36 Results of measurements on different locations in Italy, ARPAV 88 able 39 Detection values for HFPO-DA in different loc	Table 20 The use of perfluoroether non-polymers with unsaturated bonds in mixtures	56
able 23 Environmental release categories (ERCs) associated with life-cycle stages of the substances 61 able 24 Group 3 substances found in the Cape Fear River in North Carolina 62 able 25 CAS numbers, the chemical names, and the structure for Group 4 substances 64 able 26 Overview of CAS numbers in Group 4 and appearance in databases 68 able 27 Registration status for selected CAS numbers 68 able 28 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the NL 86 able 37 Results of measurements on different vater media carried out in 2018 at different locations in the NL 86 able 38 Results of measurements on different locations at Cape Fear River 88 able		
able 24 Group 3 substances found in the Cape Fear River in North Carolina 62 able 25 CAS numbers, the chemical names, and the structure for Group 4 substances 64 able 26 Overview of CAS numbers in Group 4 and appearance in databases 68 able 27 Registration status for selected CAS numbers 68 able 28 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 29 Perfluoroether non-polymers, identified use in relation to articles 73 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 36 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the Netherlands 86 able 39 Detection values for HFPO-DA in different locations in Italy, ARPAV 88 able 40 GenX Concentrations detected in different locations at Cape Fear River 88 able 41 GenX Concentrations at two different locations at Cape Fear River 88 able 42 Field data from differen	Table 22 Tonnage bands of Group 3 substancers registered under REACH	59
able 25 CAS numbers, the chemical names, and the structure for Group 4 substances 64 able 26 Overview of CAS numbers in Group 4 and appearance in databases 68 able 27 Registration status for selected CAS numbers 68 able 28 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 29 Perfluoroether non-polymers, identified use in relation to articles 73 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 36 Results of measurements on different water media carried out in 2018 at different locations in the Netherlands		
able 26 Overview of CAS numbers in Group 4 and appearance in databases 68 able 27 Registration status for selected CAS numbers 68 able 28 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 29 Perfluoroether non-polymers, identified use in relation to articles 73 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 36 Results of measurements on different water media carried out in 2018 at different locations in the Netherlands		
able 27 Registration status for selected CAS numbers 68 able 28 Perfluoroether non-polymers with saturated bonds use in mixtures 70 able 29 Perfluoroether non-polymers, identified use in relation to articles 73 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the NL86 80 able 39 Detection values for HFPO-DA in different locations in Italy, ARPAV 88 able 40 GenX Concentrations at two different sampling points. 88 able 41 GenX Concentrations at two different sampling points. 88 able 42 Field data from different monitoring exercises in the EEA 89		
able 28 Perfluoroether non-polymers with saturated bonds use in mixtures70able 29 Perfluoroether non-polymers, identified use in relation to articles73able 30 Tonnage bands of Group 4 substances registered under REACH76able 31 Industrial uses of GALDEN LMW at industrial sites78able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances80able 33 Exposure information provided by the SPIN database based on CAS numbers81able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-201583able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands86able 37 Results of measurements on different water media carried out in 2018 at different locations in the Netherlands.86able 38 Results of measurements on different water media carried out in 2018 at different locations in the NL87able 39 Detection values for HFPO-DA in different locations in Italy, ARPAV.88able 40 GenX Concentrations detected in different locations at Cape Fear River88able 41 GenX Concentrations at two different sampling points.88able 42 Field data from different monitoring exercises in the EEA89		
able 29 Perfluoroether non-polymers, identified use in relation to articles 73 able 30 Tonnage bands of Group 4 substances registered under REACH 76 able 31 Industrial uses of GALDEN LMW at industrial sites 78 able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances 80 able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the Netherlands86 86 able 39 Detection values for HFPO-DA in different locations in Italy, ARPAV 88 able 40 GenX Concentrations detected in different locations at Cape Fear River 88 able 41 GenX Concentrations at two different sampling points	Table 27 Registration status for selected CAS numbers	68
able 30 Tonnage bands of Group 4 substances registered under REACH		
able 31 Industrial uses of GALDEN LMW at industrial sites.		
able 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances		
able 33 Exposure information provided by the SPIN database based on CAS numbers 81 able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015 83 able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands 86 able 36 Results of measurements on groundwater carried out in 2018 at different locations in the Netherlands 86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the NL86 86 able 38 Results of measurements on different water media carried out in 2018 at different locations in the NL86 87 able 39 Detection values for HFPO-DA in different locations in Italy, ARPAV 88 able 40 GenX Concentrations detected in different locations at Cape Fear River 88 able 41 GenX Concentrations at two different sampling points 88 able 42 Field data from different monitoring exercises in the EEA 89		
able 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015		
able 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands		
able 36 Results of measurements on groundwater carried out in 2018 at different locations in the Netherlands86 able 37 Results of measurements on different water media carried out in 2018 at different locations in the NL86 able 38 Results of measurements on different wastewater media carried out in 2018 at different locations in the L	Table 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015	83
able 37 Results of measurements on different water media carried out in 2018 at different locations in the NL86 able 38 Results of measurements on different wastewater media carried out in 2018 at different locations in the L	Table 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands	86
able 38 Results of measurements on different wastewater media carried out in 2018 at different locations in the L	Table 36 Results of measurements on groundwater carried out in 2018 at different locations in the Netherlands.	86
L		
able 39 Detection values for HFPO-DA in different locations in Italy, ARPAV	Table 38 Results of measurements on different wastewater media carried out in 2018 at different locations in th	ie
able 40 GenX Concentrations detected in different locations at Cape Fear River		
able 41 GenX Concentrations at two different sampling points	Table 39 Detection values for HFPO-DA in different locations in Italy, ARPAV	88
able 42 Field data from different monitoring exercises in the EEA	·	
able 42 Field data from different mentions eventions contriad out in China		
	Table 43 Field data from different monitoring exercises carried out in China	
able 44 Concentrations detected by the monitoring carried out by ARPAV, between 2013-2018		
able 45 Overview of CAS numbers in Group 5 and appearance in databases		
able 46 Structures of two Fluorolink products developed by Solvay94	Table 46 Structures of two Fluorolink products developed by Solvay	94

Table 47 Side-chain perfluoroether polymers used in mixtures	95
Table 48 Side-chain perfluoroether polymers, identified use in relation to articles	96
Table 49 Overview of CAS numbers, groups and appearance in databases	102
Table 50 Group 1 substances	103
Table 51 Group 2 substances	104
Table 52 Group 3 substances	104
Table 53 Group 4 substances	105
Table 54 Group 5 substances	105
Table 55 List of CAS numbers registered using process-based naming conventions	106
Table 56 List of substances found in Cape River	108
Table 57 List of interviews conducted	111

1 Abbreviations

CAS RN	Chemical Abstract Service Registry Number					
CDGR	Compound Annual Growth Rate					
CDR	Chemical Data Reporting (USA)					
C&L	Classification and labelling					
ECHA	European Chemicals Agency					
ECF	Electrochemical fluorination process					
EEA	European Economic Area					
EFSA	European Food Safety Authority					
ERC	Environmental Release Category					
FCM	Food contact material					
FDA	U.S. Food and Drug Administration					
FKM	Fluoroelastomers					
HPF	Hexafluorophosphoric acid					
HFPO-DA	Hexafluoropropylene oxide dimer acid					
IRSA	Water Research Institute (Italy)					
KEMI	Swedish Chemical Agency					
PBT	Persistent, bioaccumulative and toxic					
PFAS	Perfluoroalkyl and polyfluoroalkyl substance					
PFBS	Perfluorobutane sulfonic acid					
PFCA	Perfluoroalkyl carboxylic acid					
PFECAs						
PFESAs						
PFNA	Perfluorononanoic acid					
PFPE						
PFOA	Perfluorooctanoic acid					
PFOS	Perfluorooctane sulfonic acid					
PFSA	Perfluoroalkane sulfonic acid/sulfonate					
РОР	Persistent organic pollutant					
POSF	Perfluorooctane sulfonyl fluoride					
PPVE	Perfluoro propyl vinyl ether					
PTFE	Polytetrafluoroethylene					
REACH	Regulation on Registration, Evaluation and Assessment of Chemicals (EU)					
RIVM	National Institute for Public Health and the Environment of The Netherlands					
SVHC	Substance of very high concern					
vPvB	Very persistent, very bioaccumulative					
NKE						
TFE	Tetrafluoroethylene					
TSCA	Toxic Substances Control Act (USA)					
UBA	German Environment Agency					
USFDA FCS	U.S Food and Drug Administration Food Contact Substances					
U.S. EPA	U.S. Environmental Protection Agency					

2 Summary

This project is aimed at providing an initial overview of a group of per- and polyfluoroalkyl substances (PFASs), namely the per- and polyfluoroalkylether substances (hereafter referred to as PFAEs). The terms of reference called for compilation of available information on the characteristics, production, import and use on European and global markets as well as exposure risks of PFAEs, linked to specific substances.

PFAEs as a group are distinguished from other PFASs by their ether-linkages between the perfluorocarbon moieties (e.g. $-C_nF_{2n}-O-C_mF_{2m}-$), but the group itself remains very diverse. Apart from a few exceptions such as GenX and ADONA, little is known about PFAEs. However, emerging evidence suggests that these chemicals have similar behaviour in the environment as their analogues without ether-linkages and can be hazardous to human health and the environment. In the interests of minimising further contamination in the future, it is therefore necessary to take steps in managing their production, use and disposal.

The study begins with the identification of 394 PFAEs from 22 chemical inventories in the EU and 18 other countries, while noting that for some substances, there is some uncertainty with regard to their chemical identities. The individual substances are assigned to five sub-groups based on their molecular structures: (1) perfluoropolyethers (PFPEs), (2) fluoropolymers, (3) perfluoroether non-polymers with unsaturated bonds, (4) perfluoroether non-polymers with saturated bonds, and (5) side-chain perfluoroether polymers.

A methodical search by CAS number is then carried out, with a focus on seven public databases from the European Economic Area (EEA) and the US, namely the REACH database of registered substances, ECHA pre-registered substances database, ECHA C&L inventory, EURL Food Contact Materials, EU Cosing, SPIN database (Norway, Sweden, Denmark and Finland) from the EEA, and the US Chemical Data Reporting databases from 2012 and 2016. The information retrieved is compiled into a database in the format of accompanying Excel spreadsheets. With this foundation in place, further desk research is performed to gather additional information on individual PFAEs. Furthermore, interviews are conducted with mainly public authorities to gather additional information.

The study confirms that little is known about most of the PFAEs identified. More than half (225 out of 394) do not appear in any of the seven databases selected for this study. Only 18 (<5%) appear in the REACH database. The REACH Regulation's exemption of polymers from registration contributes to the significant gaps in data for three sub-groups of PFAEs (Groups 1, 2 and 5). Even when a substance is registered under REACH, the information is usually kept confidential, undermining the efforts to provide a comprehensive understanding for sound management purposes. In addition, the tonnage bands used for reporting the manufacture or import of the substances under REACH are too broad for a detailed understanding of the quantities involved, and information on exposure during the chemicals' lifecycles is superficial. Information on downstream uses also seems incomplete. The information found in the other databases searched is equally scattered and even less detailed.

The desk research found a diverse and complex marketplace for PFAEs, from major producers to suppliers and downstream users. PFAEs are manufactured, sold and used in many industries from aerospace to cosmetics although It is not possible to determine quantities involved. Furthermore, the main chemical composition of a particular chemical product is often kept confidential by the manufacturers, making it difficult to link individual CAS numbers to identified uses of PFAEs in specific mixtures and articles. Information on exposure risks and environmental releases is found for only a handful of substances that have already been identified as problematic in the scientific literature, like GenX and ADONA. Little is known about the other PFAEs. Key findings for each group of PFAEs are summarized below.

Group 1 chemicals are perfluoropolyethers (PFPEs). These are different polymers made of perfluoroether monomers. PFPEs have been used in a wide range of industries for several decades. They seem to be used primarily as lubricants and are available on the market under several brand names, including Krytox (Chemours); Fomblin, Solvera, Fluorolink and Galden (Solvay); and Dennum (Daikin). However, beyond the well-known brands and partial knowledge on their uses, little is known about PFPEs in the public domain. Out of the 127 CAS numbers that constitute PFPEs, half (63 in total) are not identified in any of the databases considered. The chemical structures for only 6 CAS numbers can be retrieved. Due to the exemption of polymers from registration under the REACH regulation, little is known about their production and import volumes as well as exposure and risks. Statistical information is not available for PFPEs as a whole and there is limited information on the amounts of individual CAS numbers being produced and sold. Online research found several instances where PFPEs were advertised as environmentally friendly, non-toxic and low risk. The literature indicated that degradation at high temperatures under specific conditions may lead to lower-molecular weight contaminants being released.

The marketplace today seems to be complex, however, several CAS numbers were identified as being among the most common PFPEs on the market:

- 51798-33-5 (Poly(oxy(trifluoro(trifluoromethyl)-1,2-ethanediyl)), alpha-(1-carboxy-1,2,2,2-tetrafluoroethyl)-omega-(tetrafluoro(trifluoromethyl)ethoxy)-
- 60164-51-4 (Poly[oxy[trifluoro(trifluoromethyl)-1,2-ethanediyl]], α -(1,1,2,2,2-pentafluoroethyl)- ω -[tetrafluoro(trifluoromethyl)ethoxy])
- 69991-61-3 (Ethene, 1,1,2,2-tetrafluoro-, oxidized, polymd.))
- 162492-15-1 (tetrafluoroethylene, oxidized, oligomers, reduced, methyl esters, reduced, reaction products with ethylene oxide)

Group 2 chemicals are fluoropolymers that are made of perfluoroether monomers (Group 3) and tetrafluoroethylene (TFE). They include the group of perfluoroalkoxy alkanes (PFAs). Only 12 out of the 57 Group 2 chemicals appear in the databases selected for this study. As in the case of Group 1 substances, as polymers, Group 2 substances are exempt from registration in the REACH databases, which contributes to the lack of information. The chemical structure has been found for almost one third of the CAS numbers (20 out of 57). Main producers of Group 2 substances include 3M, AGC, Chemours, Daikin and Solvay. Group 2 fluoropolymers are used in a variety of industries, ranging from renewable energy to medical devices to fuel cell technology. They are often used as membranes and in coating applications in the food industry, amongst other uses. However, there is little information on the production, import and use volumes in the EEA and globally.

Some of the important CAS numbers identified in this group appear to be:

- 26654-97-7 Ethanesulfonyl fluoride, 2-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2tetrafluoro ethoxy]-1,1,2,2-tetrafluoro-, polymer with tetrafluoroethene)
- 31175-20-9 Ethanesulfonic acid, 2-[1-[difluoro[(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2tetrafluoroe thoxy]-1,1,2,2-tetrafluoro-, polymer with 1,1,2,2-tetrafluoroethene)

- 66796-30-3 (4-(3-Bromophenyl)-1,3-thiazol-2-amine), associated with Nafion (Chemours)
- 69462-70-0 (Ethanesulfonyl fluoride, 1,1,2,2-tetrafluoro-2-[(1,2,2-trifluoroethenyl)oxy]-, polymer with 1,1,2,2-tetrafluoroethene) associated with Aquivion (Solvay).

Group 3 substances are monomers (perfluoroether non-polymers with unsaturated bonds) **used in the production of Group 2 substances**. 31 out of the 51 CAS numbers are identified in at least one of the databases considered, and chemical structures are retrieved for 34 CAS numbers. Almost all of the substances for which there is information are used as intermediates. Producers identified in connection with these substances include 3M, AGC Europe, Chemours, Dyneon and Solvay. Information obtained from the REACH files suggest that the annual production/import quantities in the EU are between 223 and 2230 tonnes for eight substances. No other information is found for the EEA or rest of the world.

The CAS numbers that appear to be important in terms of volume are:

- 1187-93-5 (trifluoro(trifluoromethoxy)ethylene)
- 1623-05-8 (1,1,1,2,2,3,3-heptafluoro-3-[(trifluorovinyl)oxy]propane)

According to the REACH database of registered substances, they are being produced in a tonnage band of 100–1000 tonnes per year.

According to the information provided for the nine substances registered in REACH, primary exposure occurs during polymerisation processes on industrial sites, where substances can be released into the air or into water. Some of the Group 3 chemicals have been detected in the Cape Fear River in the USA, downstream from the Chemours plant at Fayetteville, North Carolina.

Group 4 substances are perfluoroether non-polymers with saturated carbon bonds. Out of the 152 CAS numbers that belong to Group 4, 90 are not identified in any of the databases considered. Internet searches on the basis of CAS numbers identify chemical structures for 103 Group 4 substances. Some Group 4 chemicals are linked to Group 1 substances, as they are used in the manufacturing of PFPEs. Beyond that, the use and applications of other PFAEs point to a complex picture: from replacement chemicals for PFOA (GenX and ADONA) in the production of polymers to ingredients in floor polishing products. Among the main producers are 3M, Unimatec, Solvay, Chemours and Omnova. Information on the six Group 4 substances available in the REACH registration files leads to an estimate of 212 to 2120 tonnes manufactured/imported annually in the EU.

Substantial information is available for GenX and ADONA. Efforts might therefore be more efficiently directed to other substances where there is almost no information. Due to their high volumes of manufacture and import (between 100 to 1000 tonnes annually), possible widespread use by workers (for the former) and possible wide range of application as lubricant and grease (for the latter), important CAS numbers in this group include:

- 382-28-5 (2,2,3,3,5,5,6,6-octafluoro-4-(trifluoromethyl)morpholine)
- 161075-00-9 (Hexafluoropropene, oxidized, oligomers, reduced, fluorinated)

Group 5 chemicals are side-chain perfluoroether polymers with non-fluorinated polymer backbones and perfluoroether moieties on the sidechains. Only seven CAS numbers are in this group and none are identified in the target databases. No chemical structures are found for any of the CAS numbers. On the other hand, several Fluorolink products (Solvay) are identified based on Group 5 substances. This points to industrial applications related to surface treatment in a wide range of sectors from automotive to construction. No information is found on production, import and use volumes. While some information is available on the sectors where Group 5 substances are used, no information is identified on the exposure and environmental releases of the substances. It is however important to note that there are indications in the literature that fluorinated side-chains can detach from the polymer backbones, releasing these substances into the environment. This indicates risks and needs to be further investigated.

Conclusions

The study revealed that a large variety of PFAEs have been produced and used and their marketplace is complex. All chemicals in the five groups have very diverse uses in a variety of industries. These include uses as processing aids, building blocks for manufacturing other chemicals and treatment agents for surfaces. They have a wide range of industrial and commercial applications including cosmetic products, food contact materials, lubricants, metal plating, paints and varnishes, fuel-cells, electronic equipment and other high-tech applications.

The study also confirmed a general lack of information on PFAEs in the public domain, including a lack of non-ambiguous chemical identities in many cases; the information that is available paints a complex picture. The public databases considered cover only a fraction of the PFAEs identified, only those that exceed certain tonnage thresholds (1 tonne per year for REACH) and meet certain criteria (for instance, non-polymers produced/imported in the EU for REACH). When available in the REACH database of registered substances, the information usually includes producers, potential health hazards and environmental exposure, albeit in an approximative way which does not account for the whole picture, nor provide clarity about the risks of individual substances.

Furthermore, since the chemicals and their industrial applications are many and varied, linking these applications to specific CAS numbers is very difficult without the cooperation from manufacturers. Currently, transparency is lacking both at the manufacturing and downstream use levels, often justified as confidential business information.

This lack of information undermines public efforts to protect the environment and the public from the risks associated with the production, use and disposal of these chemicals. In the specific context of this study, this has impeded the efforts to estimate exposure for both humans (workers and consumers) and the environment. Despite this, literature shows that some PFAEs have been identified at elevated levels in the environment and the public, often downstream to the manufacturing sites, resulting in significant human health risks. Future studies may further focus on the different industrial uses to provide a more detailed picture.

Despite their shortcomings, databases such as the REACH registered substances remain the most valuable, sometimes even the only source of information regarding these substances. That clearly suggests that such databases have a great potential for improving oversight of PFAEs if their limitations are addressed,

namely expanding their coverage to include more chemicals (such as polymers) and steps are taken to remedy the current information gaps regarding the substances that are already in the databases.

PFAEs as a sub-group of PFASs merit further scrutiny, based on emerging evidence about the risks associated with some of the substances (such as GenX), their widespread use and their high persistence in the environment. It is also important to remember that although many of these chemicals are produced or imported in small quantities in the EU (which might be a main reason why many of them fall outside the scope of relevant regulations), their combined impact may still present a significant risk to the environment and human health.

3 Introduction

3.1 Background

The per- and polyfluoroalkyl substances (PFASs) are a class of chemicals of great concern today, due to their extreme persistence. The long-chain PFASs such as PFOS and PFOA (both perfluoroalkyl acids, or PFAAs) are known to be also bioaccumulative and toxic. Efforts have been made to phase out production and use of PFOS and PFOA in Europe and North America, and both PFOS and PFOA, together with their precursors, are now regulated globally under the Stockholm Convention. However, the chemical industry has developed many other PFASs, production of which continues. To date, some 4700+ monomeric and polymeric PFASs are identified as been on the global market, including many other than long-chain PFAAs and their precursors. This study focuses on one subset of PFASs, namely per- and polyfluoroalkyl acids (PFAAs) and their precursors, but with ether-linkage(s) between the perfluorocarbon moieties (e.g. – C_nF_{2n} –O– C_mF_{2m} –).

A critical review found that due to structural similarities, many PFAEs have similar hazardous properties as PFAAs and their precursors¹. For example, perfluoroalkylether carboxylic acids (PFECAs) such as ADONA and GenX are similarly extremely persistent as PFOA, have high mobility in the environment, and can cause various toxicological adverse effects such as liver toxicity. Several PFECAs such as GenX and F-DIOX have been self-classified by their producers as "toxic" under REACH. Some current major producers of PFAAs and their precursors have also been the major producers of PFAEs since the 1970s². In recent years, some of them have additionally marketed novel PFAEs as replacements to PFAAs and their precursors³. However, in contrast to the well-studied PFAAs and their precursors, no clear overview of the production, import and use of all PFAEs is currently available in the public domain. While recent studies have focused on the two PFECAS RNw used as replacements to PFOA in fluoropolymer production, i.e. ADONA and GenX, many other PFAEs are being produced and used in a wide range of industrial and commercial applications without scrutiny. This lack of overview seriously hinders the efforts to understand, assess and manage these chemicals.

3.2 Study objectives: to provide an overview of PFAEs on the EEA market

This study on "Per- and polyfluoroalkylether substances – identity, production and use" has been carried out under the guidance of the Nordic Working Group for Chemicals, Environment and Health (NKE). The aim of the project is:

"to gather as much information as possible on the identity, use and production of [PFAEs] on the EEA market, within the available budget, in order to get an understanding of the extent of the

¹ Wang et al., (2015), <u>Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their</u> precursors: <u>Status quo</u>, <u>ongoing challenges and possible solutions</u>, Environment International Volume 75, February 2015, Pages 172-179.

² Ibid.

³ Wang et al., (2013), Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors, Environment International 60 (2013) 242–248.

presence of these substances in articles and environment and also get an idea of the transition from other long-chain PFAS to these substances".

In addition to the more readily available data on well-known PFAEs, such as GenX, the tender documents ask the consultants for information on PFAEs beyond PFECAs and PFESAs. The outcome of the project is to be a report, in English, with information on the following:

- What PFAEs are on the EEA market
- How they are being used in mixtures⁴
- How they are being used in articles, including articles imported into the EEA⁵
- The volumes of PFAEs produced in the EEA; imported into the EEA; and used in the EEA
- The volumes being produced globally and any time trends
- The potential for spills and exposure

Please note the Terms of Reference did not call for research into the hazards (e.g., toxicity, bioaccumulation) of the respective compounds, but instead focused on elements relevant to exposure.

3.3 Structure of the report

The report contains six chapters, with a separate chapter focusing on each of the five sub-group of PFAEs identified. For each group, an overview is provided, synthesising the research outcomes from the steps described in the methods section. Each chapter concludes with a section providing key messages and overview of gaps in the information. The sixth chapter provides a general discussion about the findings and challenges.

Annexes include:

- CAS numbers included in the project, indicating those for which no information was found and those that were registered using vague process-based naming conventions, but identified as PFAEs (with low to moderate uncertainty) by the study team based on available evidence.
- background information on Environmental Release Categories (From REACH registration database)
- background information on SPIN Exposure toolbox
- list of CAS numbers that have been detected in Cape Fear River, US
- glossary of terms
- list of interviews
- bibliography

⁴ REACH Article 3(3) defines the term "mixture" as "a mix or solution of two or more substances" and considers them as separate from substances when the two compounds put together do not react with each other. REACH requires producers and importers of mixtures to register each individual substance in the mixture beyond the threshold of one tonne per year.

⁵ REACH Article 3(3) defines article as 'an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition'. Producers and importers of articles need to register each individual substance in the article, given the condition that *the substance is present in the article in quantities of over one tonne per year and if the substance is intended to be release under normal conditions of use.*

3.4 Methods

This study started with an initial identification of relevant PFAEs on the global market by a review of the regulatory inventories of industrial chemicals from 19 countries and regions (Canada, US, Mexico, EU, Denmark, Finland, Norway, Sweden, Switzerland, Turkey, Russia, Japan, China, Taiwan, Philippines, Vietnam, Republic of Korea, Thailand, India, Malaysia, Australia and New Zealand).

In total, 394 CAS numbers were identified as linked to compounds containing -CnF2n-O-CmF2m- moieties. These include 104 CAS numbers registered using vague process-based naming conventions, e.g. CAS RN 101316-90-9 as "Ethene, 1,1,2,2-tetrafluoro-, oxidized, polymd., reduced, Me esters, reduced, acrylates". This is in line with the production process of PFAEs, particularly perfluoropolyethers (PFPEs), documented in the literature⁶. This is also in line with the description and visualisation of CAS number 161075-00-9 (Hexafluoropropene, oxidized, oligomers, reduced, fluorinated) as a mixture of PFAEs in the REACH dossier. These are included in the research, with clear labelling with regard to the uncertainties⁷, and in the relevant annex documents.

On the basis of their structural characteristics and similarities, the 394 CAS numbers were grouped into 5 categories:

- 1. Perfluoropolyethers (PFPEs)
- 2. Fluoropolymers
- 3. Perfluoroether non-polymers with unsaturated bonds
- 4. Perfluoroether non-polymers with saturated bonds
- 5. Side-chain perfluoroether polymers

These groups are defined at the beginning of the respective chapters below.

3.4.1 Database research based on CAS numbers

A detailed research of 7 key databases was then carried out for each of the 394 CAS numbers; for details on these databases including an overview, the information they contain and how this information is used, and their limitations if applicable, see Table 1. These databases were prioritized for the study since they provide additional information on the substances, including their commercial status (e.g. on the EEA market, on the US market). In some cases, information on production/import volumes and exposure is also available. This research aimed to provide an overview of the relevant information scattered across these databases.

⁶ Sianesi et al, (1994), Perfluoropolyethers (PFPEs) from Perfluoroolefin Photooxidation.

⁷ These 104 CAS numbers are in the overview list as well as on a separate list, to enable easy identification.

Databases searched	Description of database	Reason for use and limitations	PFAEs found
REACH Registered Substances	The REACH Regulation follows the 'one substance, one registration' principle and requires producers and/or importers of substances in quantities of 1 tonne or more to submit a registration dossier. The registration dossiers contain information depending on the substance's registration status (full registration or as an intermediate). The information provided by the registrant contains structures and inherent properties of the substance, any other names, hazard information, PBT assessment, information on the life cycle stages (how the substance is used, for which processes, in which industries, whether there is any consumer use), environmental fate and pathways, ecotoxicological information, toxicological information and guidance on safe use. The European Chemical Agency (ECHA) compiles the data from the dossiers submitted and makes it available online, except for what is back as confidential business information (CBI). As of 17.10.19, information was available for 22,468 unique substances.	 Tonnage information Despite some limitations⁸, REACH registered substances provides information on the tonnage of substances, which is crucial for this study. Because of the tonnage threshold, it is possible to deduce that substances that appear on the list are produced/imported in the EEA for a quantity that exceeds 1 tonne. In some cases, a larger specific tonnage band is provided. Use and industrial sector information is a general indication of potential for exposure for humans and the environment at different life cycle stages. Industrial information is used to determine sectors that are using the substance to manufacture mixtures or articles (both manufacture and downstream users). A major limitation of the REACH database is that it does not include polymers. Furthermore, the release factors used to indicate exposure for humans and environment are very general and are not adjusted for each chemical.	18
Pre-registered substances	The ECHA database on pre-registered substances is a list of 145,297 unique substances/entries submitted between 1.06.08 and 1.12.08 as an indication of the intention of registering them as phase-in (existing) substances under REACH.	The pre-registration of a substance indicates it is/was manufactured/imported in the EEA and whether the producer/importer of a substance requested to benefit from an extended deadline for registration under REACH. Pre- registration enabled a registrant to qualify for different registration deadlines according to the tonnage of the substance in question.	119

⁸ The calculation is based on the aggregation of all *non-confidential* quantities reported by all the registrants. The calculations exclude quantities used as intermediate in order to produce other chemicals. Beyond the fact that this system only captures the producers and importers for quantities that exceed 1 tonnes it might also create different results then what is registered by the companies as acknowledged by the ECHA.

Databases searched	Description of database	Reason for use and limitations	PFAEs found
<u>C&L Inventory</u>	This ECHA database contains classification and labelling information on notified and registered substances received from manufacturers and importers. It also includes the list of harmonised classifications. The information includes hazard labelling for physical, chemical, environmental, and human health hazards.	Although this study is not directly concerned with the intrinsic hazard properties of substances, this information can be a useful complement when discussing exposure. Furthermore, the inclusion of a substance in the C&L inventory is indicative of its use in the EEA market, whether current or in the past.	49
EURLFoodContactMaterials	The European Commission's Joint Research Centre maintains a database of substances for which information has been submitted for evaluation as a substance to be used in food contact materials.	A substance included in EURL FCM gives an important indication of the downstream uses of a substance. In some cases, information is provided on the use of the substance and maximum limits.	6
EU Cosing	The database contains substances and ingredients used in cosmetic and in some cases medicinal products.	The inclusion of a substance in this database indicates that it is used in cosmetic or related products, providing information on downstream and consumer use.	2
<u>SPIN Database</u>	This database contains information on the use of substances in products in the Nordic Countries. Rules about registration depend on the country in question. In Sweden, all chemical products should be registered whereas in the other three countries (DK, NO and FI) this is limited to dangerous products ⁹ . Consequently, information from SE is larger in scope. There are currently 28,934 substances registered in the database. It contains information about the exposure, use in different sectors. The Exposure toolbox uses an index system, which rates the substances from 1 to 3 to provide a potential worst-case exposure scenario for different targets (such as consumers or workers).	Because SPIN focuses on downstream uses of chemical substances, it complements the REACH database. It also features an exposure toolbox ¹⁰ , used to provide information on exposure for the CAS numbers for which data was available. The database uses an algorithm that accounts for direct exposure only. It excludes the impacts of diffuse pollution 'via the environment or waste disposal'. Furthermore, 'certain product types which may contribute significantly to exposure (such as toys and food packaging materials) are insufficiently represented in SPIN'. These factors contribute to underestimation ¹¹ .	22
CDR 2012 and 2016	The Chemical Data Reporting (CDR) database is maintained by the USEPA and includes substances that are on the TSCA Inventory and produced/imported in volumes of 11.4 tonnes or	The CDR database provides additional information (information on volumes, industry users, whether the substance is used in manufacturing consumer articles) and	15

 ⁹ SPIN Database, <u>Companies liable for declaration</u>, accessed November 2019.
 ¹⁰ SPIN Exposure Toolbox, <u>http://www.spin2020.com/2015/09/10/8-1-spin-exposure-toolbox/</u>

¹¹ SPIN Exposure Toolbix, <u>http://spin2000.net/?p=302</u>

Databases searched	Description of database	Reason for use and limitations	PFAEs found
	more in the US. Lower thresholds apply for substances that fall under specific regulations (1.4 tonnes). The CDR is a four-year system and each publication year covers substances which fit the description for the four years that precedes it. The information is organized based on different life cycle stages such as production, industrial use and consumer end use. Between the two reporting periods, some changes to reporting were implemented which made the scope of the CDR broader ¹² .	complements the REACH database for substances that appear in both. However, most of the information is not available to the public and withheld by the reporting companies as confidential business information.	
Inventory of Effective Food Contact Substance (USFDA FCS) Notifications	The database includes substances that are used as food contact substance and are demonstrated to be safe. It is maintained by the US Food and Drug Administration.	The presence in the database indicates the substance is used in food contact materials, an important downstream use.	15

¹² US EPA, <u>Chemical Date Reporting Results</u> 2016, Accessed December 2019.

Per- and polyfluoroalkyl ether substances: identity, production and use, January 2020

In the beginning of each section, a table is provided with an overview of the number of CAS numbers and the databases in which they appear. This information is complemented with a detailed overview of CAS numbers that appear in more than three databases. For an overview of all groups, see Table 49 in the annex.

The information gathered was then compiled into a master excel spreadsheet (available as a separate annex to this study). This spreadsheet compiles information on the CAS numbers from several databases, to the extent possible without losing user-friendliness. Information available for each substance differs greatly and this is also reflected in the database. Where information was available, the database contains name, trade names, structure of the chemical, physical form, information from REACH database on volumes, manufacturers and downstream uses, additional information from SPIN, information from C&L inventory on hazards and information from US CDR on volumes. It also provides an overview of the databases the CAS number appears in. There is also a column dedicated to the source of the information presented in the table. Following the example of the US CDR, an additional column was created for plain CAS numbers (for instance, 37382642 for CAS RN 37382-64-2), which made it possible to sort the CAS numbers, based on simple number ordering. The list was then sorted again for substance group ID (1 to 5).

Table 2 below presents several examples from the databases, excluding some information such as registration status due to space limitations.

Table 2 An example of how information is presented in the excel database which is a separate annex to this document, other columns are removed due to limitations in page size

ID	CAS RN	Chemical Name	Formula	Physical form	C&L Information	Manufacturer	Uses	Industrial Sector	Downstrea m Uses	Production/I mport Volume
1	69991-62-4	Ethene, 1,1,2,2-tetrafluoro-, oxidized, polymd., reduced	Unspecified	Unknown	No result	Solvay Specialty Polymers	Oil and water repellent	Paper, food	Food contact materials	Unknown
2	31175-20-9	Ethanesulfonic acid, 2-[1- [difluoro[(1,2,2- trifluoroethenyl)oxy]methyl]- 1,2,2,2-tetrafluoroe thoxy]- 1,1,2,2-tetrafluoro-, polymer with 1,1,2,2-tetrafluoroethene	(C7-H-F13- O5-S.C2- F4)x-	Unknown	Н315, Н319, Н335	E I Dupont de nemours & co	Several	Reparations for cleaning the hair, oil and water repellent,	Protective clothing, hair products, fuel cells	Unknown
3	1187-93-5	Trifluoro(trifluoromethoxy)ethyle ne	C3F6O	Gas	H315; H319; H220; H280; H332; H335	Chemours, Solvey, AGC Chemicals	Used in manufact uring of plastics	Plastics, thermoplastics	Anti-stick materials, food contact materials	100 - 1 000 tonnes per year
4	3330-14-1	Propane, 1- 1- difluoro(1,2,2,2- tetrafluoroethoxy)methyl - 1,2,2,2-tetrafluoroethoxy - 1,1,2,2,3,3,3-heptafluoro-	C8HF17O2	Unknown	No result	Dupont (US)	Unknown	Basic organic chemical manufacturing	Unknown	Unknown

3.4.2 Further internet search using CAS numbers

For all CAS numbers not found in any of the databases, an additional Google search was conducted. The number of results that Google search provided varied greatly, depending on the CAS number. In some cases, no matching results were found. These CAS numbers are indicated in the excel database and also in the annex. Where the search returned many results, the study team prioritised information for substance name, structure and formula.

The researchers also gathered information via company websites. This helped to compile additional data on uses of PFAEs and industry applications. The hypothesis was that the manufacturer of the substances identified in the previous stages also had other products related to other CAS numbers. Furthermore, they were likely to use the same substances for different applications. Safety Datasheets (SDSs) accompanying the products at times included the CAS numbers or the molecular formula, making it possible to connect the products and applications to the CAS numbers.

However, an exhaustive use of this approach and a thorough scanning of the product catalogues was not possible within the time limitations of this study. In order to overcome this obstacle, research on the company websites focused on industries/products and applications which were known from the CAS numbers as well as general information from the literature.

3.4.3 Research regarding human and environmental exposure

Potential for exposure to the substances that are the subject of this study is explored to a limited extent, due to the limited availability of relevant information.

3.4.3.1 Information compiled from REACH and SPIN

Registered Substances Database (REACH)

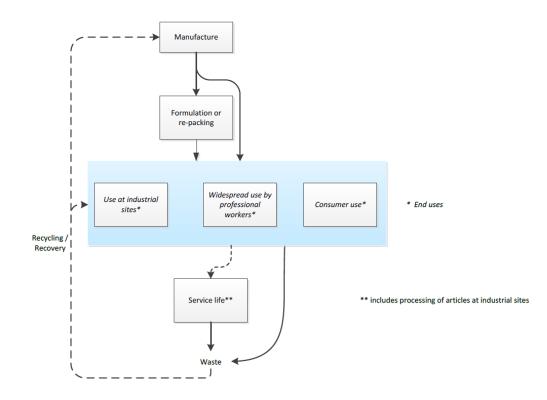
The first pillar of the information on exposure of the humans and the environment compiles data from REACH registered substances database, C&L inventory and SPIN database. The information from REACH is integrated into different sections. Furthermore, sector information is sometimes available, which gives an indication of downstream and consumer uses. Both were used to complement information on uses in articles and mixtures. The emission scenarios provided under REACH were used to give an indication of exposure, complementing other findings from desk research.

The REACH database compiles information provided by the registrants in the registration dossiers.

The registrants may provide a detailed life cycle overview for the substance, as well as exposure and risk assessments¹³. The lifecycle stages include manufacture (M), formulation or re-packing (F), use at industrial sites (IS), widespread use by professional workers (PW), consumer use and service life (SL)¹⁴. The following section briefly describes the life cycle stages based on the REACH Guidance Document.

 ¹³ ECHA, <u>Guidance on Information Requirements and Chemical Safety Assessment Chapter R.12</u>: Use description.
 ¹⁴ Ibid.





Life cycle stage 1: Manufacturing

This stage refers to all activities which are related to manufacturing of the substance from raw materials and *'all handling'* operations which are inherent to its manufacturing process.

Life cycle stage 2: Formulation or re-packing

All types of operations necessary to use the manufactured substance in mixtures to create products to be put on the market falls under this stage. It also encompasses activities which involve repackaging of the substance, for instance into smaller amounts, even if there is no mixing taking place. These operations take place at industrial sites.

Life cycle stage 3: Uses at industrial sites

According to the Guidance document "all end-uses of the substance (as such or in mixture) carried out at industrial sites should be reported under this stage". It applies to cases where the substance is a 'reactive agent, a non-reactive ingredient in an article and is released completely during the industrial process or transformed into waste.' If the substances become a part of the article, the registrant has to report information on service life stage.

Life cycle stage 4: Use by professional workers

This stage refers to the use of the chemical substances by professionals, however at a different scale than industrial sites. Whereas uses at industrial sites refers to large operations, use by professional workers

include smaller scale operations usually not requiring a permit (for instance under Industrial Emissions Directive).¹⁵. The REACH guidance document provides useful examples to illustrate such uses: façade cleaning services, car washes, hairdressing or other beauty services, indoor cleaning services, maintenance for office-household equipment and micro companies which operate in building and construction¹⁶. As such, uses by professional workers involve smaller scale but more numerous activities in a very large number of sectors. The total amounts of chemicals used will most likely be low per operation, but together, these uses may amount to considerable volumes, when all sectors are aggregated. This also implies a wider geographical spread. This distinction is useful to assess downstream users with regard to uses of per-fluorinated compounds. For instance, the leather industry in Italy falls under this category and places like Veneto where such businesses are concentrated could have been a potential diffuse source of contamination for PFAS¹⁷.

Life cycle stage 5: End use by professionals or consumers (Article Service Life)

This stage is pertinent for potential exposure to chemicals through use of articles. In such instances, the registrant must provide information on the safe uses of the article¹⁸.

Environmental release category (REACH)

The lifecycle stages explained above lead to different exposure and release scenarios. The REACH guidance document provides the following description for the ERCs (Environmental Release Categories): describes the activity from the environmental (release) perspective. One ERC is assigned to one contributing activity (environmental perspective) but it can be linked to one or more contributing activities from an occupational perspective (e.g. several PROCs per ERC). This means that one set of environmental conditions for a use can be connected to several sets of operational conditions (OC)/ risk management measures (RMM) for the different activities of workers carried out at this site¹⁹.

The environmental release categories (ERC) that are referred to in the relevant sections for each group mainly describe the manufacturing of the substance and its use at industry sites. Following are some examples:

- ERC1 Manufacture of the substance
- ERC2 Formulation into a mixture
- ERC4 Used as non-reactive processing aid at industrial site (no inclusion onto or into the article)
- ERC6a Use of intermediate
- ERC6b Use of reactive processing aid at industrial site (no inclusion into or onto article)
- ERC6c Use of monomer in polymerisation processes at industrial site (inclusion or not into/onto article)
- ERC7– Use of functional fluid at industrial site

¹⁵ REACH (2015), <u>Guidance on Information Requirements and Chemical Safety Assessment, Chapter R: 12</u>.

¹⁶ REACH (2015), <u>Guidance on Information Requirements and Chemical Safety Assessment, Chapter R: 12</u>.

¹⁷ Nordic Council of Ministers (2018), <u>The cost of inaction: A socioeconomic analysis of environmental and health impacts linked</u> to exposure to PFAS.

 ¹⁸ REACH, Newsletter, <u>New consumer exposure example helps companies to comply with REACH</u>.
 ¹⁹ Ibid.

Each of these categories have assigned release factors to air, water (before treatment) and to soil. The emissions are described as '*default worst case release factors resulting from the conditions of use*' in each ERC. The complete list of ERCs and release factors is provided in Annex 10.4. However, these are values developed as general guidance to help their exposure estimation and are not fine-tuned to the chemical substance (unless provided by the registrant)²⁰. They have been also criticised for being too conservative because of this general aspect²¹.

Process Categories

Registrants of the substances also provide information on the process within the life cycle, which are categorised using a harmonised system of process categories (PROCs). This information provides further details regarding the circumstances under which exposure can happen for each of the stages of the life cycle, based on type of activity. Different activities and processes result in different levels of exposure risk.

Following are examples of PROCs most commonly reported for substances included in this report:

- Transfer of substances or mixtures to 'dedicated facilities'
- Transfer of a substance or mixtures into small containers, for example on a filling line
- Use as a laboratory reagent
- Manual maintenance (cleaning and repair) of machinery
- 'Manufacture or formulation in the chemical industry in closed batch processes with occasional controlled exposure or processes with equivalent containment conditions'

The SPIN database

The SPIN database uses an algorithm to indicate worst case exposure scenarios for humans and environment from the products (excluding the impacts of diffuse pollution, focusing only to the environment that is in the proximity of the point source)²². It provides indicative and approximative indicators, but it is useful in order to see the steps in the lifecycle where potential for exposure arises. The detailed list of indicators is provided in the annex.

C&L (Classification and Labelling) Inventory

Only the sections about health and environmental hazards of the chemicals are included in the excel datasheet. The complete list of hazard codes can be found <u>here</u>²³.

3.4.3.2 Desk research using keywords

Desk research to identify additional information varied across different substance groups. For Group 4 substances where there is information on specific substances like GenX, reports from the public authorities of countries where there is a known production facility was prioritised. Information was complemented by academic literature focusing on environmental releases. For the groups 1, 2, 3 and 5, this was not possible since general group names provided little information. For these groups, an

²⁰ ECHA, <u>Guidance on Information requirements and Chemical Safety Assessment Chapter 16</u>.

²¹ ECOTOC (2009), <u>Addendum to ECOTOC Targeted Risk Assessment</u>, Report No. 93

²² SPIN Exposure Toolbox, available at: <u>http://www.spin2020.com/2015/09/10/8-1-spin-exposure-toolbox/</u>, accessed November 2019.

²³ ECHA, What is an infocard?

additional CAS number-based Google search was conducted using a pre-selected list of keywords. These keywords were: exposure, sample, release, monitoring, screening, pollution and contamination. This exercise was not carried out for all CAS numbers, since most of the CAS numbers did not return any results on the previous stage explained in the section 3.4.2. Therefore, only the CAS numbers that returned a significant number of hits from the previous research was included in this step. Other information identified using the CAS numbers as described in the section 3.4.2 above was also synthesised in this section.

3.4.4 Interviews

To gather additional information, interviews were conducted with various stakeholders. Interviews focused on two different types of stakeholders: the first group of interviews were with competent authorities involved in the research or regulation of PFAEs. The second groups mostly consisted of private companies and industry associations. Little information was gathered from contacts at the private companies.

4 Findings: Group 1: Perfluoropolyethers (PFPEs)

4.1 Overview of the substances in Group 1

4.1.1 Characteristics of Group 1 substances, including chemical structure

Group 1 consists of perfluoropolyethers (PFPEs), which are polymers from perfluoroether monomers. One structural trait is that they have moieties of –CnF2n-O-CmF2m- in the polymer backbone. There are three main families of PFPEs on the market, marketed under the brand names Krytox (Chemours), Fomblin/Fluorlink/H-Galden/Solvera (Solvay), and Demnum (Daikin).

PFPEs are mostly advertised as being very stable, relatively non-toxic, and not having impacts on the environment. For example, the Solvay website²⁴ identifies the key features of Fomblin as solvent resistance; non–reactive with metal, plastic, elastomers and rubber; non-flammable; environmentally safe; not a volatile organic chemical; and non–toxic behaviour, among many other properties.

127 CAS numbers have been identified in this group. It is worth noting that desk research identified several additional substances that were not identified using CAS number searches (e.g., Demnum, which does not have a CAS number). Desk research also shows that substances marketed under the same brand name may have distinct chemical characteristics and are thus allocated to different groups in this study (e.g., some substances under the brand "Fluorolink" are allocated to Group 1, whereas other are allocated to Group 5). This, coupled with the fact that very little information is available in the public domain, would suggest PFPEs are both complex and little-researched.

The table below lists the CAS numbers, chemical names, and structure for those substances that appeared in three or more databases prioritised for this study²⁵.

²⁴ Solvay, <u>Fomblin® PFPE Lubricants</u>, accessed November 2019

²⁵ Unless stated otherwise, all structures presented in the table are retrieved from <u>PubChem</u>, provided by the US National Library of Medicine.

CAS RN	Chemical name	Listed in	Structure
60164-51-4	Poly[oxy[trifluoro(trifluoromethyl)-1,2-ethanediyl]], α-(1,1,2,2,2-pentafluoroethyl)-ω- [tetrafluoro(trifluoromethyl)ethoxy]-	Pre-registered substances, C&L, SPIN	
69991-61-3	Ethene, 1,1,2,2-tetrafluoro-, oxidized, polymd.	Pre-registered substances, C&L, SPIN	Not available
69991-67-9	1-Propene, 1,1,2,3,3,3-hexafluoro-, oxidized, polymd.	Pre-registered substances, C&L, SPIN, US EPA CPCAT	F = F = F = F = F = F = F = F = F = F =
88645-29-8	Polyperfluoroethoxymethoxy difluoroethyl peg ether	Pre-registered substances database, C&L, US FDA FCM	Not available
161075-14-5 Hexafluoropropene, oxidized, oligomers, reduced I		Pre-registered substances database, C&L, SPIN	Not available
162492-15-1 Tetrafluoroethylene, oxidized, oligomers, reduced, P		Pre-registered substances database, C&L, SPIN	Not available
200013-65-6Diphosphoric acid, polymers with ethoxylated reduced methyl esters of reducedPre date		Pre-registered substances database, US FDA FCM, SPIN, CDR 2016	Not available

Table 3 The CAS numbers, chemical names, and molecular structures of the Group 1 substances that appeared in 3 or more databases, as of November 2019.

Limited chemical structures are available for the Group 1 substances in the public domain. Structures have been retrieved for only six substances, and even then, in several cases it seems the structures published were not accurate²⁶. In general, very little is known about polymer structures, often with ambiguous terms in their chemical names.

More than 10 substances have been identified only in Japanese and Korean databases. These databases have not been systematically checked due to language barriers. And no further information was available from a Google search.

4.1.2 Group 1 substances identified on the EEA market

None of the CAS numbers in Group 1 are listed in ECHA's Registered substances database. 60 CAS numbers are in the Pre-registered substances database. Nine CAS numbers appear in the C&L inventory and nine CAS numbers in the SPIN database. Half of the substances do not appear in any of the databases. The table below provides an overview of the Group 1 substances that have been identified in the databases:

Databases searched	CAS numbers that appear in the database
ECHA registered substances database	0
ECHA pre-registered substances	60
C&L inventory	9
EU FCM	1
EU Cosing	2
SPIN Database	9
USFDA FCS	3
CDR 2012 (USA)	0
CDR 2016 (USA)	1
None of the above	63
Total	127

Table 4 Overview of CAS numbers in Group 1 and appearance in databases

The table below summarises the substances set out on the C&L Inventory and the SPIN (indicating if they were also identified as pre-registered substances). Further details for all CAS numbers are provided in the annex.

Table 5 Registration sta	tus for selected CAS numbers
--------------------------	------------------------------

CAS RN	Name	Registered Substances	Pre- registered substances ²⁷	C&L Inventory	SPIN
51798-33-5	Poly(oxy(trifluoro(trifluoromethyl)-1,2- ethanediyl)), alpha-(1-carboxy-1,2,2,2- tetrafluoroethyl)-omega- (tetrafluoro(trifluoromethyl)ethoxy)-			х	x
60164-51-4	Poly[oxy[trifluoro(trifluoromethyl)-1,2- ethanediyl]], α -(1,1,2,2,2-pentafluoroethyl)- ω -[tetrafluoro(trifluoromethyl)ethoxy]-		Х	Х	x

²⁶ E.g. For CAS 88645-29-8 and CAS 162492-15-1 diagrams showed tetrafluoroethylene, which are not relevant here.

²⁷ Not all Pre-registered substances are listed in this table due to space constraints, please see the annex for a full list.

CAS RN	Name	Registered Substances	Pre- registered substances ²⁷	C&L Inventory	SPIN
69991-61-3	Ethene, 1,1,2,2-tetrafluoro-, oxidized, polymd.		х	х	х
69991-67-9	1-Propene, 1,1,2,3,3,3-hexafluoro-, oxidized, polymd.		х	х	х
88645-29-8	Polyperfluoroethoxymethoxy difluoroethyl peg ether		х	Х	
156559-18-1	2-Oxiranemethanol, polymers with reduced Me esters of reduced polymd. oxidized tetrafluoroethylene			х	
161075-02-1	Tetrafluoroethylene, oxidized, oligomers, reduced, decarboxylated		х		x
161075-14-5	Hexafluoropropene, oxidized, oligomers, reduced and hydrolyzed		х	х	х
161212-22-2	Hexafluoropropene, oxidized, oligomers, telomers with chlorine, reduced, reaction products with methanol and octadecylamine		х		х
162492-15-1	Tetrafluoroethylene, oxidized, oligomers, reduced, methyl esters, reduced, reaction products with ethylene oxide		х	х	х
200013-65-6	Diphosphoric acid, polymers with ethoxylated reduced methyl esters of reduced polymerized oxidized tetrafluoroethylene		х		х
769967-14-8	[No public or meaningful name is available]			Х	

4.2 Group 1 substances used in mixtures

Several areas of application in a wide range of industries have been identified, and different commercial products are available (see Table 6). Some of these products are mixtures used as such (for instance, lubricants) and others are used to give certain characteristics to other products, such as emulsifiers in cosmetics or grease/water proofing of paper. PFPEs as liquid lubricants have been used in a number of industries for decades²⁸; specific uses include greases used in the chemical, electronic, military, nuclear, data processing, and other industries in need of high-performance lubrication. In addition, PFPEs have also been used in medical research, especially for MRIs. It is worth noting that both Krytox and Fomblin are represented several times in Table 6, as there are many different products under the same brand names²⁹.

²⁸ See for example Chemours, <u>Krytox</u>, accessed December 2019.

²⁹ For example, one commercial database lists 40 different safety datasheets for different Fomblin products. The exact chemical identities including CAS numbers are not available, so a comparison of different products was not possible: Matweb, FOMBLIN® Technical Data Sheets

CAS RN	Company	Mixture	Used
			as/function
51798-33-5	Chemours	Used to make Krytox™ 157FSH (90-100% of total product)	Lubricant ³⁰
60164-51-4	Chemours	Used to make Krytox [®] Sodium Nitrite Inhibited PFPE/PTFE Greases (71 - 80% of total product) ³¹ Krytox [®] PFPE High Performance Lubricant (60 – 100% of	Lubricant
		total product) ³²	
		Laboratory chemicals	
		Manufacture of substances	
		Scientific research and development	
		Used to make Fomblin,	
		FOMBLINCR 862 (50-55% of total product) ³³	
		Fomblin Z60 (100% of total product) ³⁴	
69991-61-3	Solvay	Fomblin Z-15 (Reg):100% of total product ³⁵	Not specified
	,	Personal Care Product	
		Chemical Industrial	
		Cosmetics: Personal Care Products	
		Lubricants and additives	
		Welding and soldering agents	
		Manufacture of machinery and equipment	
		Lubricants	
		Lubricating grease and oil	
		Used to make Fomblin Y	
		Fomblin [®] HC ³⁶	
		FOMBLIN [®] Y LVAC (99.9% of total product) ³⁷	
		Galden HT-90 Assay (100% of total product) ³⁸	
69991-67-9	Solvay	SOLKATHERM [®] SES 36 (35% of total product) ³⁹	Not specified
		Lubricating Oil	
76415-97-9	Castrol	Used to make Brayco 815Z ⁴⁰	Lubricant
88645-29-8	Solvay	Lubricant for disk drives	Lubricant ⁴¹

Table 6 Perfluoropolyethers used in mixtures, identified via CAS number

³⁰ Chemours, <u>2018, SAFETY DATA SHEET Krytox™ 157FSH</u>, accessed November 2019.

³¹ DuPont, (2015), <u>Safety Data Sheet: Krytox® Sodium Nitrite Inhibited PFPE/PTFE Greases</u>, accessed November 2019.

³² Henkel, (2011), <u>Material Safety Data Sheet</u>, accessed November 2019.

³³ Edwards, <u>MATERIAL SAFETY DATA SHEET PRODUCT NAME : GREASE - FOMBLINÆ CR 862</u>, accessed November 2019.

³⁴ Synquest Laboratoires, (2015), <u>Fomblin Z60 (Average MW = 13000) Safety Data Sheet 2108260</u>, accessed November 2019.

³⁵ Synquest Laboratoires, (2015), <u>Fomblin Z-15</u>, accessed November 2019.

³⁶ Solvay Solexis, <u>Fomblin HC Classic</u>, accessed November 2019.

³⁷ SOLVAY SPECIALTY POLYMERS USA, LLC, (2015), Safety Data Sheet: FOMBLIN® Y LVAC, accessed November 2019.

³⁸ Fluorochem Ltd, (2011), <u>Safety Data Sheet</u>, accessed November 2019.

³⁹ SOLVAY FLUORIDES, (2015), <u>SAFETY DATA SHEET, SOLKATHERM [®] SES 36</u>, accessed November 2019.

⁴⁰ American Chemicals, <u>Brayco 815Z</u>, accessed November 2019.

⁴¹ United States International Trade Commission, 2012, <u>MEMORANDUM ON PROPOSED TARIFF LEGISLATION of the 112th</u> <u>Congress</u>, accessed November 2019.

CAS RN	Company	Mixture	Used as/function
156559-18-1	Solvay	Reacted with other polymers to improve surface properties Used to make Immersol-w (Zeiss) making 50%-60% ⁴² . Used to increase the resolving power of a microscope	Lubricant, water/oil repellent ⁴³
		used as a heat transfer media, a lubricant, and a solvent in	
161075-02-1	Solvay	semiconductor device fabrication	Not specified ⁴⁴
161075-14-5	Solvay	lubricants and corrosion inhibitors in fluorinated greases and, used for various release and surface treatment applications effective in sub-zero temperatures ⁴⁵ Used to make CARBAFLO XTR S5 F80; 1-2,4% total weight ⁴⁶ , used in automotive industry ⁴⁷	Lubricant
		Used to make GOLDSEAL GLASS COATING CONCENTRATE	
161212-21-1	GoldSeal	4000m2 PART B (20% of total product)	Not specified ⁴⁸
162492-15-1	Solvay	Polymer additive, used to make Fluorolink [®] E10-H (100% of total product) ⁴⁹	Non-stick coating
162567-74-0		Cosmetics	Surfactant, Emulsifier ⁵⁰
162567-75-1		Cosmetics	Surfactant, emulsifier ⁵¹
200013-65-6	Solvay	Possibly Fomblin: FOMBLIN HC/P2-1000 Lubricants, Paper manufacturing Finishing agent	Lubricants, finishing agent
		Possibly Fomblin: FOMBLIN HC/P2-1000	Lubricant
		Lubricants and lubricant additives/Paper	Water/grease
200013-65-6	Solvay	manufacturing/Finishing agents/Food packaging	repellent ⁵²

⁴² Zeiss, <u>Safety Data Sheet Immersol W</u>, accessed November 2019.

Cadre inc. <u>RFHC [®] Surface Treatment Series</u>, accessed November 2019.

⁵² United States International Trade Commission (2012), <u>Memorandum On Proposed Tariff Legislation</u>

⁴³ United States Trade Commission (2012), <u>Memorandum On Proposed Tariff Legislation Of The 112th Congress</u>, accessed November 2019.

⁴⁴ United States Trade Commission (2012), <u>Memorandum On Proposed Tariff Legislation Of The 109th Congress</u>, accessed November 2019.

⁴⁵ United States Trade Commission (2012), <u>Memorandum On Proposed Tariff Legislation Of The 112th Congress</u>, accessed November 2019.

⁴⁶ Fuchs (2015), <u>Safety Data Sheet according to Regulation (EC) No. 1907/ 2006 (REACH): CARBAFLO XTR S5 F80, accessed</u> November 2019, accessed November 2019.

⁴⁷ FUCHS LUBRITECH GMBH, <u>CARBAFLO XTR 5F</u>, accessed November 2019.

⁴⁸ CF Supplies Intern Ltd, <u>Product Name : GOLDSEAL GLASS COATING CONCENTRATE 4000m2 PART B Material Safety Data</u> Sheet, accessed November 2019.

⁴⁹ Solvay, <u>Fluorolink[®] E10H</u>, accessed November 2019.

⁵⁰ ParChem, <u>POLYPERFLUOROETHOXYMETHOXY PEG-2 PHOSPHATE</u>, accessed November 2019.

⁵¹ Trade Navi, <u>LISTADO DE INGREDIENTES PERMITIDOS EN PRODUCTOS COSMÉTICOS</u>, accessed November 2019.

Of The 112th Congress, accessed November 2019.

Trier, X., Taxvig, C., Rosenmai, A. K., & Pedersen, G. A. (2018). <u>PFAS in paper and board for food contact: Options for risk</u> management of poly-and perfluorinated substances. Nordic Council of Ministers.

CAS RN	Company	Mixture	Used as/function
223557-70-8	Chemwill		Not specified 53
	(Asia)	Hair and skin conditioning products	
		Used in a mixture (5%) creating GEARBOX LUBRICANT -	
370097-12-4		DRYNERT 25/6 and GREASE - FOMBLINÆ CR 861 (7-13%)	Not specified 54
	Akzo	Used to make INTERSLEEK 1100SR PART C (50 – 75%),	
1260733-08-1	Nobel	anti-fouling marine coating ⁵⁵	Not specified

One substance (CAS Number 162567-74-0, Hexafluoropropene, oxidized, oligomers, reduced, reaction products with methanol, reduced, reaction products with ethylene oxide and phosphoryl trichloride, hydrolysed), a product under the brand of Fomblin (RFHC Reactive Fomblin⁵⁶) has been banned in cosmetics by H&M⁵⁷.

4.3 Group 1 substances used in articles

Many of the substances in Group 1 have been also used to treat polymers, mixtures, and other materials to impart certain properties (see Table 7).

CAS RN	Company	Article	Used as/function
69991-62-4	Solvay	Food-contact paper/paperboard	oil and water repellent ⁵⁸
69991-67-9	Solvay	Personal Care Product Chemical Industrial Cosmetics: Personal Care Products Lubricants and additives Welding and soldering agents Manufacture of machinery and equipment Lubricants Lubricating grease and oil Used to make Fomblin Y	
		Fomblin [®] HC59 FOMBLIN [®] Y LVAC (99.9% of total product) ⁶⁰	

Table 7 Perfluoropolyethers identified use in relation to articles

⁵⁴ Chemical Book, <u>https://www.chemicalbook.com/ProdSupplierGWCB91448370_EN.htm</u> accessed November 2019.

Edwards 2011, <u>MATERIAL SAFETY DATA SHEET PRODUCT NAME : GEARBOX LUBRICANT - DRYNERT 25/6</u>, accessed November 2019.

⁵³ Google Patents, <u>Korrosionsschutzgel und Korrosionsschutzbeschichtung für elektronische und/oder mikromechanische</u> <u>Bauteile</u>, accessed November 2019.

Edwards, <u>MATERIAL SAFETY DATA SHEET PRODUCT NAME : GREASE - FOMBLINÆ CR 861</u>, accessed November 2019.

⁵⁵ Akzon Nobel, <u>Safety Data Sheet (2017) INTERSLEEK 1100SR PART C</u>, accessed November 2019.

⁵⁶ Cadre inc. <u>RFHC [®] Surface Treatment Series</u>, accessed November 2019.

⁵⁷ H&M GROUP, 2018, <u>H&M Group Chemical Restrictions 2018: Restricted Substances List (RSL), Cosmetic Products</u> accessed November 2019.

⁵⁸ U.S. Food and Drug Administration, <u>Inventory of Effective Food Contact Substance (FCS) Notifications: FCN No. 538</u> <u>Solvay Specialty Polymers USA, LLC</u>, accessed November 2019.

⁵⁹ Solvay Solexis, <u>Fomblin HC Classic</u>, accessed November 2019.

⁶⁰ SOLVAY SPECIALTY POLYMERS USA, LLC, 2015, <u>Safety Data Sheet: FOMBLIN® Y LVAC</u>, accessed November 2019.

CAS RN	Company	Article	Used as/function
		Galden HT-90 Assay (100% of total product) ⁶¹ SOLKATHERM [®] SES 36 (35% of total product) ⁶²	
88645-29-8	Solvay	Contact lenses, disk drives	Lubricant ⁶³
161075-02-1	Solvay	Semiconductor device	Heat transfer media ⁶⁴
200013-65-6	Solvay (Possibly FOMBLIN HC/P2- 1000)	Paper products	Water and oil repellent ⁶⁵⁶⁶
200013-65-6	Solvay (Possibly Fomblin: FOMBLIN HC/P2-1000)	Paper/Food contact articles	Water/grease repellent ⁶⁷

4.4 Key producers and suppliers

It is clear that there are several manufacturers heavily involved in the industry: Chemours produces Krytox, and Daikin produces Demnum. A Google search suggests that the following companies are involved in the PFPE market, according to their company websites: and some (for example M&I Materials Limited) also clearly manufacture the substance:

- Dow Corning⁶⁸
- Kluber Lubrication⁶⁹
- ICAN⁷⁰
- M&I Materials Limited⁷¹
- Nye Lubricants⁷²
- IKV Tribology⁷³

It is clear that some of these companies, such as M&I Materials Limited, manufacture the greases and lubricants themselves, however it is not clear which of these companies have produced/supplied PFPEs in Europe, even when they have a European presence. There is a complex web of relations within the

⁶⁸ Dow Corning Automotive, <u>Smart Lubrication Solutions</u>, accessed November 2019.

⁶¹ Fluorochem Ltd, 2011, <u>Safety Data Sheet</u>, accessed November 2019.

⁶² Solvay Fluorides, 2015, <u>SAFETY DATA SHEET, SOLKATHERM [®] SES 36</u>, accessed November 2019.

⁶³ United States International Trade Commission, 2012, <u>Memorandum On Proposed Tariff Legislation of the 112th Congress</u>, accessed November 2019.

⁶⁴ United States International Trade Commission, 2006, <u>Memorandum On Proposed Tariff Legislation of the 109th Congress</u>, accessed November 2019.

⁶⁵ U.S. Food and Drug Administration, <u>Inventory of Effective Food Contact Substance (FCS) Notifications: FCN No. 962</u> <u>Solvay Specialty Polymers USA, LLC,</u> accessed November 2019.

⁶⁶ Trier, X., Taxvig, C., Rosenmai, A. K., & Pedersen, G. A. (2018). <u>PFAS in paper and board for food contact: Options for risk</u> management of poly-and perfluorinated substances. Nordic Council of Ministers.

⁶⁷ United States International Trade Commission, 2012, <u>Memorandum On Proposed Tariff Legislation Of The 112TH Congress</u>, accessed November 2019. Fejl! Linkreferencen er ugyldig.

⁶⁹ Klueber, <u>PFPE Products for the Chemical Industry</u>, accessed November 2019.

⁷⁰ <u>http://web.icanchem.com.cn/</u>

⁷¹ https://www.apiezon.com/

⁷² https://www.nyelubricants.com/uniflor

⁷³ http://www.ikvlubricants.com/

industry and its supply chains. For example, a Google search unearthed a press release from 2011 that Solvay was to increase its production capacity for FOMBLIN-Y[®] and GALDEN in Spinetta Marengo, Italy, following a 15 million Euro upgrade⁷⁴. In 2013, Klüber Lubrication München SE & Co. KG acquired the PFPE grease business from Solvay Specialty Polymers Italy S.P.A.⁷⁵. In April 2016, IMCD was chosen by Solvay Specialty Polymers to distribute its Fomblin PFPE lubrication grades in Europe, Middle East and Africa⁷⁶.

4.5 Volumes of Group 1 substances

4.5.1 Within the EEA

Information regarding the production volumes of the chemicals in Group 1 is scarce in the public domain; however, a non-verified commercial market report suggested that UK, Germany, France, and Italy are the main producers and users⁷⁷.

According to the SPIN database, around 1 tonne of CAS RN 60164-51-4 (one Krytox product) was used in nine preparations (mixtures) in Sweden in 2017. For Fomblin Y (CAS RN 69991-67-9), Sweden reported a total use of 0.5 tonnes in 2017, whereas Denmark reported 0.3 tonnes in 2016. The two countries reported the use of Fomblin Y in 17 and 5 preparations, respectively.

On the basis of a Google search, several documents were found on the website for the United States International Trade Commission⁷⁸ concerning tariff legislation for several substances in Group 1. Dated 2012, these documents concern a request by Solvay to import several PFPEs tariff free into the US from Italy (see Table 8), as no US-based companies were making either the substance or a competing product. While these documents are certainly limited in scope, they suggest that in 2012, the US were not manufacturing these substances and Italy/Solvay was, and show estimated values of dutiable imports in the following five years by 2017.

CAS RN	Chemical Name	Estimated value of dutiable imports by 2017 (\$)
156559-18-1	No public name is available	2,000,000
161075-14-5	Hexafluoropropene, oxidized, oligomers, reduced and hydrolyzed	2,000,000
200012 65 6	Diphosphoric acid, polymers with ethoxylated reduced methyl esters of reduced	13,000,000
200013-65-6	polymerized oxidized tetrafluoroethylene	

Table 8 Estimated value of Group 1 substances imported into the US, based on documentation from US International Trade Commission

⁷⁴ Chemical Parks in EU, (2011), <u>SOLVAY increases FOMBLIN-Y®</u> and <u>GALDEN®</u> production capacity to continue serving fast growing demand, accessed November 2019.

⁷⁵ Klüber Lubrication, (2013), <u>Klüber Lubrication acquires PFPE grease business from Solvay</u>, accessed November 2019.

⁷⁶ CHEManager, (2016), <u>IMCD Distributes Solvay Fluorinated Lubricants</u>, accessed November 2019.

⁷⁷ Global Market Insights, 2019, <u>Perfluoropolyether Market By Product (PFPE-K, PFPE-M, PFPE-Z, PFPE-Y, PFPE-D), By Type (Grease, Oil), By End-Use (Automotive, Aerospace, Electronics, Chemical & Petrochemical, Food Processing, Metal Processing, Medical Industry Equipment, Power Generation, Textile, Pulp & Paper), Industry Outlook Report, Regional Analysis, Application Potential, Price Trends, Competitive Market Share & Forecast, 2019 – 2025, accessed November 2019.</u>

⁷⁸ United States International Trade Commission, <u>Congress Bill Reports – 112th Congress</u>, accessed November 2019.

88645-29-8	Polyperfluoroethoxymethoxy difluoroethyl peg ether	8,000,000	

Information was available for at least one other substance but was dated earlier, and the amounts were less than 1 million dollars: in 2006 CAS RN 161075–02–1, Ethene, tetrafluoro, oxidized, polymerized, reduced, decarboxylated was predicted to have an estimated dutiable value of \$82,000 by 2010⁷⁹.

⁷⁹ United States International Trade Commission, <u>Memorandum On Proposed Tariff Legislation of the 109th Congress</u>, accessed December 2019.

4.5.2 Globally

Statistics regarding the global manufacture and use of the substances in Group 1 are not identified.

One substance (CAS RN 200013-65-6, Diphosphoric acid, polymers with ethoxylated reduced methyl esters of reduced) was registered in the US CDR database. The amount of the substance manufactured in the USA was 'withheld' or considered as confidential business information. However, because of the legal reporting threshold, it can be deduced that these substances are produced or imported in volumes of 25,000 pounds (11,340 kg) or more at two sites in the US⁸⁰. It was reported that the site producing/importing 99% of the total volume of the substances has between 100 and 500 employees, and this site concerns the manufacture of finishing agents for paper. The other site, representing 1% of the total volume, makes lubricants.

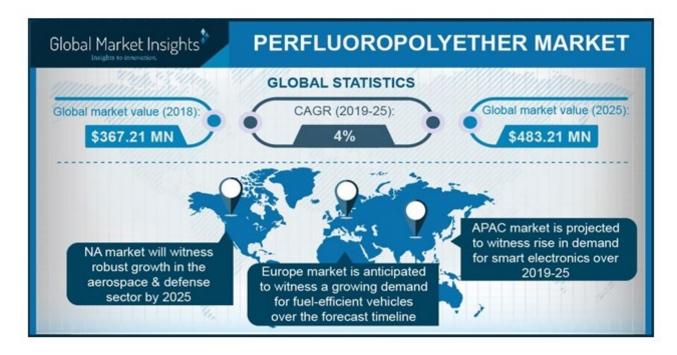
A number of market reports on the value of the PFPE market globally were noted⁸¹, they cost several thousand USD each. Considering the authenticity of such reports is often in doubt, they were not accessed in the context of this study. According to the "teaser" of one such non-verified report on their websites, the Perfluoropolyether Market size exceeded USD 350 million globally in 2018 and was estimated to grow over 4% compound annual growth rate between 2019 and 2025⁸². The same report linked the PFPE market to uses in fuel-efficient vehicles and predicted an increase in demand for Europe.⁸³⁸⁴

⁸⁰ EPA, Chemical Data Reporting, <u>The Basics</u>, accessed October 2019.

 ⁸¹ See for example "GLOBAL (UNITED STATES, EUROPEAN UNION AND CHINA) PFPE MARKET RESEARCH REPORT 2019-2025" https://www.absolutereports.com/global-united-states-european-union-and-china-pfpe-market-research-report-2019-2025-14484077, "Perfluoropolyether Market By Product Type (PFPE Oil and PFPE Grease), By Application (Aerospace, Electronics, Chemicals, Others), And Region - Global Forecast To 2023" https://marketresearch.biz/report/perfluoropolyether-market/
 ⁸² Global Market Insights, (2019), Perfluoropolyether Market By Product (PFPE-K, PFPE-M, PFPE-Z, PFPE-Y, PFPE-D), By Type (Grease, Oil), By End-Use (Automotive, Aerospace, Electronics, Chemical & Petrochemical, Food Processing, Metal Processing, Medical Industry Equipment, Power Generation, Textile, Pulp & Paper), Industry Outlook Report, Regional Analysis, Application Potential, Price Trends, Competitive Market Share & Forecast, 2019 – 2025, accessed November 2019.

⁸³ Products included in the report: PFPE-K, PFPE-M, PFPE-Z, PFPE-Y, PFPE-D Type: Grease, Oil End-use: Automotive, Aerospace, Electronics, Chemical & Petrochemical, Food Processing, Metal Processing, Medical Industry Equipment, Power Generation, Textile, Pulp & Paper. Companies covered (15): Solvay, Daikin Industries, Inc., Klüber Lubrication, The Chemours Company, Nye Lubricants, M&I Materials Limited, LUBRILOG SAS, Miller-Stephenson, Inc., Metalubgroup, TECCEM GmbH, IKV Tribology, HUSK-ITT Corporation, Fluorotech USA, Setral Chemie GmbH, Jet lube.

⁸⁴ Global Market Insights, (2019), Perfluoropolyether Market By Product (PFPE-K, PFPE-M, PFPE-Z, PFPE-Y, PFPE-D), By Type (Grease, Oil), By End-Use (Automotive, Aerospace, Electronics, Chemical & Petrochemical, Food Processing, Metal Processing, Medical Industry Equipment, Power Generation, Textile, Pulp & Paper), Industry Outlook Report, Regional Analysis, Application Potential, Price Trends, Competitive Market Share & Forecast, 2019 – 2025, accessed November 2019.



*Figure 2 Infographic providing overview of PFPEs global market*⁸⁵ *from a non-verified market research study*

4.6 The potential for exposure

4.6.1 Information from ECHA and SPIN

The SPIN database provides information on several CAS numbers. Among the Group 1 substances, 5 substances have information on exposure, mostly covering Denmark, Norway, and Sweden. The indicators use 1 to 5 and a 1 to 3 assessment scale (for use in articles), 1 meaning 'very low or no exposure' or 'very narrow range of application' and 5 referring to 'very probably exposure' and 'wide range of applications' depending on the index. The article index (last column in table 9) refers to use of the chemical in production of articles. 1 refers to 'potential use', whereas 3 refers to 'very probable use'⁸⁶. According to the assessment, in most cases there is a fairly low potential for environmental exposure. Occupational exposure is rather higher, three substances identifying a very probable exposure. The range and quantity for all substances is low (with one exception in Sweden where an intermediate range of applications was reported), and there seems to be at least probable potential for use in an article in most substances.

 ⁸⁵ Global Market Insights, (2019), Perfluoropolyether Market By Product (PFPE-K, PFPE-M, PFPE-Z, PFPE-Y, PFPE-D), By Type (Grease, Oil), By End-Use (Automotive, Aerospace, Electronics, Chemical & Petrochemical, Food Processing, Metal Processing, Medical Industry Equipment, Power Generation, Textile, Pulp & Paper), Industry Outlook Report, Regional Analysis, Application Potential, Price Trends, Competitive Market Share & Forecast, 2019 – 2025, accessed November 2019.
 ⁸⁶ Please see Table 10.5 in the annex for complete guide on SPIN exposure toolbox indicators.

CAS RN		Year	Surface Water	Air	Soil	Waste water	Human consumer	Worker- occupational	Range	Quantity	Article
60164-51-4	DK	2017	2	4	3	4	4	5	1	1	2
	NO	2017	3	3	3	4	4	4	1		1
	SE	2017	3	3	3	3	2	5	2	2	3
69991-61-3	SE	2017	1	3	1	3	2	3	1	2	2
69991-67-9	DK	2017	2	5	3	3	4	5	2	1	2
	NO	2017	3	3	4	4	3	5	1		1
	SE	2017	3	3	4	4	4	5	3	2	2
	DK	2009	2	2	3	1	2		1		
162492-15-1	NO	2009									
	SE	2017	2	2	2	2	1	5	1	1	2
200013-65-6	SE	2017	3	2	1	2	2	3	1	1	3

Table 9 Exposure information provided by SPIN database based on CAS numbers

4.6.2 Information from literature

There is little information in literature on the environmental risk of PFPEs, in general they are highlighted as a way to reduce contamination and pollution by improving lubrication, and renowned for their inertness (mirroring the sales pitches on the producers, as discussed above). For example, a public report⁸⁷ prepared by the National Industrial Chemicals Notification and Assessment in Australia in 2012 concluded that Fluorolink E10H would not be available to the public, and as the product would be imported ready for use, the risk of exposure during preparation was minimal. The report also concluded that as the paint cures and dries, it becomes inert, meaning the public would not be affected by coming into contact with the painted surface, and waste (e.g. used paintbrushes) can be disposed of in landfills once dried. The report also noted that "Given the high molecular weight of > 1000 Da, the notified polymer is not considered to be bioaccumulative in organisms", and further testing on the effects on aquatic life was not carried out, due to the low risk.

At the same time, literature highlights several points which may raise potential impacts. One patent filed in the United States⁸⁸ highlights the fact the Krytox is susceptible to wash-out, when used underwater (for example in submarine hangers). Similarly, information brochures⁸⁹ acknowledge that PFPEs may suffer degradation at high temperatures (usually above 204°C) in the presence of certain construction materials, especially non-passivated aluminium and titanium alloys, and small amounts of gases released by such degradation are toxic and corrosive. It is not clear how often such conditions would be encountered through normal use, nor what is meant by "small amounts". In addition, another study⁹⁰ suggested that some PFPEs have a huge potential impact on global warming on a 100-year time scale; however, it was

⁸⁷ National Industrial Chemicals Notification And Assessment Scheme, (2012), <u>Public Report for Polymer in Intersleek</u> 970.

⁸⁸ Bulluck et al. United States Patent: WASH-OUT RESISTANT UNDERWATER Grease, Accessed December 2019.

⁸⁹ See for example Huskey Specialty Lubricants, Applications and Benefits of Perfluoropolyether (PFPE) Lubricants, accessed December 2019.

⁹⁰ Young, Cora & Hurley, Michael & Wallington, Timothy & Mabury, Scott. (2006). <u>Atmospheric Lifetime and Global Warming</u> <u>Potential of a Perfuoropolyether</u>. Environmental science & technology. 40. 2242-6. 10.1021/es052077z.

not clear what the impacts from normal use would be. Furthermore, the low molecular weight manufacturing by-products and impurities are not considered in any of the literature.

4.7 Key messages for Group 1 PFPE

- PFPEs have had a range of uses for decades, owing to the fact that they are durable, relatively inert, and are effective at high or widely varying temperatures. Uses range from cosmetics to aeronautics.
- There is a lack of information on PFPEs in general formulae and structures of the substances are not easy to find, and manufacturers such as Solvay do not provide CAS numbers for their products.
- There is a lack of information on the use of PFPEs in Europe because polymers are exempt from the REACH registration obligation.
- Environmental exposure appears to occur through the use of PFPEs as lubricants, especially with regard to releases to air and water. However, a lack of information means it cannot be generalized for all PFPEs.

5 Group 2: PFAEs that are fluoropolymers

5.1 Overview of the substances in Group 2

5.1.1 Characteristics of Group 2 substances, including chemical structure

Substances included in Group 2 are fluoropolymers that are made from perfluoroether monomers and tetrafluoroethylene (TFE) or hexafluoropropylene (HFP). They include perfluoroalkoxy alkanes (PFAs) and fluoroelastomers. One structural trait of these fluoropolymers is that they have no ether linkages between perfluorocarbon moieties on the polymer backbone, but only on the side chains. Table 10 below lists the CAS numbers and chemical names for those Group 2 substances that appeared in more than one database.⁹¹ As mentioned above, REACH Regulation does not require polymers to be registered.⁹² Thus, not surprisingly, substances from Group 2 are not found in the REACH databases of registered substances. Also included in the table below are the chemical structures for the monomers of the three substances are included in the accompanying electronic database that has been compiled from our research for the project. We were able to identify chemical structures for 20 of 57 substances that were identified as being in Group 2 (fluoropolymers).

⁹¹ Compared to other groups, fewer substances of the Group 2 were found in the key databases considered. Only one substance appeared in three databases, therefore substances that were found in two databases were also included in Table 10. ⁹² Regulation (EC) No 1907/2006, article 2(9).

CAS RN	Name	Appears in	Structure
26425-79-6	Ethene, tetrafluoro-, polymer with trifluoro(trifluoromethoxy)ethene	SPIN, USFDA FCS	$F \xrightarrow{F} F$ $F \xrightarrow{F} F$ $F \xrightarrow{F} F$ $F \xrightarrow{F} F$
31175-20-9	Ethanesulfonic acid, 2-[1- [difluoro[(1,2,2- trifluoroethenyl)oxy]methyl]-1,2,2,2- tetrafluoroe thoxy]-1,1,2,2- tetrafluoro-, polymer with 1,1,2,2- tetrafluoroethene	ECHA, US EPA CPCAT	$\left[\left[\left[\begin{array}{c} r & r & r & r & r & r & r & r & r & r $
56357-87-0	Ethene, tetrafluoro-, polymer with 1,1-difluoroethene and trifluoro(trifluoromethoxy)ethene	SPIN, USFDA FCS	$F \xrightarrow{F} F$

Table 10 CAS numbers, the chemical names, and the structure for Group 2 substances that appeared in 2 or more databases, as of November 2019.

5.1.2 Group 2 substances identified on the EEA market

As explained in the previous section, due to the fact that polymers are not required to be registered under the REACH legislation, no substances in Group 2 were found in the REACH registered substance database, although two were found in the Classification and Labelling (C&L) Inventory. SPIN contained four of the 57 PFAE substances identified as being fluoropolymers. A total of 45 of the substances were found in none of the databases that were searched.

Databases searched	CAS numbers that appear in the database
ECHA registered substances database	N/A
ECHA pre-registered substances	N/A
C&L inventory	2
EU FCM	N/A
EU Cosing	0
SPIN Database	4
USFDA FCS	6
CDR 2012 (USA)	0
CDR 2016 (USA)	2
None of the above	45
Total	57

Table 11 Overview of CAS numbers in Group 2 and appearance in databases

Table 12 Registration status for selected CAS numbers

CAS RN	Name	Registered Substances	Pre- registered substances	C&L Inventory	SPIN
26425-79-6	Ethene, tetrafluoro-, polymer with trifluoro(trifluoromethoxy)ethene				Х
26655-00-5	Propane, 1,1,1,2,2,3,3-heptafluoro-3- [(trifluoroethenyl)oxy]-, polymer with tetrafluoroethene				Х
31175-20-9	Ethanesulfonic acid, 2-[1-[difluoro[(1,2,2- trifluoroethenyl)oxy]methyl]-1,2,2,2- tetrafluoroe thoxy]-1,1,2,2-tetrafluoro-, polymer with 1,1,2,2-tetrafluoroethene			Х	
56357-87-0	Ethene, tetrafluoro-, polymer with 1,1- difluoroethene and trifluoro(trifluoromethoxy)ethene				Х
108144-05-4	1-Propene, 1,1,2,3,3,3-hexafluoro-, polymer with (2-bromo-1,1,2,2- tetrafluoroethoxy)trifluoroethene, 1,1- difluoroethene and tetrafluoroethene				X
111173-25-2	Ethanesulfonic acid, 1,1,2,2-tetrafluoro-2- [(trifluoroethenyl)oxy]-, polymer with tetrafluoroethene			X	

While there was a lack of information available from database searches, examples of important brand names of PFAE fluoropolymers were found in the scientific literature reviewed. Table 13 collects together some of the major brand names of PFAE fluoropolymers containing TFE⁹³. It brings together four different families of substances: perfluoroalkoxy (PFA) resins, fluoroelastomers, perfluoroelastomers and perfluorosulfonic acids (PFSA). It also sheds light on some of the major manufacturers of these substances: 3M-Dyneon, AGC, Chemours, Daikin, Dupont, Saint-Gobain and Solvay.

Table 13 Trade name, family name, composition and manufacturer of PFAE co- and terpolymers of tetrafluoroethylene. Source: Hercules, Cameron, Parrish and Thrasher 2016, 'Research and Non-major Commercial Co- and Terpolymers of Tetrafluoroethylene' in Fluorinated Polymers: Volume 2: Applications

Trade name	Family name	Composition	Manufacturer
Chemfluor PFA	Perfluoroalkoxy	Poly (TFE-co-PAVE)	Saint-Gobain
Chemware PFA	 copolymer resin		Performance
Norton PFA			Plastics
Dyneon PFA	_		3M-Dyneon
Hyflon-MFA	_	Poly (TFE-co-PMVE)	Solvay Specialty Polymers
Hyflon-PFA	_	Poly (TFE-co-PPVE)	
Neoflon PFA			Daikin
Teflon PFA		Poly (TFE-co-PMVE)	Chemours
		Poly (TFE-co-PEVE)	
		Poly (TFE-co-PPVE)	
Aflon PFA	_	Poly (TFE-ter-PAVE-ter-PFBE)	Asahi Glass
Viton GLT	Fluoroelastomer	Poly (TFE-ter-VDF-ter-PMVE)	Chemours
Viton ETP		Poly (TFE-ter-E-ter-PMVE)	Chemours
Kalrez		Poly (TFE-ter-PMVE-ter	DuPont
		8CNVE)	
Tecnoflon-PL		Poly (TFE-ter-PMVE-ter-VDF)	Solvay Specialty
Tecnoflon-VPL		Poly (TFE-ter-MOVE-ter-VDF)	Polymers
Tecnoflon-BR		Poly (TFE-ter-VDF-ter-P) or	-
		Poly (TFE-penta-HPF-penta-VDF-	
		penta-E-penta-PMVE)	_
Tecnoflon PFR, PFR-	Fluoroelastomer	Perfluorinated rubbers of	
HT, PFR-LT		1polymethylene type having all	
		fluoro, perfluoroalkyl or	
		perfluoroalkoxy substituent	
		groups on the polymer chain. (e.g. TFE and PMVE)	
Nafion	Perfluorosulfonic	Poly (TFE-co-PFSVE)	Chemours
Aquivion PFSA	acid resin	Poly (TFE-co-SFVE)	Solvay Specialty
			Polymers

⁹³ Hercules, Cameron, Parrish and Thrasher (2016), 'Research and Non-major Commercial Co- and Terpolymers of Tetrafluoroethylene' in *Fluorinated Polymers: Volume 2: Applications*.

5.2 Group 2 substances used in mixtures

Table 14 lists substances by CAS number that were identified in the databases searched, the manufacturer and their usage in mixtures as described in the database.

Substances from Group 2 were linked primarily to articles; the polymers in Group 2 are made from (some of) the monomers found in Group 3 of this report.

CAS RN	Company	Mixture	Used as/function
26425-79-6	3M Dyneon	Peroxide Cure Perfluoroelastomer	Cleaning, wet chemical and fluid handling in manufacture of semiconductors and flat panel displays, chemical etching processes. ⁹⁴
31175-20-9	Chemours (Nafion pellets)	Resin	Chemical processing: Catalyst for acid- catalysed organic synthesis ⁹⁵
35397-13-8	Solvay Specialty Polymers USA, LLC	Processing agent	Plating agents and surface treating agents. ⁹⁶
56357-87-0	Solvay Specialty Polymers Italy S.p.A.	Surfactant	 Used to produce copolymers to be used for components of gaskets or seals used in food processing equipment Cleaning and washing agents⁹⁷
69462-70-0	Solvay (Aquivion pellets)	Resin	Chemical processing ⁹⁸

Table 14 Fluoropolymers used in mixtures, identified via CAS number

5.3 Group 2 substances used in articles

Table 15presents the uses of Group 2 substances used in articles that were identified using CAS numbers. A main source of information was the US Inventory of Food Contact Substances; that they are found in this inventory means that these substances have been cleared as food contact substances in the US. Limit values are attached on the percentage content of certain substances within the mixtures.

Table 15 Fluoropolymers identified use in relation to articles

CAS RN	Company	Related Article	Used as/function
26425-79-6	Precision Polymer Engineering, Ltd. (downstream user) Solvay Specialty Polymers Italy S.p.A (copolymer manufacturer) 3M Dyneon	Gaskets or seals for food preparation.	Used to produce a copolymer ⁹⁹

⁹⁴ 3M 2019, <u>3M[™] Dyneon[™] Peroxide Cure Perfluoroelastomer PFE 80Z</u>, accessed December 2019.

⁹⁵ Chemours 2019, <u>Nafion[™] Membranes</u>, <u>Dispersions</u>, and <u>Resins in Chemical Processing</u>, accessed December 2019.

⁹⁶ EPA 2019, <u>2016 Chemical Data Reporting Results</u>, accessed November 2019.

⁹⁷ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed November 2019.

⁹⁸ Solvay 2015, <u>Technical Data Sheet: Aquivion P87S-SO2F perfluorosulfonyl fluoride</u>, accessed December 2019.

⁹⁹ US FDA 2019, Inventory of Effective Food Contact Substance (FCS) Notifications

CAS RN	Company	Related Article	Used as/function
26654-97-7	Chemours	Fuel cells	Nafion-layered silicate nanocomposite membrane for fuel cell application ¹⁰⁰
26655-00-5	Merck (supplier in EU)	Construction materials and electrical machinery and apparatus. ¹⁰¹	Used in the manufacture of rubber and plastics used in the construction materials and electrical machinery and apparatus.
31175-20-9	Chemours (Nafion)	Fuel cells; hydrogen production; energy storage applications such as flow batteries	Unreinforced membranes in fuel cells, hydrogen generation and electrolytic processes. Reinforced membranes for specialty applications – electrolytic processes and chor-alkali for potassium service ¹⁰²
31784-04-0	Quadrant EPP AG (Symalit 1000) Chemours	Repeat-use, food-contact articles. Components used in petro- chemical, chemical, metallurgical, food, paper, textile, semiconductor, pharmaceutical and nuclear industries ¹⁰³	For use in contact with all food types (I-IX) under Conditions. ¹⁰⁴
63654-41-1	AGC Europe (Fluon CD 90)	Wire coating; small diameter transparent tubing ¹⁰⁵	Coating
66796-30-3	Chemours (Nafion)	Energy storage, hydrogen generation, electrolytic processes ¹⁰⁶	Membrane
105656-63-1	The Chemours Company FC, LLC	O-rings and gaskets in food processing equipment ¹⁰⁷	Industrial use
106108-23-0	Greene, Tweed and Company, Inc.	Perfluorocarbon-cured elastomers used in the production of moulded parts for food processing equipment, such as O-rings, gaskets, diaphragms and	Used in different combinations with other substances to create several different perfluorocarbon- cured elastomers (PCE) used for food contact.

¹⁰⁰ Alfa Aesar 2019, <u>44626 Nafion® R-1100 resin, sulfonyl fluoride form,</u> accessed December 2019.

¹⁰¹ Nordic Council of Ministers Chemical Group 2019, <u>SPIN database</u>, accessed October 2019.

¹⁰² Chemours 2019, <u>Nafion[™] Sulfonic Membranes</u>, accessed December 2019.

¹⁰³ Quadrant 2007, <u>SYMALIT PFA-HP 1000,</u> accessed December 2019.

¹⁰⁴ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed October 2019.

¹⁰⁵ AGC 2019, <u>Fluon PTFE</u>, accessed December 2019.

¹⁰⁶ Chemours 2019, <u>Nafion[™] Sulfonic Membranes</u>, accessed December 2019.

¹⁰⁷ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed October 2019.

CAS RN	Company	Related Article	Used as/function
		other materials used for sealing. ¹⁰⁸	
190062-24-9	Solvay Specialty Polymers Italy S.p.A.	Gaskets or seals for food processing equipment ¹⁰⁹	Industrial use

Those substances referenced above for rubber O-rings or moulded parts for food contact materials can also be named as fluoroelastomers (FKM). Fluoroelastomers are prized for their high resistance to oxygen and heat and to swelling by oils and fuels¹¹⁰. Viton, perhaps the most well-known of these, is the registered trade name for elastomers produced by Chemours. As well as the food-processing industry, fluoroelastomers such as Viton are used in the car industry for seals and valves, the aerospace industry for seals and lubricants, and general industry for gaskets and seals.

Another major brand name here is Nafion. Nafion is the trade name of PFSA substances produced by Chemours. It is an ionomer, a polymer with ionised groups attached to the polymer backbone. Nafion polymers are made by combining sulfonate-group-terminated perfluorovinyl ether groups onto polytetrafluoroethylene (PTFE).¹¹¹ Nafion polymers are available in different formulae and forms. They are used as membranes in various applications, including fuel cells, medical tubing, transportation, stationary power and energy flow battery storage¹¹². The Nafion brand name was associated with at least three CAS numbers in the database compiled for this report: 26654-97-7; 31175-20-9; and 66796-30-3.

Other chemical companies produce very similar polymers with similar properties to Nafion, e.g. Aquivion, which is also associated with a CAS number in the database for this report: 69462-70-0. Produced by Solvay, Aquivion is also an ionomer. Like Nafion, Aquivion polymers are used both as membranes and dispersions, and in the production of end-products including fuel cells and flow batteries. Both Chemours and Solvay emphasise the role that their respective products can play in the development of emission-free energy sources.

A further family of substances is PFAs (perfluoroalkoxy alkanes), a group of fluoropolymers composed of tetrafluoroethylene and Group 3 substances (see Table 13). PFAs are highly resistant to heat and to corrosion and have anti-adhesive properties. They are used as a coating for pipes or tubes for handling aggressive chemicals, in medical tubing and in valve liners. Important PFA brand names include Dyneon PFA, Hyflon PFA (Solvay), Teflon PFA (Chemours), Neoflon PFA (Daikin) and Chemfluor PFA (Saint-Gobain).

¹⁰⁸ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed November 2019.

¹⁰⁹ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed November 2019.

¹¹⁰ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed November 2019.

¹¹¹ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications</u>, accessed November 2019.

¹¹² Chemours, <u>Nafion</u>, accessed December 2019.

5.4 Key producers and suppliers

Chemours and Solvay would appear to be among the most important manufacturers of Group 2 substances; both have factories in Europe (Chemours in Dordrecht in the Netherlands and Solvay in Tavaux, France and Spinetta-Argeno, Italy). Known producers of Group 2 substances with fluoropolymer production sites in Europe include:

- AGC (Blackpool, UK)¹¹³
- Chemours (Dordrecht, Netherlands)
- Daikin Chemical France (Pierre-Bénite, France);
- Dyneon (Gendorf, Germany); Solvay (Spinetta-Argeno, Italy)

5.5 Volumes of Group 2 substances

5.5.1 Within the EEA

Information about use volume is very limited. While four Group 2 substances were identified on the SPIN database, information on use volume was only publicly available for one: TFE-PPVE (CAS RN 26655-00-5) with 14.6 tonnes used in Sweden in 2017. Information on the use of the other three substances in one or more of the Nordic countries (usually Sweden) was contained in the database but classified as confidential, and non-accessible for the public.

5.5.2 Globally

Two Group 2 substances were identified in the US CDR databases:

- 1-Propene, 1,1,2,3,3,3-hexafluoro-, polymer with 1,1-difluoroethene, ethene, 1,1,2,2tetrafluoroethene and 1,1,2-trifluoro-2-(trifluoromethoxy)ethene (CAS RN 149935-01-3); and
- Propane, 1,1,1,2,2,3,3-heptafluoro-3-[(1,2,2-trifluoroethenyl)oxy]-, polymer with 1-chloro-1,2,2-trifluoroethene and ethene (CAS RN 35397-13-8).

For both substances, the use volumes were non-accessible because it was classified as 'confidential business information' (CBI).

Information on PFA global production is provided in Wang et al. in their 2014 paper on 'Global Emission Inventories for C4–C14 Perfluoroalkyl Carboxylic Acid (PFCA) Homologues from 1951 to 2030'¹¹⁴. Production volumes are based on estimated volumes for Japan, Western Europe and the US, as it is assumed in the paper that production occurred mainly in these countries, with the amount produced elsewhere negligible.

¹¹³ It was not possible to discern for certain whether PFAE fluoropolymers are produced at these specific sites. Nordic Council of Ministers (2018), The cost of inaction: A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS.<u>https://www.accessdata.fda.gov/scripts/fdcc/index.cfm?set=FCN&id=126</u>

¹¹⁴ Wang et al. (2014), Global Emission Inventories for C4–C14 Perfluoroalkyl Carboxylic Acid (PFCA) Homologues from 1951 to 2030. Part I: Production and Emissions from Quantifiable Sources', *Environment International*, Volume 70, September 2014, pp. 62-75.

Table 16 shows the evolution in the annual global production of PFA since 1973. Figures for the period 1973 to 2002 are estimated. The table shows a clear evolution in the production volume of PFA over the 42-year period, with particularly strong growth during the 1990s and early 2000s, before decreasing and slowing following the economic crisis.

Period	PFA production [kilotons/year]
1973 – 1979	0.2 – 0.6
1980 – 1989	1.0 – 1.5
1990 – 1994	1.9 – 2.7
1995 – 2002	3.0 – 3.9
2003 – 2005	4.0 - 5.3
2006 – 2010	5.2 – 5.7
2011	5.2
2012	5.5
2013	5.7
2014	5.7
2015	5.8

Table 16 Reported and estimated PFA production between 1973 and 2015 in kilotons per year [figures for 1973 – 2002 estimated]¹¹⁵

5.6 The potential for exposure

5.6.1 Information from literature

Given that polymers are not registered under REACH, it was not possible to find information directly related to the Group 2 substances in the REACH database. However, given that the monomers in Group 3 are used to produce fluoropolymers, and these monomers and the processes of their polymerisation are included in the REACH database of registered substances, it is possible to look at the exposure information found for Group 3 substances and extrapolate from that. For example, REACH Registered substances documentation on monomers used in polymerisation states that the polymerisation process at industrial sites can lead to a recognised risk of environmental emissions into air and to water.¹¹⁶ Exposure to the environment can also occur at the disposal phase, for example through littering and improper treatment, including landfilling. An example of emissions into water in industrial processes can be found in the US, related to pollution of the Cape Fear River in North Carolina. By-products of Nafion discharged from the Chemours plant at Fayetteville were also found in the river, following the well-publicised discovery of GenX compounds. Analysis by the US Environmental Protection Agency identified the compounds in the waste stream of the Chemours plant and found that the concentrations of these compounds were not

¹¹⁵ Wang et al. (2014), Global Emission Inventories for C4–C14 Perfluoroalkyl Carboxylic Acid (PFCA) Homologues from 1951 to 2030. Part I: Production and Emissions from Quantifiable Sources', Environment International, Volume 70, September 2014, pp. 62-75.

¹¹⁶ See Section 6.6.1.

decreasing¹¹⁷. Researchers found a Nafion copolymer (CAS RN 66796-30-3) in the water. They also found transformation products that they suspect resulted from the use of the another substance under Group 3, 1,1,2,2-tetrafluoro-2-[1,2,2-trifluoro-1-(trifluoromethyl)-2-[(trifluorovinyl)oxy]ethoxy]ethanesulphonyl fluoride (CAS RN 16090-14-5). Other Group 3 substances found in the Cape Fear River are listed in the chapter on Group 3 in Section 6.6.2 of this report.¹¹⁸ Considerable media attention has been given to these findings, associated with similar findings regarding the substance known as GenX, described in the Chapter on Group 4 substances. A full list of substances found in the Cape Fear River is included in the Annex 10.6.

Information in safety data sheets can also be an indication on possible toxicity to the environment. Safety data sheets consulted for several of the most referenced substances (for example: CAS RN 26425-79-6 or 26655-00-5) state that the substances should not be released into the environment. But they can also state that the substance is not known to be hazardous to the environment, or that it is not known to be not degradable in waste water treatment plants.¹¹⁹ Others do not contain information on ecotoxicology or chemical fate, despite having sections dedicated to these topics, simply asking the reader to contact the company for more information,¹²⁰ or stating that no information is available.¹²¹

5.7 Key messages for Group 2 PFAEs

- PFAEs that are fluoropolymers have an extensive range of uses. These include technologies such as the ionomer membranes, that could be important for decarbonisation or for medical advances.
- Releases of PFAEs related to Group 2 substances into the environment appears to occur mostly during the production stage, and into water and air.
- There is a lack of information on the uses of PFA fluoropolymers in Europe because polymers are exempt from the REACH registration obligation.

¹¹⁷ Winkel V, '<u>GenX: What Is Nafion', And Why Is It In The Water?</u>, *WHQR Public Media*, August 31 2017, accessed November 2019.

¹¹⁸ Strynar et al. 2015, 'Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)', Environ. Sci. Technol. 2015, 49, 19, 11622-11630.

¹¹⁹ See, for example:

ThermoFisher Scientific 2018, <u>Safety Data Sheet Ethanesulfonyl fluoride, 2-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-, polymer with tetrafluoroethene, accessed December 2019.</u> ¹²⁰ See, for example, for CAS 26425-79-6:

³M 2018, <u>Safety Data Sheet 3M[™] Dyneon[™] Perfluoroelastomer PFE 80Z</u>, accessed December 2019. ¹²¹ See, for example for CAS 26655-00-5.

³M 2011, <u>Safety Data Sheet 3M[™] CCM105-GRN-246</u>, accessed December 2019.

6 Group 3: Perfluoroether non-polymers with unsaturated bonds

6.1 Overview of the substances in Group 3

6.1.1 Characteristics of Group 3 substances, including chemical structure

Group 3 substances are perfluoroether non-polymers with unsaturated bonds. These are the monomers for the fluoropolymers found in Group 2. There were 51 substances identified as part of this group.

The table below lists the CAS numbers and chemical names for those substances that appeared in three or more databases. Seven of the substances in Group 3 were found in both the EU REACH database and at least one of the US databases.

We were able to identify chemical structures for 34 of the 51 Group 3 substances. The table below provides the chemical structures for the four substances that appeared most frequently in the selected databases. The chemical structures for the other Group 3 substances are in the accompanying electronic database.

CAS RN	Name	Appears in	Structure
1187-93-5	Trifluoro(trifluoromethoxy)- ethylene	Registered substances, Pre-registered substances, C&L, EU FCM, USFDA FCS, CDR 2012, CDR 2016	$F \to 0 \to F$ $F \to F$ $F \to F$
1644-11-7	1,1,1,2,3,3-hexafluoro-2- (heptafluoropropoxy)-3- [(trifluorovinyl)oxy]propane	Registered substances, Pre-registered substances, C&L	
10493-43-3	Trifluoro(pentafluoroethoxy) ethylene	Registered substances, Pre-registered substances, C&L, USFDA FCS, CDR 2012, CDR 2016	$F \xrightarrow{F} F \xrightarrow{F} F$

Table 17 The CAS numbers, chemical names, and chemical structure of Group 3 substances that appeared in 3 or more databases, as of November 2019.

CAS RN	Name	Appears in	Structure
13846-22-5	1,1,2,2,3,3-hexafluoro-1,3- bis[(trifluorovinyl)oxy]propan e	Registered substances, Pre-registered substances, C&L	$F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F$
16090-14-5	1,1,2,2-tetrafluoro-2-[1,2,2- trifluoro-1-(trifluoromethyl)- 2- [(trifluorovinyl)oxy]ethoxy]et hanesulphonyl fluoride	Pre-registered substances, CDR 2012, CDR 2016	
1623-05-08	1,1,1,2,2,3,3-heptafluoro-3- [(trifluorovinyl)oxy]propane	Registered substances, Pre-registered substances, C&L, USFDA FCS, CDR 2012, CDR 2016	

CAS RN	Name	Appears in	Structure
29514-94-1	1,1,2,2-tetrafluoro-2- [(trifluorovinyl)oxy]ethanesul fonyl fluoride	Registered substances, Pre-registered substances, USFDA FCS	

6.1.2 Group 3 substances identified on the EEA market

A total of 29 CAS numbers of Group 3 substances were found in the ECHA databases (registered substances, pre-registered substances and C&L Inventory). No Group 3 substances were found in the Nordic SPIN database; nine were found in non-EU databases. Table 18 shows the breakdown for each of the databases searched (note that some substances appear in several databases). Further details for all CAS numbers are provided in the annex. A total of 20 CAS numbers were located in none of the databases searched.

- 9 were found in the REACH database of registered substances;
- 27 were found in the pre-registered substances database;
- 6 were found in the C&L database.

Table 18 Overview of C	CAS numbers in Group 3	and appearance in databases
------------------------	------------------------	-----------------------------

Databases searched	CAS numbers that appear in the database
ECHA registered substances database	9
ECHA pre-registered substances	27
C&L inventory	6
EU FCM	2
EU Cosing	0
SPIN Database	0
USFDA FCS	6
CDR 2012 (USA)	5
CDR 2016 (USA)	4
None of the above	20
Total	51

The table below summarises the substances found in the Reach databases for registered substances and pre-registered substances and the C&L Inventory.. Further details for all CAS numbers are provided in the annex.

Table 19 The registration status of Group 3 substances in the Europe-related databases.

CAS RN	Name	Registered Substances	Pre- registered substances	C&L Invent ory
1187-93-5	Trifluoro(trifluoromethoxy)ethylene	х	х	Х
1623-05-8	1,1,1,2,2,3,3-heptafluoro-3-[(trifluorovinyl)oxy]propane	Х	Х	Х
1644-11-7	1,1,1,2,3,3-hexafluoro-2-(heptafluoropropoxy)-3- [(trifluorovinyl)oxy]propane	Х	Х	Х
10493-43-3	Trifluoro(pentafluoroethoxy)ethylene	х	х	Х
13846-22-5	1,1,2,2,3,3-hexafluoro-1,3- bis[(trifluorovinyl)oxy]propane	x	x	Х
19190-61-5	methyl 2,2,3,3,4,4-hexafluoro-4-[(1,2,2- trifluoroethenyl)oxy]butanoate	Х		Х
29514-94-1	1,1,2,2-tetrafluoro-2-[(trifluorovinyl)oxy]ethanesulfonyl fluoride	Х		

CAS RN	Name	Registered Substances	Pre- registered substances	C&L Invent ory
40573-09-9	1,1,2,2,3,3-hexafluoro-1-trifluoromethoxy-3- trifluorovinyloxypropane	X		
700874-87-9	1-[Difluoro(trifluoromethoxy)methoxy]-1,2,2- trifluoroethene	X		

6.2 Group 3 substances used in mixtures

As mentioned in the introduction to this chapter, the monomers classed in Group 3 are used to produce fluoropolymers. The table below details the different substances that are produced in the EU which have been identified as being part of Group 3. This information is primarily taken from the REACH database of registered substances, which describes all substances as being used as intermediates for industrial processes of polymerisation. According to the REACH database, three of these monomers are imported into the EU already bound in a polymer (CAS RN 1187-93-5, 1623-05-8 and 10493-43-3). The first two appear to be only used in the polymerisation process *outside of the EU* (this is used as a justification for the registrant of the substance not registering a 'use' of the substance), whereas the third is indicated as being both imported as part of a polymer and used in the EU.

CAS RN	Company	Mixture	Used as/function
1187-93-5	AGC Chemicals Europe; Chemours; Solvay	Used as an intermediate in polymer production	Used with other compounds to make perflourocarbon cured elastomers. In EU not authorised for use as additive or polymer production aid for food-contact materials; authorised for use as a monomer later used in fabrication of articles intended for repeated use in contact with food. The substance can only be used in non-stick coatings and fluoro- and perfuoropolymers intended for repeated use applications where the contact ratio is 1 dm2 surface in contact with at least 150 kg food. ¹²² ¹²³
1623-05-8	3M Belgium; AGC Chemicals Europe; Ambofluor Gmbh; Chemours; DELACAMP Aktiengesellschaft;	Used as an intermediate	Used for the production of polymers ¹²⁴

Table 20 The use of perfluoroether non-polymers with unsaturated bonds in mixtures, identified using CAS numbers

¹²² EU Regulation 10/2011 on plastic materials and articles intended to come into contact with food.

¹²³ The REACH database gives no identified uses for this monomer, based on the justification that 'The monomer is bound in an imported polymer. There are therefore no identified uses in the EU for the bound monomer in the polymer substance.' ECHA 2019, <u>Registration dossier: Trifluoro(trifluoromethoxy)ethylene.</u>

¹²⁴ The REACH database gives no identified uses for this monomer, based on the justification that the 'substance is a monomer used outside the EU to produce polymers that are subsequently imported into the EU. The monomer itself is not imported'. ECHA 2019, <u>Registration dossier: 1,1,1,2,2,3,3-heptafluoro-3-[(trifluorovinyl)oxy]propane.</u>

CAS RN	Company	Mixture	Used as/function
	Dyneon; Merck KGaA; Solvay		
1644-11-7	Dyneon	Used as an intermediate	Used for the production of thermal plastics and in polymerisation processes. ¹²⁵
10493-43-3	Chemours	Used as an intermediate	Plastic material and resin manufacturing; production of polymers ¹²⁶
13846-22-5	Dyneon	Used as an intermediate	Production of polymers ¹²⁷
19190-61-5	Registration dossier now inactive ¹²⁸	Surfactant	
29514-94-1	Caffaro Industrie; Solvay	Intermediate	A monomer used in polymerisation processes. In the US it is used to produce a polymer that can be used as a component of coatings for repeat-use food filtration membranes, except for use in contact with infant formula or ingredients used for making infant formula. ¹²⁹ Used in the manufacture of PFSVE.
40573-09-9	3M Belgium; Dyneon	Used as an intermediate	Production of polymers ¹³⁰
700874-87-9	Caffaro Industrie; Solvay	Used as an intermediate	Production of polymers from monomer MOVE 3. ¹³¹

6.3 Group 3 substances used in articles

Group 3 substances are used primarily as intermediates in the production of fluoropolymers during polymerisation processes. The table below gives some examples of possible end use of Group 3 substances in articles.

¹²⁷ ECHA 2019, <u>Registration dossier: 1,1,2,2,3,3-hexafluoro-1,3-bis[(trifluorovinyl)oxy]propane</u>, accessed October 2019.

¹²⁵ ECHA 2019, <u>Registration dossier: 1,1,1,2,3,3-hexafluoro-2-(heptafluoropropoxy)-3-[(trifluorovinyl)oxy]propane,</u> accessed October 2019.

¹²⁶ The REACH database gives no identified uses for this monomer, based on the justification that there is 'additional import as monomer in imported polymer'.

ECHA 2019, <u>Registration dossier: Trifluoro(pentafluoroethoxy)ethylene</u>, accessed October 2019.

 ¹²⁸ ECHA 2019, <u>Registration dossier: Methyl 2,2,3,3,4,4-hexafluoro-4-(trifluoroethenyloxy)butanoate</u>, accessed October 2019.
 ¹²⁹ US FDA 2019, <u>Inventory of Effective Food Contact Substance (FCS) Notifications: FCN No. 1805</u>, accessed October 2019.

ECHA 2019, <u>Registration dossier: 1,1,2,2-tetrafluoro-2-[(trifluorovinyl)oxy]ethanesulfonyl fluoride</u>, accessed October 2019. ¹³⁰ ECHA 2019, <u>Registration dossier: 1-[difluoro(trifluoromethoxy)methoxy]-1,2,2-trifluoroethylene</u>, accessed October 2019. ¹³¹ ECHA 2019, <u>Registration dossier: 1,1,2,2,3,3-hexafluoro-1-trifluoromethoxy-3-trifluorovinyloxypropane</u>, accessed October 2019.

Table 21 Perfluoroether non-polymers with unsaturated bonds, identified use in relation to articles

CAS RN	Company	Related Article	Used as/function
6037-91-8	Unavailable	Medical devices	Coating used on nanostructured surfaces ¹³²
13269-86-8	Unavailable	Fire extinguishing equipment	Fire-extinguishing foam ¹³³

It has been difficult to find links between the monomers identified under Group 3 and specific Group 2 fluoropolymers. However, common uses of the fluoropolymers made from Group 3 monomers touch a large range of industries and uses. These include the automobile industry, non-stick coatings for cookware, water resistant fabrics for high-performance clothing, flame retardant coatings for articles and fire-fighting foam, O-rings and gaskets for food processing, membranes in fuel cells and coatings for medical devices.

6.4 Key producers and suppliers

Based on information gathered through research, particularly from the REACH databases, the following companies produce or import Group 3 substances in the EU:

- 3M Belgium SPRL/BVBA (BE);
- AGC Chemicals Europe Ltd (UK);
- Ambofluor Gmbh (DE);
- Caffaro Industrie S.p.A (IT);
- Chemours Netherlands B.V. (NL);
- DELACAMP Aktiengesellschaft (DE);
- Dyneon GmbH (DE);
- Merck KGaA (DE);
- Solvay Specialty Polymers Italy S.p.A. (IT).

It is possible that Group 3 substances are also produced in the US by companies such as Chemours and Solvay and imported into the EU.

6.5 Volumes of Group 3 substances

6.5.1 Within the EEA

The table below provides the tonnage bands for those Group 3 substances registered under REACH.

¹³² This use is taken from <u>a list of patents</u> that have been taken out on this substance, produced by the USA National Institute of Health.

¹³³ WIPO IPC A62D1/00.

Identified in a list of patents associated with the substance produced by the USA National Institute of Health.

CAS RN	Name	Number of registrants (active)	Submissions	Tonnage band (tonnes/year)
1187-93-5	Trifluoro(trifluoromethoxy)ethylene	6	1 (joint)	100 - 1000 ¹³⁴
1623-05-8	1,1,1,2,2,3,3-heptafluoro-3- [(trifluorovinyl)oxy]propane	11	1 (joint) 2018 & 2019	100 - 1000 ¹³⁵
1644-11-7	1,1,1,2,3,3-hexafluoro-2- (heptafluoropropoxy)-3- [(trifluorovinyl)oxy]propane	1	1 (joint) 2018	1-10 ¹³⁶
10493-43-3	Trifluoro(pentafluoroethoxy)ethylene	1	1 (joint) (2018)	1-10 ¹³⁷
13846-22-5	1,1,2,2,3,3-hexafluoro-1,3- bis[(trifluorovinyl)oxy]propane	1	1 (individual)	Unavailable – intermediate use only ¹³⁸
19190-61-5	methyl 2,2,3,3,4,4-hexafluoro-4- [(1,2,2-trifluoroethenyl)oxy]butanoate	0 (2 inactive registrations)	1 (joint)	0 ¹³⁹
29514-94-1	1,1,2,2-tetrafluoro-2- [(trifluorovinyl)oxy]ethanesulfonyl fluoride	2	1 (joint) (2018)	1-10
40573-09-9	1,1,2,2,3,3-hexafluoro-1- trifluoromethoxy-3- trifluorovinyloxypropane	2	1 (joint) (2018)	10-100 ¹⁴⁰
700874-87-9	1- [Difluoro(trifluoromethoxy)methoxy]- 1,2,2-trifluoroethene	2	1 (joint) (2018)	10-100 ¹⁴¹
Total				223-2230

 Table 22 Tonnage bands of Group 3 substancers registered under REACH
 Image bands of Group 3 substancers registered under REACH

No CAS numbers related to Group 3 substances were identified in the SPIN database.

6.5.2 Globally

Statistics regarding the global manufacture and use of the substances in Group 3 were not available.

6.6 The potential for exposure

6.6.1 Information from ECHA

ECHA 2019, Registration dossier: Trifluoro(pentafluoroethoxy)ethylene

¹³⁴ ECHA 2019, Registration dossier: Trifluoro(trifluoromethoxy)ethylene

¹³⁵ ECHA 2019, <u>Registration dossier: 1,1,1,2,2,3,3-heptafluoro-3-[(trifluorovinyl)oxy]propane</u>

¹³⁶ ECHA 2019, <u>Registration dossier: 1,1,1,2,3,3-hexafluoro-2-(heptafluoropropoxy)-3-[(trifluorovinyl)oxy]propane</u>

¹³⁷ The REACH database gives no identified uses for this monomer, based on the justification that there is 'additional import as monomer in imported polymer'.

¹³⁸ ECHA 2019, <u>Registration dossier: 1,1,2,2,3,3-hexafluoro-1,3-bis[(trifluorovinyl)oxy]propane</u>

¹³⁹ This is an inactive registration. The REACH database describes there as being 'no exposure to the substance in the EU. It is not imported or manufactured or used in the EU.'

ECHA 2019, Registration dossier: Methyl 2,2,3,3,4,4-hexafluoro-4-(trifluoroethenyloxy)butanoate

¹⁴⁰ ECHA 2019, <u>Registration dossier: 1,1,2,2,3,3-hexafluoro-1-trifluoromethoxy-3-trifluorovinyloxypropane</u>

¹⁴¹ ECHA 2019, <u>Registration dossier: 1-[difluoro(trifluoromethoxy)methoxy]-1,2,2-trifluoroethylene</u>

Nine substances in Group 3 were located in the REACH database of registered substances. Information based on the environmental release category given for different substances potential for exposure in different circumstances is summarised in the table below for these nine substances. It uses the table of default parameters that details worst-case release factors associated with different environmental release categories, as described in the introduction. Most exposure related to Group 3 substances occurs through release into the air during manufacture of the substance and when a substance is used as an intermediate or as a monomer in polymerisation at industrial sites. Release into water is also a concern, particularly during manufacturing but also at industrial sites. The risk of release into soil would appear to be minimal.

Manufacturing phase

Information is available for six substances for the manufacturing phase (see Table 23). All are listed under Environmental Release Category 1 (ERC1) meaning that primary risk is through exposure to air and water. Risk to workers comes from processes such as transfer of substances at dedicated facilities and transfer of substance into small containers, for example at a filling line. For two substances (CAS RN 1623-05-8 and 700874-87-9) there is also risk as use as a laboratory reagent. The latter of these two has been the subject of a far more extensive Chemical Safety Report¹⁴².

Formulation and re-packaging phase

Only one substance is listed as at risk of exposure during formulation and re-packing phase (CAS RN 1623-05-8). For workers, this comes in transfer of the substance at non-dedicated and dedicated facilities, and in use as a laboratory reagent.

Uses at industrial sites

Eight of the nine substances in the REACH database were listed as posing a risk of exposure at industrial sites. Environmental release came under use of a monomer in polymerisation processes at an industrial site (ERC6c) and the use of an intermediate (ERC6a). Risks to workers mentioned generally include occasional controlled exposure. Taking one substance as an example, PMVE (CAS RN 1187-93-5), which is registered with major chemicals manufacturers such as Solvay, Chemours and AGC, many different working processes are mentioned as posing a risk of exposure. These include occasional controlled exposure in chemical production, manufacture or formulation; mixing or blending in batch processes; transfer of substances; use as a laboratory reagent; tabletting and palletisation; and polymer preparations and compounds. This is partly due to the substance being linked to many different processes, all including stages of polymerisation.

¹⁴² ECHA 2019, <u>Registration dossier: 1-[difluoro(trifluoromethoxy)methoxy]-1,2,2-trifluoroethylene</u>

	Manuf	acture		Formul	ation or re-packing		Indus	trial sites		by p	espread u rofession kers			sumer use vice life	and
CAS RN	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil
1187-93-5	5%	6%	0.01%				5% 5%	2% 5%	0.1% 0%						
1623-05-8	5%	6%	0.01%	2.5%	2%	0.01%	5% 0.1% 5%	2% 5% 5%	0.1% 0.025% 0%						
1644-11-7	5%	6%	0.01%				5% 5%	2% 5%	0.1% 0%						
10493-43-3							5%	5%	0%						
13846-22-5							5%	2%	0.1%						
19190-61-5 ¹⁴³															
29514-94-1	5%	6%	0.01%				5%	5%	0%						
40573-09-9	5%	6%	0.01%				5%	5%	0%						
700874-87-9	5%	6%	0.01%				5%	5%	0%						

Table 23 Environmental release categories (ERCs) associated with life-cycle stages of the substances, based on REACH registrations.

¹⁴³ No information is available because 'There is no exposure to the substance in the EU. It is not imported or manufactured or used in the EU. It is a monomer bound within an imported polymer.'

ECHA 2019, Registration dossier: Methyl 2,2,3,3,4,4-hexafluoro-4-(trifluoroethenyloxy)butanoate, accessed November 2019.

6.6.2 Information from literature

As mentioned in section 5.6.1 for Group 2 substances, several Group 3 substances are listed as having been released into the Cape Fear River in North Carolina from the Dupont-Chemours factory at Fayetteville (see Table 24). These were identified using a time-of-flight mass spectrometry detector. Substances identified include monomers suspected as being related to manufacture of Nafion that are Group 2 substances. The study also located the presence of GenX, among other substances. This is discussed further in the Chapter about Group 4 substances. Suspect and non-target screening using high-resolution mass spectrometry was suggested as the most effective technique for discovering PFAEs released into the environment.¹⁴⁴

CAS RN	Chemical Name
10493-43-3	Trifluoro(pentafluoroethoxy)ethylene
1187-93-5	Trifluoro(trifluoromethoxy)ethylene
1623-05-8	1,1,1,2,2,3,3-heptafluoro-3-[(trifluorovinyl)oxy]propane
16090-14-5	1,1,2,2-tetrafluoro-2-[1,2,2-trifluoro-1-(trifluoromethyl)-2 [(trifluorovinyl)oxy]ethoxy]ethanesulphonyl fluoride

Table 24 Group 3 substances found in the Cape Fear River in North Carolina

6.7 Key messages for Group 3 PFAEs

- Group 3 substances are primarily used as intermediates in industrial polymerisation processes in the EU to make the fluoropolymers described in Group 2. The fluoropolymers produced are used in a vast range of industries, including automobiles, cooking and homeware, fire protection, apparel, fuel cells and medical technology.
- Substances from this group are registered in the REACH database of registered substances as being produced in volumes of up to 1000 tonnes per year. Major chemical companies including Chemours, Solvay and 3M are registered as manufacturing or using these substances in the EU.

The major risk of exposure to this group of substances comes during the manufacturing stage and the industrial processes stage in the life cycle of the substance. During the manufacturing stage, the highest risks of exposure come from emissions into water or air. During the use in industrial production of other substances, the greatest risk is emissions into the air, followed by emissions into the water.

¹⁴⁴ Strynar et al. (2015), Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)', Environ. Sci. Technol. 2015, 49, 19, 11622-11630

7 Group 4: Perfluoroether non-polymers with saturated bonds

7.1 Overview of the substances in Group 4

7.1.1 Characteristics of Group 4 substances, including chemical structure

This group consists of perfluoroether non-polymers (defined as with fewer than 20 carbon atoms in this study) with only saturated carbon bonds. 152 CAS numbers were identified in this group. Among those, chemical structures for 103 Group 4 substances were found and included in the accompanying electronic database.

The table below provides the CAS numbers, names, chemical structures for the substances found most frequently in the selected databases. We used the number of databases in which a substance appears as an indicator of whether or not the substance is in widespread use within the EEA.

CAS RN	Chemical name	Listed in	Structure ¹⁴⁵
335-36-4	2,2,3,3,4,4,5-heptafluorotetrahydro-5- (nonafluorobutyl)furan	Pre-registered substances, C&L, SPIN	
382-28-5	2,2,3,3,5,5,6,6-octafluoro-4- (trifluoromethyl)morpholine	REACH, pre-registered substances, C&L, SPIN, CDR 2012 and 2016	
2062-98-8	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionyl fluoride	Pre-registered substances, C&L, CDR 2012 and 2016	

Table 25 CAS numbers, the chemical names, and the structure for Group 4 substances that appeared in 3 or more databases, as of November 2019.

¹⁴⁵ Unless stated otherwise, all structures are found via CAS number search on <u>PubChem</u>, provided by the US National Library of Medicine.

CAS RN	Chemical name	Listed in	Structure ¹⁴⁵
2641-34-1	2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2- (heptafluoropropoxy)propoxy]propionyl fluoride	Pre-registered substances, C&L, CDR 2012 and 2016	
4089-58-1	2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2- [1,1,2,2-tetrafluoro-2- (fluorosulphonyl)ethoxy]propoxy]propionyl fluoride	Pre-registered substances, C&L, CDR 2012 and 2016	
13252-13-6	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	Pre-registered substances, C&L, EU FCM, CDR 2012 and 2016	

CAS RN	Chemical name	Listed in	Structure ¹⁴⁵
62037-80-3 (GenX)	Ammonium 2,3,3,3-tetrafluoro-2- (heptafluoropropoxy)propanoate	REACH, C&L, CDR 2012 and 2016	H H H H H H H H H H H
144728-59-6	2-(1,2-dichloro-1,2,2-trifluoroethoxy)-1,1,2,2- tetrafluoroethanesulfonyl fluorid	REACH, pre-registered substances, C&L	
161075-00-9	Hexafluoropropene, oxidized, oligomers, reduced, fluorinated	REACH, Pre-registered substances database, C&L	norman

¹⁴⁶ ECHA, <u>REACH Registration Dossier for CAS RN 161075-00-9</u>, accessed October 2019.

CAS RN	Chemical name	Listed in	Structure ¹⁴⁵
1190931-27-1 ¹⁴⁷	Ammonium difluoro{[2,2,4,5-tetrafluoro-5- (trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate	REACH, C&L, EU FCM	

¹⁴⁷ ECHA, Registered Substances Database, <u>Infocard</u> for CAS number 1190931-27-1.

7.1.2 Group 4 substances identified on the EEA market

European databases list a number of Group 4 substances:

- 9 CAS numbers in the REACH Registered Substances Database.
- 32 CAS numbers in the C&L Inventory (including all substances that appear in the Registered Substances Database)
- 32 CAS numbers in the pre-registered substances database (not entirely overlapping with C&L)
- 9 CAS numbers in the SPIN database, with only one overlap with the Registered Substances Database.
- A very important majority (90 out of 152) of the substances do not appear in any of the databases.

Table 26 Overview of CAS numbers in Group 4 and appearance in databases

Databases searched	CAS numbers that appear in the database
ECHA registered substances database	9
ECHA pre-registered substances	32
C&L inventory	32
EU FCM	3
EU Cosing	0
SPIN Database	9
USFDA FCS	0
CDR 2012 (USA)	10
CDR 2016 (USA)	8
None of the above	90
Total ¹⁴⁸	152

The table below recapitulates the findings for the substances that are in the Registered Substances and SPIN databases. Further details for all CAS numbers are provided in the annex.

Table 27 Registration status	for selected CAS numbers
------------------------------	--------------------------

CAS RN	Name	Registered Substances	Pre- registered substances	C&L Inventory	SPIN	
335-35-3	2,2,3,3,4,4,5,5,6-nonafluoro-6- (heptafluoropropyl)tetrahydro-2H-pyran		X		Х	
335-36-4	2,2,3,3,4,4,5-heptafluorotetrahydro-5-X(nonafluorobutyl)furan					
382-28-5	2,2,3,3,5,5,6,6-octafluoro-4- (trifluoromethyl)morpholine	X	X	Х	Х	
646-85-5	Furan, 2,2,3,3,4,5,5-heptafluorotetrahydro-4- (nonafluorobutyl)-				Х	
801-26-3	2H-Pyran, 2,2,3,3,4,4,5,6,6-nonafluoro-5- (heptafluoropropyl)tetrahydro-				Х	

CAS RN	Name	Registered Substances	Pre- registered substances	C&L Inventory	SPIN	
1600-71-1	Morphline, 2,2,3,3,5,5,6,6-octafluoro-4- [1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]- (SPIN)	2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-				
55716-11-5	Morpholine, 2,2,3,3,5,5,6,6-octafluoro-4- (1,1,2,2,2-tentafluoroethyl)-				Х	
62037-80-3 (GenX)	Ammonium 2,3,3,3-tetrafluoro-2- (heptafluoropropoxy)propanoate	Х		X		
133080-89-4	Hexane, 1,1,2,2,3,3,4,4,5,5,6,6,6- tridecafluoro-1-(pentafluoroethoxy)-				X	
133881-46-6	Heptane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7- pentadecafluoro-7-(trifluoromethoxy)-				Х	
144728-59-6	2-(1,2-dichloro-1,2,2-trifluoroethoxy)-1,1,2,2- tetrafluoroethanesulfonyl fluorid	X	X X X			
161075-00-9	Hexafluoropropene, oxidized, oligomers, reduced, fluorinated	х	X			
874288-98-9	1,2-dichloro-1- [difluoro(trifluoromethoxy)methoxy]-1,2,2- trifluoroethane	x		X		
919005-14-4	2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3- (trifluoromethoxy)propoxy]propanoic acid	Х		Х		
957209-18-6	2,3,3,4,4-pentafluoro-2,5-bis(1,1,1,2,3,3,3- heptafluoropropan-2-yl)-5- methoxytetrahydrofuran	X		X		
1190931-27-1	Ammonium difluoro{[2,2,4,5-tetrafluoro-5- (trifluoromethoxy)-1,3-dioxolan-4- yl]oxy}acetate	Х		X		
1190931-39-5	Potassium difluoro{[2,2,4,5-tetrafluoro-5- (trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate	X X				

7.2 Group 4 substances used in mixtures

Group 4 substances have several areas of application in a wide range of industries. Direct links were identified between certain CAS numbers and products developed by chemical companies (see Table 28). Some of these products are mixtures used as such (e.g. cooling liquids). Others are used in the process of production of other chemicals such as fluorinated polymers, particularly as replacements to APFO (ammonium perfluorooctanoate) in the production of PTFE, such as GenX and ADONA¹⁴⁹. Some others are also used as main ingredients in consumer mixtures such as mascaras and varnishes.

¹⁴⁹ Wang, Z., Cousins, I., Scheringer, M. and Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environment International, 60, pp.242-248.

CAS RN	Company	Mixture	Used as/function
335-36-4	3M	Functional fluids	Heat transfer applications in semi-conductor package testing, power electronics and computer cooling ¹⁵⁰
382-28-5	3M	PF-5052 Performance Fluid ¹⁵¹	Non-reactive processing aid, functional, widespread use of non-reactive processing aid, widespread use of functional fluid (indoor) ¹⁵²
1644-10-6	Unimatec	Not specified	Monomer and processing promoters for fluorine polymers ¹⁵³
2062-98-8	Unimatec	Not specified	Intermediate monomers for PFPE oligomers production ¹⁵⁴
2641-34-1	Unimatec	Not specified	Intermediate monomers for PFPE oligomers production ¹⁵⁵
13252-14-7	Unimatec	Waterproof Powder, Mascara	Cosmetic additive for colour brilliance, water resistance, reduces the shine by natural skin secretions ¹⁵⁶
13252-14-7	Unimatec	Surfactant	Additive for electroplating ¹⁵⁷
13252-15-8	Unimatec	Not specified	Intermediate monomers for PFPE oligomers production ¹⁵⁸
26131-32-8		Not specified	Intermediate monomers for PFPE oligomers production
26537-88-2	Unimatec	Not specified	Intermediate monomers for PFPE oligomers production ¹⁵⁹
26537-88-2	Tikkurila	Hardener 008 7067 ¹⁶⁰ (Between 25% to 50% of the product)	Hardener for industrial coatings ¹⁶¹
27617-34-1	Unimatec	Waterproof Powder, Mascara	Cosmetic additive for colour brilliance, water resistance, reduces the shine by natural skin secretions ¹⁶²
62037-80-3 (GenX)	Chemours	pH-regulators, flocculants, precipitants, neutralisation agents, formulations, polymer	non-reactive processing aid, used in mixtures ¹⁶⁴¹⁶⁵

Table 28 Perfluoroether non-polymers with saturated bonds use in mixtures, identified via CAS number

¹⁵⁹ Ibid.

¹⁵⁰ 3M, <u>3M[™] Fluorinert[™] Electronic Liquid FC-3284</u>, accessed December 2019.

¹⁵¹ 3M, (2018) <u>Safety Sheet for 3M[™]PF-5052 Fluide Performance</u>,, accessed November 2019 (French).

¹⁵² REACH Registration Dossier for CAS RN 382-28-5.

¹⁵³ Unimatec product range for <u>Monomers and Processing Promoters for Fluorine Polymers</u>, accessed November 2019.

¹⁵⁴ Unimatec product range for <u>Perfluoroether-Oligomers</u>, accessed November 2019.

¹⁵⁵ Ibid.

¹⁵⁶ Unimatec <u>product range for Cosmetic Additives</u> accessed October 2019 (German).

¹⁵⁷ Unimatec <u>product range for Coating Additives</u> accessed October 2019 (German).

¹⁵⁸ Unimatec product range for <u>Perfluoroether-Oligomers</u>, accessed November 2019.

¹⁶⁰ Tikkurila, <u>Hardener 008 7067</u>, accessed November 2019.

¹⁶¹ Safety Data Sheet for Tikkurila, <u>Hardener 008 7067</u>, accessed November 2019.

¹⁶² Unimatec Product Range on Germany Website, <u>http://www.unimatec-chemicals.de/index.php?id=135</u> (German) accessed October 2019.

¹⁶⁴ REACH Registration Dossier for CAS RN 62037-80-3, accessed October 2019.

¹⁶⁵ REACH Registration Dossier for CAS RN 62037-80-3, accessed October 2019.

CAS RN	Company	Mixture	Used as/function
		preparations and compounds ¹⁶³	
161075-00-9	Solvay ¹⁶⁶	Galden PFPE fluid (heat transfer fluids, polymers and semiconductors), lubricant	Used in the formulation as ingredient ¹⁶⁷
874288-98-9	Solvay	MOVE Adduct 3 (Not specified)	Used as intermediate in the production of other substance ¹⁶⁸
957209-18-6	3M	Heat-transfer fluids	Not specified ¹⁶⁹
1190931-27-1	Solvay	Surfactant, emulsifier	Used in polymerization process, manufacture of other substance (polymers) ¹⁷⁰
1190931-39-5	NA	Large scale chemicals (including petroleum products)	Used as intermediate ¹⁷¹
Classified	Omnova	Floor polish products	Surfactant ¹⁷²
Classified	Omnova	Coating formulations (paint and varnish)(possibly PolyFox) ¹⁷³	Flow, level, and wetting additive ¹⁷⁴

In addition to the mixtures identified above, several substances are also sold as chemical products available on the market. The majority of these substances are sold for research and development and no further information is available by the suppliers about their uses. These include CAS RN 26738-51-2, 27639-98-1, 37486-69-4, 55154-18-2, 85720-80-5, 97571-69-2, 133609-46-8, 147492-57-7, 330562-41-9, 330562-44-2, and 510774-77-3. Some of these chemicals can be ordered online. The available quantities are generally very limited. For instance, the substance with CAS number 97571-69-2 (Perfluoro-15-crown-5-ether) can be purchased as packs of 1 or 5 g from Matrix Scientific¹⁷⁵. Another one, Perfluoro-3,6,9-trioxatridecanoic acid (CAS RN 330562-41-9) can be bought in quantities up to 100g from Cymit Quimia¹⁷⁶, a chemical marketplace where one can buy from several different sellers. Another substance, also known

¹⁶³ REACH Registration Dossier for CAS RN 62037-80-3, accessed October 2019.

¹⁶⁶ Solvay, <u>Galden PFPE, FAQ</u>, accessed November 2019.

¹⁶⁷ REACH Registration Dossier for CAS RN 161075-00-9, accessed October 2019.

¹⁶⁸ REACH Registration Dossier for CAS RN 874288-98-9, accessed October 2019.

¹⁶⁹ REACH Registration Dossier for CAS RN 957209-18-6, accessed October 2019.

¹⁷⁰ REACH Registration Dossier for CAS RN 1190931-27-1, accessed October 2019.

¹⁷¹ REACH Registration Dossier for CAS RN 1190931-39-5, accessed October 2019.

¹⁷² The Danish Environmental Protection Agency (2005), <u>More environmentally friendly alternatives to PFOS-compounds and PFOA</u>.

¹⁷³ UNEP, (2018) Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

¹⁷⁴ The Danish Environmental Protection Agency (2005), <u>More environmentally friendly alternatives to PFOS-compounds and PFOA</u>.

¹⁷⁵ Matrix Scientific, <u>Product Page for CAS RN 97571-69-2</u>, accessed September 2019.

¹⁷⁶ Cymit Quimica, <u>Product Page for CAS RN. 330562-41-9</u>, accessed November 2019.

as the potassium salt of F-53B (CAS RN 736606-19-6), can be purchased from Alfa Chemistry¹⁷⁷ and Howei Pharm¹⁷⁸, both of which are outside the EEA.

The following additional information was found: 3M uses 95-100% of 2,2,3,3,5,5,6,6-octafluoro-4-(trifluoromethyl)morpholine (CAS RN 382-28-5) for the manufacturing of PF 5052 Performance fluids,¹⁷⁹ which are sold under the category of electronic solutions for larger public¹⁸⁰. Performance fluids are also used as coating materials in printed circuit boards and hard disk drives to improve protection against corrosion, grime and contamination, which ultimately leads to greater production efficiency¹⁸¹.

Novec 7700 engineered fluid from 3M, which is constituted of Furan, 2,3,3,4,4-pentafluorotetrahydro-5methoxy-2,5bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl] (CAS RN 957209-18-6), has been commercialised under the segment 'coating solvents for electronics'¹⁸². Little additional information was found through desk research. The existence of other CAS numbers in the EU and USA database presents evidence of their large-scale use, but no information on their uses was available.

7.3 Group 4 substances used in articles

Group 4 chemicals are used in the manufacturing of articles in complex ways (see Table 29). One role is supporting the production of fluoropolymers, which are then used in the production of consumer articles. One of the best known among these is the ammonium salt of hexafluoropropylene oxide dimer acid (CAS RN 62037–80–3, also known as GenX, FRD-902 or C3 Dimer salt¹⁸³), which was commercialized by Dupont (now Chemours) to replace PFOA in the fluoropolymer production¹⁸⁴. These fluoropolymers are then used in a wide range of industries including construction, textile, automotive sector, cabling materials, food processing, manufacturing of pharmaceutical and biotechnology and electronics¹⁸⁵. Several other uses were identified through desk research, although it was not possible to link them to specific CAS numbers. Some fluorinated substances developed as alternatives to PFOA and PFOS may be Group 4 substances, as in the case of GenX, but their chemical identities are not always known by CAS numbers¹⁸⁶. The following uses might be further investigated:

- alternatives to PFOS- and PFOA-related substances in the impregnation of a wide range of textile products including rugs, leather, carpets, upholstery. Fluorinated alternatives provide stain- and oil-

¹⁷⁷ Alfa Chemistry, <u>Product Page for CAS RN 73606-19-6</u>, accessed October 2019.

¹⁷⁸ Howei Pharm, <u>Product Page for CAS RN 73606-19-6</u>, accessed November 2019.

¹⁷⁹ 3M, <u>Safety Datasheet for Performance Fluid 5052</u>, accessed via ACOTA website, accessed November 2019.

¹⁸⁰ 3M France, <u>Performance Fluids for Consumers</u>, accessed November 2019 (French).

¹⁸¹ UNEP, (2018) Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

¹⁸² 3M, (2019) <u>Safety Datasheet for 3M[™] Novec[™] 7700 Engineered Fluid</u>, accessed November 2019.

¹⁸³ Beekman et al, for Netherlands National Institute of Public Health, (2016), Evaluation of substances used in the GenX technology by Chemours, Dordrecht. RIVM Letter report 2016-0174.

¹⁸⁴ Bao, Yixiang et al. (2018). Degradation of PFOA Substitute - GenX (HFPO-DA ammonium salt): Oxidation with UV/Persulfate or Reduction with UV/Sulfite?. Environmental Science & Technology. 52. 10.1021/acs.est.8b02172.

¹⁸⁵ US Environment Protection Agency, (2018), <u>Human Health Toxicity Values for Hexafluoropropylene Oxide (HFPO) Dimer Acid</u> and Its Ammonium Salt (CAS RN 13252-13-6 and CAS RN 62037-80-3).

¹⁸⁶ UNEP, (2018) Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

repellency in a way non-fluorinated alternative cannot achieve and are used worldwide in textiles where these specific qualities are critically important¹⁸⁷.

- Other plastics products than listed in the Table 29 above, in which fluorinated PFOS alternatives may be used as release agents used in moulding and casting¹⁸⁸.

CAS RN	Company	Related Article	Used as/function
335-36-4	3M	Solar cells, computers, mobile phones, digital home appliance	Fluoropolymer manufacture aid
16090-14-5	US Dupont	Polymer electrolyte fuel cell (PEFCs)	Used as monomer in copolymer production ¹⁸⁹
37486-69-4	Dyneon (3M)	Food contact materials for single use: films, bags, plates, sheets	processing aid in sintered and non- sintered fluoropolymers ¹⁹⁰
37486-69-4	Dyneon (3M)	Food contact materials for repeated use: pans gaskets, seals, conveyor belts, pipes, liners, and other articles that come into contact with foodstuffs for repeated use	processing aid in sintered and non- sintered fluoropolymers ¹⁹¹
62037-80-3 (GenX) ¹⁹²	Chemours	Cable and internet infrastructure, non-stick cookware, breathable outdoor garments, garments for medical use, electronic devices, insulation cabling for data centers, aircraft, ships, garments for military, plastic products including compounding and conversion ¹⁹³	Processing aid for fluoropolymer resins ¹⁹⁴¹⁹⁵
73606-19-6 (F- 53B)	Several producers in China	A diverse use for coating of metal articles	Mist suppressant ¹⁹⁶
161075-00-9	Solvay	Polyurethane insulation foam panels	Process regulator ¹⁹⁷

Table 29 Perfluoroether non-polymers, identified use in relation to articles

194 Ibid.

¹⁸⁷ UNEP, (2018) Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

¹⁸⁸ Ibid.

¹⁸⁹ Wang, Z., Cousins, I., Scheringer, M. and Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environment International, 60, pp.242-248.

¹⁹⁰ EFSA Scientific Opinion (2012), <u>Scientific Opinion on the safety evaluation of the substance</u>, <u>2H-perfluoro-[(5,8,11,14-tetramethyl)-tetraethyleneglycol ethyl propyl ether]</u> CAS RN 37486-69-4 for use in food contact materials.

¹⁹¹ Ibid.

¹⁹² Chemours Website no longer provides information on GenX. The information comes from a <u>Dupont brochure dating 2010</u> found on the internet, accessed November 2019.

¹⁹³ REACH Registration file for CAS RN 62037-80-3, accessed November 2019.

¹⁹⁵ REACH Registration file for CAS RN 62037-80-3, accessed November 2019.

¹⁹⁶ Wang, Z., Cousins, I., Scheringer, M. and Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environment International, 60, pp.242-248.

¹⁹⁷ REACH Registration Dossier for CAS RN 161075-00-9, accessed November 2019.

CAS RN	Company	Related Article	Used as/function
754925-54-7 (F53)	Several producers in China	A diverse use for coating of metal articles	Mist suppressant ¹⁹⁸
957209-18-6	3M	Small devices, electric and electronic articles	Used as functional fluid ¹⁹⁹
1190931-27-1	NA	Cast film, fittings, valves, tapes, anti-stick coating (food contact materials),	processing aid in manufacture fluoropolymers ²⁰⁰
919005-14-4	Dyneon (3M)	Non-stick cookware and other food contacts materials ²⁰¹ (this may include popcorn boxes, cardboard pizza boxes, wraps ²⁰²	replace ammonium perfluorooctanoate (APFO), emulsifier ²⁰³ for coatings
1190931-27-1	Solvay	Rubber products, plastic products	Used in polymer formulations ²⁰⁴

7.4 Key producers and suppliers

Two main types of companies are identified: the main registrants of the chemicals in Group 4 under REACH (3M, Chemours, Solvay, Dyneon (3M), Miteni (bankrupt since 2018)), and some other potential manufacturers of specialty chemicals (Unimatec, Asahi Kasei, Chemos, ABCR (DE)). Apart from these companies registered in the EU, some of the substances are also produced in the US (Chemours). Some other companies which appear to have their own production facilities but mainly for small quantities and supplying to research companies were also identified. Among them, Alfa Aesar has offices in DE and UK but has a global presence as part of the larger group of Thermo Fisher Scientific. CM Fine Chemicals has its headquarters in Switzerland but also has a production facility in China. Other manufacturers are outside of the EEA: Exfluor, Fluorotech, Omnova (all in the US, but Omnova Solutions has production facility in France), Hangzhou Dayangchem, Howei Pharm, Huanxinfluoro (all in China). China seems to host many other producers which could not be verified.

The second type of company are mainly operating as resellers/distributers. Some have started as distributers but then started to manufacture fine chemicals of their own, or to provide synthesis services to the customers. The research suggests there is a complex supply chain with inter-connected manufactures, suppliers and distributers. As in the case of major manufacturers, there might be company acquisitions, which further complicates this picture. It is challenging to create a full picture of this complex

¹⁹⁸ Wang, Z., Cousins, I., Scheringer, M. and Hungerbühler, K. (2013). Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environment International, 60, pp.242-248.

¹⁹⁹ REACH Registration Dossier for CAS RN 957209-18-6, accessed November 2019.

²⁰⁰ EFSA Journal 2014;12(6):3718, Scientific Opinion on the safety assessment of the substance, Perfluoro {acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt, CAS RN 1190931-27-1, for use in food contact materials.

²⁰¹ Gordon S. for 3M Corporation, (2011) <u>Toxicological evaluation of ammonium 4,8-dioxa-3H-perfluorononanoate, a new</u> <u>emulsifier to replace ammonium perfluorooctanoate in fluoropolymer manufacturing</u>, Regulatory Toxicology and Pharmacology 59 (2011) 64–80.

²⁰² UNEP, (2018) Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

²⁰³ 3M Dyneon Press Release, (2008) <u>New Dyneon Emulsifier Eliminates APFO from Production of Fluoropolymers</u>, accessed November 2019.

²⁰⁴ REACH Registration Dossier for CAS RN 1190931-27-1, accessed October 2019.

marketplace. The companies listed below are identified through CAS number search as selling (or sometimes manufacturing in small quantities) at least one chemical from Group 4. Where available, more information is provided.

- Apollo Scientific, UK (also manufacturer)
- Carbone Scientific, UK
- Clearsynth, European office in HU with global offices
- CM Fine Chemicals, (also manufacturer), CH with production in China)
- CPH Chemicals, (online marketplace)
- Cymitquimica, (online marketplace)
- Finetech, (also manufacturer) UK with production in China,
- Fluorochem UK
- Generon, IE
- Manchester Organics, UK, (also manufacturer and other services)
- Nova Chemistry, UK
- TCIC Chemicals Offices in BE, DE and UK (Manufacturer, supplier)
- VWR (Avatar), (Online Supplier)

In addition to these, some other were identified outside of EEA, mainly the US and China. These are Alfa Chemistry, (USA) Fluoryx (USA), FUDI Chemical CO (China), Martrix Scientific (USA, CA, also manufacturer), Santa Cruz Biotech (USA, also product development and biotech research), Kinbeste, Shouyuan (both in China), Synquest Labs (USA, also manufacturer), Pallmer Holland (USA), TRC Canada (CA, also manufacturer). As in the case of manufacturers, Chinese market is likely to have many more suppliers than identified in the research.

7.5 Volumes of Group 4 substances

7.5.1 Within the EEA

Information regarding the production volumes of the chemicals in group 4 is scarce in the public domain. One source of information is the ECHA databases, particularly the Registered Substances Database. The table below provides the tonnage bands for those Group 4 substances registered under REACH. The tonnage bands reported to REACH are large. That does not allow a detailed view and leads to a rough estimate between 212 tonnes to 2120 tonnes annual production or import, which is too broad to draw any meaningful conclusions. Furthermore, the data is not available for the substances that are used as intermediates, e.g. exclusively used in the production of other substances. This is particularly pertinent for efforts to monitor and regulate these substances since the estimations of exposure and releases to the environment are directly related to volumes produced²⁰⁵. The SPIN database does not provide information about total use volumes of the CAS numbers that appear in the database. For all nine CAS numbers in the SPIN, the information on total use is confidential.

²⁰⁵ OECD, (2015) Working Towards a Global Emission inventory of PFAS: Focus on PFCAS - Status Quo and The Way Forward.

CAS RN	Name	Number of registrants (active)	Submissions	Tonnage band (tonnes/year)
382-28-5	2,2,3,3,5,5,6,6-octafluoro-4- (trifluoromethyl)morpholine	1	1 (Joint)	100-1000
62037-80-3 (GenX)	Ammonium 2,3,3,3-tetrafluoro-2- (heptafluoropropoxy)propanoate	1	1 (Ind)	10-100
144728-59-6	2-(1,2-dichloro-1,2,2-trifluoroethoxy)- 1,1,2,2-tetrafluoroethanesulfonyl fluorid	1	1(Ind)	Unavailable- intermediate use only
874288-98-9	1,2-dichloro-1- [difluoro(trifluoromethoxy)methoxy]-1,2,2- trifluoroethane	1	1(Joint)	Unavailable- intermediate use only
919005-14-4	2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3- (trifluoromethoxy)propoxy]propanoic acid	1	1(Ind)	Unavailable- intermediate use only
957209-18-6	2,3,3,4,4-pentafluoro-2,5-bis(1,1,1,2,3,3,3- heptafluoropropan-2-yl)-5- methoxytetrahydrofuran	1	1(Ind)	1-10
1190931-27-1	Ammonium difluoro{[2,2,4,5-tetrafluoro-5- (trifluoromethoxy)-1,3-dioxolan-4- yl]oxy}acetate	1	1(Joint)	1 - 10
1190931-39-5	Potassium difluoro{[2,2,4,5-tetrafluoro-5- (trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate	1	1(Ind)	Unavailable- intermediate use only
161075-00-9	Hexafluoropropene, oxidized, oligomers, reduced, fluorinated	1	1(Joint)	100-1000
Total				212-2120

Table 30 Tonnage bands of Group 4 substances registered under REACH

The information on substances proposed as alternatives to PFOA and PFOS might be useful for some of the estimates, albeit in very general terms. A KEMI report from 2015 estimates the following volumes for PFOS use in the EU annually: 562 kg for photographic industry, 9.3 kg for semi-conductor industry, 600 to 730 for hydraulic aviation industry²⁰⁶. It is safe to assume that alternatives will replace PFOS in these industries as their exemption from the Stockholm Convention has ended in 2019²⁰⁷.

When it comes to PFOA, the substance was produced only by Miteni (IT) until 2010, therefore the use remains dependent exclusively on imports²⁰⁸. The imports of PFOA were estimated to be around 20 tonnes/year as substances, 10 tonnes as mixtures, 10 tonnes as imported in articles. A further 100-1000 tonnes as PFOA related substances and 1000-10,000 as PFOA related substances in textiles²⁰⁹. Following the latest amendments to the Annex XVII of the REACH Regulation, manufacture, use and placing on the

209 Ibid.

²⁰⁶ KEMI Report (2015), <u>Occurrence and use of highly fluorinated substances and alternatives</u>.

²⁰⁷ Chemical Watch (2019), <u>Geneva Meeting agrees global ban on PFOA, with exemptions</u>, accessed 28.01.2020.

²⁰⁸ ECHA, <u>Committee for Risk Assessment</u>, (2015) Background Document to the o the Opinion on the Annex XV dossier proposing restrictions on Perfluorooctanoic acid (PFOA), PFOA salts and PFOA-related substances.

market will be restricted starting from July 2020, with certain exemptions²¹⁰. This will increase the use of alternatives, including Group 4 substances, to replace at least some of these quantities mentioned above. It is also important to note that some alternatives to PFOS and PFOA are likely to be used in greater quantities to achieve the same results due to less efficiency²¹¹.

7.5.2 Globally

Statistics regarding the global manufacture and use of the substances in Group 4 is not available. For the CAS numbers that are listed in USEPA CDR database, all information is 'withheld' or considered as confidential business information²¹². However, because of the legal reporting threshold, it can be deduced that these substances are produced or imported in volumes of 25,000 pounds (11,340 kg) or more at any single site in the US²¹³. With the 8 substances²¹⁴ reported for 2016 under CDR, it can be concluded that the total volumes are at least 90 tonnes per year from US data alone. The threshold for reporting in the US is more than 10 times higher than in Europe; therefore, the US CDR reporting system excludes chemical substances produced/used under these thresholds. For instance, 3 of the substances registered under REACH are produced/imported 1-10 tonnes a year and thus they would not be reported in the US, even if they were used in the same quantities.

7.6 The potential for exposure

7.6.1 Information from ECHA and SPIN

REACH registration dossiers

Information is available for the 9 substances registered under REACH (listed in the table below), but it is either incomplete or withheld as confidential information. Based on the general information provided by the REACH registration dossier, emission into the air and water from industrial sites can be a concern especially for chemicals such as GenX, 2,2,3,3,5,5,6,6-octafluoro-4-(trifluoromethyl)morpholine (CAS RN 382-28-5), and 2,3,3,4,4-pentafluoro-2,5-bis(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-5-methoxytetra-hydrofuran (CAS RN 957209-18-6). Furthermore, both of the aforementioned substances (CAS RN 382-28-5 and 957209-18-6) are categorised as being widely used by workers with high levels of potential worst-case release factors. Only two CAS numbers are associated with end use by consumers (CAS RN 957209-18-6 and 1190931-39-5). Only the most relevant information is provided in the section below. All information from REACH dossiers can be found in the annex.

Manufacturing phase

For the manufacturing phase, information is available for three CAS numbers. For all of them (CAS RN 382-28-5, 1190931-39-5 and 161075-00-9) several processes are reported, sometimes based on different formulations using the same substance. All three are being used in processes where there is no likelihood of exposure with equivalent containment conditions. For CAS RN 382-28-5, the possibility of exposure is

²¹⁰ ECHA, <u>Annex XVII to REACH, Conditions of Restriction</u>.

²¹¹ KEMI Report (2015), Occurrence and use of highly fluorinated substances and alternatives.

²¹² US Environmental Protection Agency, Chemical data reporting 2016 results, downloaded from <u>EPA website</u>, September 2019.

²¹³ US Environmental Protection Agency, Chemical Data Reporting, <u>The Basics</u>, accessed October 2019.

²¹⁴ These are 382-28-5, 2062-98-8, 2641-34-1, 3330-14-1, 4089-58-1, 13252-13-6, 62037-80-3 and 69116-73-0.

noted. For CAS 1190931-39-5, occasional controlled exposure for workers was found. For GenX (CAS RN 62037-80-3), there is no information.

Formulation and re-packaging phase

Only one substance is listed as relevant during the formulation phase (CAS RN 382-28-5). The transfer of the substances between different containers is said to have no likelihood of exposure with equivalent containment conditions.

Uses at industrial sites

Except for CAS RN 919005-14-4, some level of exposure or likelihood of exposure is reported for all the substances for which data is provided. Likelihood of exposure is reported for CAS RN 382-28-5, but the substance is not included in the article nor does it remain on the finished article being manufactured. The registration dossier for GenX (CAS RN 62037-80-3) reports different processes, all of which are related to the main use of the chemical as a processing aid for polymerisation. The dossier states that there is no inclusion of the substances into or onto the article.

Under process categories, several are reported which range from no likelihood of exposure to occasional controlled exposure. The most detailed information on exposure in this group is provided for hexafluoropropene, oxidized, oligomers, reduced, fluorinated (CAS RN 161075-00-9) also known as GALDEN LMW, which is registered by Solvay. The case illustrates the difficulty of assigning a particular risk category to a substance, since different processes lead to different scenarios of exposure in different industries. For instance, the registration dossier for GALDEN LMW reports four different uses at industrial sites: as heat transfer agent in organic rankine cycle, in production of PU rigid foam panel, as heat transfer fluid and in PFPE lubricant. Each of these uses have different compositions of the substance, different process categories and different exposure/environmental release factors. The table below summarizes the information based on different uses of the GALDEN LMW²¹⁵.

Use	Process Code and exposure
Heat Transfer Agent in Organic Rankine Cycle	PROC 1: Chemical production or refinery in closed process without likelihood of exposure or processes with equivalent containment conditions PROC 2: Chemical production or refinery in closed continuous process with occasional controlled exposure or processes with equivalent containment conditions PROC 8b: Transfer of substance or mixture (charging and discharging) at dedicated facilities
Production of PU rigid foam panels	 PROC 8a: Transfer of substance or mixture (charging and discharging) at non-dedicated facilities PROC 2: Chemical production or refinery in closed continuous process with occasional controlled exposure or processes with equivalent containment conditions PROC 4: Chemical production where opportunity for exposure arises PROC 15: Use as laboratory reagent PROC 21: Low energy manipulation of substances bound in materials and/or articles
Heat transfer fluid	PROC 1: Chemical production or refinery in closed process without likelihood of exposure or processes with equivalent containment conditions

Table 31 Industrial uses of GALDEN LMW a	at industrial sites
--	---------------------

²¹⁵ All information in the table comes from the Registration Dossier for CAS RN 161075-00-9.

	PROC 2: Chemical production or refinery in closed continuous process with occasional controlled exposure or processes with equivalent containment conditions PROC 8b: Transfer of substance or mixture (charging and discharging) at dedicated facilities
PFPE Lubricant	 PROC 10: Roller application or brushing PROC 13: Treatment of articles by dipping and pouring PROC 7: Industrial spraying PROC 8b: Transfer of substance or mixture (charging and discharging) at dedicated facilities

Only one of the indicated uses, use of GALDEN LWM in the production of rigid foam panels, has a section on the different exposure and environmental release scenarios. However, no values are communicated for PECs (predicted environmental concentrations) for environmental releases, exposure of the environment or exposure of the workers.

Use by professional workers

Only two CAS numbers (382-28-5 and 957209-18-6) have information on use by professional workers, which indicates a widespread use by small scale industries. For CAS RN 382-28-5 which is used as a non-reactive processing aid and as functional fluid indoors, the processes mainly involve transfer of substance or mixture in dedicated and non-dedicated facilities or transfer into small containers. Processes also involve chemical production or refinery without likelihood of exposure and uses as laboratory agents. Two different uses are reported for CAS RN 957209-18-6 which includes transfer of substance or mixture at non-dedicated facilities and laboratory use. For both uses, insignificant exposure of workers (via oral, dermal, eye and inhalatory routes) and insignificant release into the environment (via water, soil, air and waste) is reported. These are classified as accidental and infrequent.

Article service life

As the Group 4 substances registered under REACH are mainly used as intermediates, only two have a dedicated section on this life cycle stage. The registration dossier for CAS RN 957209-18-6 states that this substance is used as a functional fluid in articles such as machinery, mechanical appliance, electrical and electronic articles covered by WEEE (Waste Electrical and Electronic Equipment) directive. Low release is expected as well as insignificant worker exposure via oral, dermal, eye and inhalatory routes. Insignificant/accidental release might occur into the environment via water, air, soil and waste. This indicates a business use, not a consumer end use. The other substance, CAS RN 1190931-39-5 is an intermediate; it has a section on article service life, but no information is provided.

The table below provides an overview of the ERCs (Environmental Release Categories) for all Group 4 substances registered under REACH.

Manufacture			Formu	Formulation or re-packing			Industrial sites			Widespread use by professional workers			Consumer use and service life		
CAS RN	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil	To Air	To water (before SPT)	To soil	To Air	To water (befor e SPT)	To soil
										100%	100%	n.a			
382-28-5	5%	6%	0.01%	2.5%	2%	0.01%	100%	100%	5%	5%	5%	n.a			
62037-80-3 (GenX)							100%	100%	5%						
							5%	5%	5%						
161075-00-9	5%	6%	0.01%	2,5%	2%	0.01%	50%	50%	1%						
919005-14-4							5%	2%	0.1%						
													0,05%	3,2%	3,2%
							5%	5%	5%	5%	5%	n.a	0,05%	0,05%	n.a
957209-18-6							100%	100%	5%	100%	100%	n.a	0,05%	0,05%	0,05%
1190931-27-1	5%	6%	0.01%				35%	0,005%	0,025%						
	5%	2%	0,1%				5%	2%	0,1%				5%	2%	0,1%
1190931-39-5	5%	6%	0.01%				5%	6%	0.01%				5%	6%	0.01%

Table 32 Environmental release categories (ERCs) associated with life-cycle stages of the substances, based on REACH registrations

The SPIN Database

Among the Group 4 substances, four substances have information on exposure in the SPIN database, solely from Sweden (see Table 33). According to the assessment results provided in the SPIN database, for all four substances, there is limited application field (which is reported under Range of Use Index 1-minimum). In a similar vein, the quantities consumed (column "Quantity) remain low for all substances, with CAS RN 1600-71-1 and CAS RN 55716-11-5 being used only at a 'medium low' level (indicated as 2 out of 5). When it comes to exposure of the environment to these substances, air emissions seem to be the biggest risk, among others (indicated as 3 out of 5), with 'potential exposure". The impact on wastewater, surface water and soil remain minimum. Risk of exposure for occupational workers is also indicated as 3 out of 5 (potential exposure). More details on exposure indicators used by SPIN database can be found in the Annex 10.5.

CAS RN	Year	Surface Water	Air	Soil	Waste water	Human consumer	Worker- occupational	Range of Use Index	Quantity	Article
335-36-4	2012	1	2	1	1	1	3	1	1	1
382-28-5* ²¹	2015	1	3	1	2	1	3	1	1	1
1600-71-1	2015	1	3	1	2	1	3	1	2	1
55716-11-5	2015	1	3	1	2	1	3	1	2	1

Table 33 Exposure information provided by the SPIN database based on CAS numbers

7.6.2 Information from the relevant literature

Information is limited regarding human and environmental exposure to Group 4 substances. Monitoring of these substances rarely happens, and information mainly comes from efforts made by the public authorities focusing on several substances. For instance, both ADONA and GenX were evaluated under REACH by Germany in 2015 and 2017, respectively. In the justification documents for inclusion in the CORAP (Community rolling action plan)²¹⁷ substance list, wide-dispersive use and environmental exposure was listed as concerns for ADONA,²¹⁸ environmental exposure was listed as a concern for GenX²¹⁹. Finally, GenX was recognised as a Substance of Very High Concern by the Member State Committee, which led to the information on the substance to be compiled together, for instance in the Supporting Document for the identification of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid, its salts and its acyl halides as substances of very high concern²²⁰.

²¹⁶ CAS RNs Marked with * are registered substances, therefore they are produced/imported 1 tonne/year or more in the EEA.
²¹⁷ CoRAP includes substances that have been or will be evaluated by a Member State based on concerns for human health or potential impacts to environment resulting from their manufacture and/or use. More information can be found here: https://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan

²¹⁸ CoRAP File on Ammonium 2,2,3 trifluor-3-(1,1,2,2,3,3-hexafluoro-3-trifluormethoxypropoxy)propionate submitted by Germany, (2015) Justification for the selection of a substance for CoRAP inclusion.

²¹⁹ CoRAP File on Ammonium 2,3,3,3-tetrafluoro-2(heptafluoroporpoxy)propanoate submitted by Germany, (2015) <u>Justification</u> for the selection of a substance for CoRAP inclusion.

²²⁰ ECHA, (2019), Member State Committee Support Document for Identification Of 2,3,3,3-Tetrafluoro-2

⁽Heptafluoropropoxy)Propionic Acid, Its Salts And Its Acyl Halides (Covering Any Of Their Individual Isomers And Combinations

Currently, existing studies on the environmental and human exposure to Group 4 substances have mainly focused on:

- PFECAs as a larger group, and within this group:
 - FRD-902 (CAS RN 62037-80-3-GenX)
 - FRD-903, (CAS RN 13252-13-6-)²²¹ which is used in the production of FRD-902 (these two substances are sometimes referred to as HFPO-DA interchangeably)
 - ADONA (CAS RN 919005-14-4) and related substances
- PFESAs as a larger group, which contains chemicals such as F-53 acid (CASN RN 754925-54-7) and F-53B potassium salt (CAS RN 73606-19-6) and F53B acid (CAS RN 756426-58-1).

Available information on the substances listed above suggests that the biggest share of releases seems to occur during the manufacturing phase. Therefore, risks for human exposure are mainly explored concerning the exposure of workers during the manufacture of the substance itself or its downstream use at industrial sites. However, as in the case for all PFAS contaminants, human exposure may occur through different pathways (such as contaminated drinking water, fish or agricultural products) which originated at or close to the production sites. The information concerning general exposure is largely missing. In the same vein, the information related to exposure of consumers is very limited and remains mostly generalized to broader groups of PFAS without addressing the particular substances in Group 4.

As stated above, there is little information on the exposure of the environment to the substances in Group 4. The information reported by the companies to REACH usually suggest limited release. However, some of these substances have been detected in the environment. The information in this section is organised by individual substances, on which there is information from the literature.

GenX (HFPO-DA) and related substances, FRD-902, FRD-903, E1²²²

The Chemours (Dupont until 2015) plant in Dordrecht, Netherlands, is the company's most important production site for fluoropolymers such as Teflon²²³ in Europe. The plant started using GenX (CAS RN 62037-80-3) technology in 2012, as a replacement for PFOA as a processing aid in fluoropolymer production. Concern over releases of GenX to the environment led to the Netherlands' temporary action framework on PFAS²²⁴ and a proposal to add GenX to the EU list of Substances of Very High Concern (SVHC) under Article 57 of REACH. The proposal was unanimously agreed upon by the Member State Committee in June 2019²²⁵.

The research and monitoring in the Netherlands concerning PFAS emissions from the Dordrecht plant started in 2015 with a focus on emissions into air, which was then expanded to monitoring of PFAS in

Thereof) As Substances Of Very High Concern <u>https://echa.europa.eu/registry-of-svhc-intentions/-/dislist/details/0b0236e1832708a2</u>.

²²¹ Netherlands National Institute for Public Health and the Environment (RIVM),(2018), Risk Management Option Analysis Conclusion Document.

²²² This section uses the terminology of the reports overviewed, which sometimes use FRD-902. FRD, GenX, HDPO-DA interchangeably.

²²³ Chemours, <u>Dit is Chemours in Dordrecht</u>, accessed November 2019.

²²⁴ ABO Consulting, <u>Grote gevolgen (tijdelijk) handelingskader PFAS (en GenX)</u>, accessed November 2019.

²²⁵ ECHA, <u>MSC unanimously agrees that HFPO-DA is a substance of very high concern</u>, accessed December 2019.

waters, waste, soil and food²²⁶. This process gathered an important body of information, complemented by an increasing focus within the research community. As a result, GenX is the Group 4 substance which has the most information on exposure available.

As indicated above, substances related to GenX include FRD-902 (Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate), FRD-903 (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid) and E1 (1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane). FRD-902 is a processing agent with the same CAS number as GenX; it is imported into the Netherlands from the USA. FRD-903 is a precursor (CAS 13252-13-6)²²⁷, while E1 is another Group 4 substance (CAS 3330-15-2). During the production process, both FRD-903 and E1 are released into the environment²²⁸. An RIVM evaluation document from 2016 provides information on the permitted emissions of FRD-903 and E1 compared to actual emissions from different processes (see Table 34).

Table 34 Release of FRD-903 and E1, from the Chemours Plant between 2012-2015, Source: RIVM

Substance	Permitted Em	nissions (year/kg)	Actual emissions 2012-2015 total (kg)		
	PTFE production FEP production		PTFE	FEP production	
			production		
FRD-903	600	40	1163	95	
E1	750	450	1176	147	
Total			2339	242	

The annual average concentrations of FRD-903 in the air were calculated to be 20 ng/m³ for the nearest area. Calculations based on recorded emissions led to a lower concentration, 15 ng/m³. These were compared to the 73 ng/m³ exposure limits for inhalation. Since the main exposure to these substances is via air, it was concluded that '*No health risk is expected for people living in the vicinity of the plant due to the emissions of these substances*'²²⁹.

However, two years later, RIVM issued an RMOA (Risk Management Option Analysis) document that identified concerns about the *unpredictable and uncontrollable* emissions of HFPO-DA (GenX) and concluded that even very low concentrations in wastewater could result in high environmental concentrations. Water contamination is a primary concern in the Netherlands, where approximately 40% of river waters are potential sources of drinking water²³⁰. The monitoring data collected from water samples showed the presence of HFPO-DA even in areas where no point sources were identified. The same substance was also found in different environmental media such as drinking water, fish and garden

²²⁶ Netherlands National Institute for Public Health and the Environment (RIVM), (2019), Verspreiding van GenX-stoffen in het milieu: Metingen in Nederland - 2013-2018 (Dutch).

²²⁷ Netherlands National Institute for Public Health and the Environment (RIVM), (2016) Evaluation of substances used in the GenX technology by Chemours, Dordrecht.

²²⁸ Netherlands National Institute for Public Health and the Environment (RIVM), (2016) Evaluation of substances used in the GenX technology by Chemours, Dordrecht.

²²⁹ Netherlands National Institute for Public Health and the Environment (RIVM), (2016) Evaluation of substances used in the GenX technology by Chemours, Dordrecht.

Netherlands National Institute for Public Health and the Environment (RIVM), (2018), Risk Management Option Analysis Conclusion Document.

²³⁰ Brandsma, S.H., Koekkoek, J.C., van Velzen, M.J.M., de Boer, J., (2019), <u>The PFOA substitute GenX detected in the environment</u> <u>near a fluoropolymer manufacturing plant in the Netherlands</u>, Chemosphere.

vegetables. These findings also contributed to increased attention to exposure via water and other pathways apart from inhalation. Because the substance has only been produced in the Netherlands since 2012, the report concluded that the substance was very mobile in the environment, spreading to large areas in a very limited amount of time²³¹. The high mobility of the substance in the environment, especially in water, was one main evidence to have HFPO-DA identified as an SVHC²³², amongst others.

Between 2017 and 2018, while monitoring surface waters for biocides, the Dutch Ministry of Infrastructure and Water Management looked for 17 different PFASs and found 11 in concentrations beyond detection limits. High concentrations of FRD-902 were found in the sewage treatment plants of Eindhoven and Bath²³³. Furthermore, in an effort to provide an overview of PFASs in the Dutch environment, the PFAS Expert Centre²³⁴ identified 29 risk locations for potential contamination. The project considered the production facilities where GenX is used (both the production and the processing of Teflon) as high-risk locations. Chrome plating facilities were also considered high risk locations. Other industries using different PFAS chemicals (textile, semiconductor, photo printing, paper and packaging, hydraulic liquids, cosmetics) were considered locations of limited risk, along with landfills and wastewater treatment plants. Samples were taken from 182 different wells in 29 locations, and 3% of all samples were analysed for GenX. A maximum concentration of 0.66 mg/l was detected in groundwater samples during a monitoring for air deposition in 6 different locations around Drechtsteden²³⁵²³⁶.

In 2017, the Dutch Ministry of Health and Environment carried out a risk analysis that focused on vegetable gardens situated within 4km of the Chemours production plant²³⁷. GenX was present at measurable quantities in 14% of the 81 samples collected. The study recognised that residents are exposed to the chemical not only via consuming these vegetables but also through emissions through air and drinking water. The analysis concluded that the levels were not above the threshold values and the produce from the vegetable gardens could be consumed in moderation, even with the additional exposure paths²³⁸.

In another study, GenX was found in leaves and grass as well as in drinking water within the immediate vicinity of the production plant in Dordrecht, markedly decreasing in concentrations as the distance of sampling location increased from the plant. In the figure below, concentrations of PFOA and GenX are provided, showing that GenX has higher concentrations than PFOA²³⁹.

²³¹ Netherlands National Institute for Public Health and the Environment (RIVM), (2018), Risk Management Option Analysis Conclusion Document.

²³² Chemical Watch, <u>Dutch SVHC action agains GenX first of his kind</u>, accessed December 2019.

²³³ BACO Adviesbureau (2017), Onderzoek naar biociden in efflienten van rwzi's najaar 2017 (deel 1).

²³⁴ The PFAS Expert Centrum is a team of experts commissioned by the Dutch Ministry of Infrastructure and Environment to work on PFAS with the local authorities. It involves expert from Arcadis, TTE Consultants and Witteveen + Bos.

²³⁵ Expertisecentrum PFAS, (2018), Aanwezigheid van PFAS in Nederland: Deelrapport B - Onderzoek van PFAS op potentiële risicolocaties.

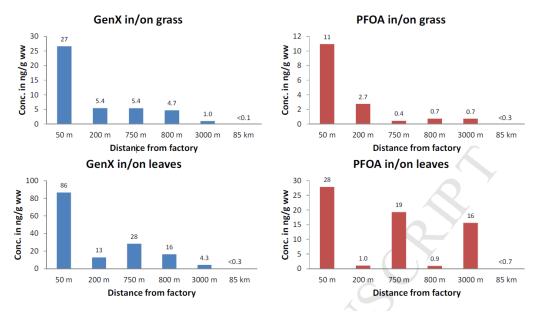
²³⁶ The exact location of these samples is not mentioned in the report. Drechtsteden refers to a group of cities which include Alblasserdam, Dordrecht, Hendrik-Ido-Ambacht, Papendrecht, Sliedrecht and Zwijndrecht

²³⁷ RIVM, (2018), Risicobeoordeling van GenX en PFOA in moestuingewassen in Dordrecht, Papendrecht en Sliedrecht (In Dutch).

²³⁸ RIVM, (2018), Risicobeoordeling van GenX en PFOA in moestuingewassen in Dordrecht, Papendrecht en Sliedrecht (In Dutch).

²³⁹ Brandsma, S.H., Koekkoek, J.C., van Velzen, M.J.M., de Boer, J., (2019), <u>The PFOA substitute GenX detected in the environment</u> <u>near a fluoropolymer manufacturing plant in the Netherlands</u>, Chemosphere.

Concentration of GenX and PFOA in samples collected



Source: Brandsma, S.H., Koekkoek, J.C., van Velzen, M.J.M., de Boer

Another location, Helmond in North-Brabant, was identified as a high-risk location for air emissions because of the presence of Custom Powders, a PTFE powder and granule processing company that dries products containing GenX. Calculations based on modelling resulted in a range of 2.85 ng/m³ and 48 ng/m³ as realistic and worst-case scenarios²⁴⁰. In the 2018 monitoring, samples from a sewer near the facility provided the highest concentrations recorded in water (6,700,000 ng/L) as well as the highest concentrations in soil (1,300 ng/L)²⁴¹.

Contaminations were also detected in areas where there were no known point sources. One of them was at the Suez Almelo waste processing company, which regularly monitors their waste stream for FRD 903. Above 1000 ng/L of FRD 903 was detected during the monitoring. The company does not receive waste from the only known source of FRD 903 (Chemours), but their clients include metal working industry. However, the contamination could not be traced back to those clients, which led the authorities to conclude the contamination might be due to the coating of trucks that deliver the waste²⁴². This document also states that Chemours emits 27,255 kg of FRD²⁴³ via waste, 2,000 kg via water, 500 kg via air and less than 25 kg via products²⁴⁴.

The most detailed report published in the Netherlands to date provides an overview of different measurements from across the country and different media including air, water, groundwater and waste²⁴⁵. The number of measurements is classified by region, year and environmental medium,

²⁴⁰ Netherlands National Institute for Public Health and the Environment (RIVM), (2019), Verspreiding van GenX-stoffen in het milieu: Metingen in Nederland - 2013-2018 (Dutch).

²⁴¹ Ibid.

²⁴² Dutch Ministry of Infrastructure and Water, (2019), Vervolgonderzoek afvalstromen Chemours (Dutch).

²⁴³ The report does not distinguish between FRD-902 and FRD-903.

²⁴⁴ Dutch Ministry of Infrastructure and Water, (2019), Vervolgonderzoek afvalstromen Chemours (Dutch).

²⁴⁵ Netherlands National Institute for Public Health and the Environment (RIVM), (2019), Verspreiding van GenX-stoffen in het milieu: Metingen in Nederland - 2013-2018 (Dutch).

amounting to more than 1000 measurements for years 2013, 2016, 2017 and 2018. It also provides an overview of the results, using the thresholds that are defined as risk limits for exposure. The tables below provide a very broad summary of the measurement data, but the interested parties are encouraged to consult the report (in Dutch) for more details.

Environmental Medium	Total number of samples (2018)	#of Samples exceeding lowest limit for nature (>3 μg/kg ds)	#of Samples exceeding lowest limit for vegetable gardens (>8 μg/kg ds)	Detectior (µg/kg ds	
				Median	Maximum
Soil	40	15	7	1,3	1,300

Table 35 Results of measurements on soil carried out in 2018 at different locations in the Netherlands, 2018

Table 36 Results of measurements on groundwater carried out in 2018 at different locations in the Netherlands,2018

Environmental Medium	Number of samples (2018)	#of samples exceeding risk limits for surface water >118 ng/L)	#of samples exceeding provisional guide value for drinking water (>150 ng/L)	#of samples exceeding risk limit for direct use of groundwater as drinking water (>660ng/L)	Detectior (ng/L)	n values
					Median	Maximum
Groundwater	8	6	6	5	2185	36.000

Table 37 Results of measurements on different water media carried out in 2018 at different locations in the NL, 2018

Environmental Medium	Number of samples (2018)	#of Samples exceeding risk limits for fish consumption (>118 ng/L)	#of Samples exceeding risk limits for bathing waters (>403 ng/L)	#of samples exceeding provisional guide value for drinking water (>150 ng/L)	Detection (ng/L)	n values
					Median	Maximum
Surface water	196	38	18	32	25	400
Drinking water samples	23	NA	NA	0	2,3	4

Environmental Medium	Number of samples (2018)	nples exceeding risk limits limits for bathing water		Detection values (ng/L)	
				Median	Maximum
Wastewater affluent	190	112	98	515	6.700.000
Sewage Treatment Plant effluent	47	10	6	15	3000

Table 38 Results of measurements on different wastewater media carried out in 2018 at different locations in the NL, 2018

Finally, the production process of GenX at the Chemours plant in Dordrecht creates waste, half of which is recycled for reuse²⁴⁶. Chemours has sent the remaining waste to another fluorochemical production facility in Italy, namely Miteni, which also had a waste processing activity²⁴⁷. According to Greenpeace Italy, Chemours has been sending around 100 tonnes/year of GenX waste to Italy between 2014 and 2017²⁴⁸. After Miteni declared bankruptcy in October 2018, this operation was no longer possible, creating problems with the recycling and treatment of the waste from Chemours. Some of the waste had already been transported to Miteni at the time. Chemours initially asked permission from the Dutch authorities to store the waste amounting to 15 tonnes in the Netherlands under Wabo Licence²⁴⁹. The company also asked the US EPA permission to ship this waste to its facility in North Carolina. In fact, Chemours had been shipping waste from the Netherlands to Fayetteville since 2014 and exported 90 metric tons of GenX to the US in 20 shipments between November 2016 and October 2017²⁵⁰. The additional shipment resulting from the Miteni bankruptcy however has been considered as a second waste stream, which created confusion among the public authorities. The request for the additional shipment was temporarily refused by the US authorities who asked for clarifications on the matter from the company²⁵¹. There are also reports that the waste retrieved from Italy has been stored in Antwerp to be incinerated there,²⁵² which might have been counter to rules regulating waste in the EU²⁵³. This case illustrates the waste management for such substances being problematic and creating a burden for local communities, in this case in 4 different countries, all of which refused to have the GenX-contaminated waste stored in their proximity.

GenX and other related substances are an increasing concern in Italy as well. The source of extensive PFAS groundwater contamination in the Veneto region was traced to the Miteni factory already in 2013²⁵⁴,

²⁴⁶ Dutch Ministry of Infrastructure and Water, (2018), Afvalstromen van Chemours (Dutch).

²⁴⁷ Dutch Ministry of Infrastructure and Water, (2018), Afvalstromen van Chemours (Dutch).

²⁴⁸ Greenpeace, <u>Sette scomode verità sul GenX</u>, 13 July 2018 (Italian).

²⁴⁹ Dutch Ministry of Infrastructure and Water, (2019) Vervolgonderzoek afvalstromen Chemours

²⁵⁰ Lisa Sorg, <u>Chemours says it's been "re-importing" GenX waste from Netherlands to Fayetteville plant for five years</u>, *NC Policy Watch*, January 25 2019. accessed December 2019.

²⁵¹ EPA, (2018). <u>Notice of Temporary Objection</u>, accessed November 2019.

²⁵² <u>Chemours exporteerde illegaal GenX</u>, *RTV Dordrect*, November 14 2019, accessed November 2019.

²⁵³ <u>Chemours ontstemd over ministersbrief over 'illegale PFAS-export' naar België</u>', *Process Control*, November 19 2019.

²⁵⁴ WHO, (2016), Keeping our water clean: the case of water contamination in the Veneto Region, Italy.

which led to a high concern and interest in PFAS substances and their monitoring. Due to the GenX waste imported from the Netherlands since 2012, the Veneto region has added HFPO-DA to the list of substances for monitoring efforts as of 2018²⁵⁵. In 2018 the following concentrations of the substance were found²⁵⁶:

Table 39 Detection values for HFPO-DA in different locations in Italy, ARPAV

Sample location	HFPO-DA (ng/L)
Poscola stream	<25 ng/L for all samples
Incoming stream to Trissiono treatment facility	28 ng/L (June 2018)
Piezometer MW18	Lowest 33 ng/L (May 2018) to highest 1240 ng/L (November 2018)
Piezometer MW25	<25 ng/L for all samples
Piezometer MW40	Highest 40 ng/L (December 2018), <25 ng/L for all other samples

In the US, attention to environmental releases of GenX has recently focused on the Chemours plant on the Cape Fear River in North Carolina. GenX was introduced in 2009 as a new technology and has likely been used at the Fayetteville plant since then. Contamination has been documented in Cape Fear River Basin in North Carolina, sometimes linked to specific CAS numbers, including GenX: 1682-78-6, 2062-98-8, 2927-83-5, 3330-14-1, 3330-15-2, 4089-58-1, 13140-29-9, 13252-13-6, 62037-80-3, 137780-68-8, 1132933-86-8²⁵⁷. GenX was detected in different concentrations in samples collected at different sites:

Table 40 GenX Concentrations detected in different locations at Cape Fear River

Sample Site	GenX Concentrations (ng/g dry sediments) ²⁵⁸
Site 1	12.8
Site 2	21.6
Site 3	3.1
Site 4	4.0

The following quantities were detected by Eurofins laboratory following the demand from Cape Fear Public Utility Authority, both from Sweeney Water Treatment Plant²⁵⁹:

Table 41 GenX Concentrations at two different sampling points

Sample N.	GenX Concentrations (ng/L)
3735383	185
3735384	128

Because the Cape Fear River is a major source of drinking water, the private water wells close to the Chemours plant have also been tested for GenX and other PFAS substances. Among 837 private wells

²⁵⁵ ARPAV, (2019) Contaminazione da PFAS Azioni ARPAV (Italian).

²⁵⁶ ARPAV, (2019) Contaminazione da PFAS Azioni ARPAV (Italian).

 ²⁵⁷ Strynar et al, (2015), Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS), Environ. Sci. Technol. 2015, 49, 11622–11630
 ²⁵⁸ <u>Report to the Environmental Review Commission from The University of North Carolina at Wilmington Regarding the</u> <u>Implementation of Section 20.(a)(2) of House Bill 56</u> (S.L. 2017-209)

²⁵⁹ Eurofins, <u>Chain of custody record</u> (no date), accessed December 2019.

tested in 2018, 25% of them had GenX levels that exceeded the provisional risk limit, which is set to 0,14 ng/L. Maximum concentration was 4 ng/L²⁶⁰. The North Carolina Department of Environmental Quality has been investigating the issue since June 2017 and a consent order was signed between the State of North Carolina and the Chemours company in February 2019. The company has agreed to install technologies to reduce GenX emissions into the air and temporarily cut the emissions at least 92% compared to emissions at the beginning of December 2018. They will also continue to capture off-site disposal of wastewater from the facility and take measures to remediate the groundwater contamination and providing alternative drinking water supplies²⁶¹.

The SVHC supporting document for HFPO-DA provides additional monitoring data from other EEA countries, based on previous literature. The table below provides some examples, including studies focusing on human biomonitoring with the source and the year, (see Table 42). Monitoring data from the countries outside the EEA is also provided, some examples can be found in the table below (see Table 43).

Country (Year)	Location/Sample Population	Detected values	Study
DE (2013)	Scheur river	91.4 ng/L	Heydebreck et al., 2015, Heydebreck, 2017
DE (2013)	Rhine-Leverkusen	108 ng/L	Heydebreck et al., 2015, Heydebreck, 2017
DE (2013)	Ems delta	1.80 ng/L	Heydebreck et al., 2015, Heydebreck, 2017
DE/NL (2014)	North Sea and the Wadden Sea multiple locations	average concentration of 2.3 ± 0.9 ng/L	Heydebreck et al., 2015, Heydebreck, 2017
UK (2016)	6 locations in Thames River	between 0.70 to 1.58 ng/L	Pan et al. 2018
NL (20117- 2018)	Blood samples from 24 employees of a fluorochemical plant	Median: 1.55 ng/mL, highest values were 26.6, 51.2 and 169 ng/mL which were much higher than the other values.	Van den Berg 2017
DE (2018)	20 locations along Mainz river	between 0.59 to 1.98 ng/L	Pan et al. 2018
SE (2016) River Svartån and lake Hjälmar		Between 0.88 and 2.68 ng/L	Pan et al. 2018

Table 42 Field data from different monitoring exercises in the EEA, compiled by the SVHC supporting document for HPFO-DA²⁶²

²⁶⁰ Centers for Disease Control and Prevention, <u>Notes from the Field: Targeted Biomonitoring for GenX and Other Per- and</u> <u>Polyfluoroalkyl Substances Following Detection of Drinking Water Contamination — North Carolina, 2018</u>, accessed December 2019.

²⁶¹ North Carolina State, <u>Consent Order 17 CVS 580</u>, accessed December 2019.

²⁶² ECHA (2019), Support document for identification of 2,3,3,3-tetrafluoro-2(heptafluoropropoxy)propionic acid, its salts and its acyl halides (covering any of their individual isomers and combinations thereof) as substances of very high concern (article 57f).

Country Location/Sample **Detected values** Study (Year) Population China **Xiaoqing River** <100 ng/L with peak Heydebreck, 2015, 2017 (2014) concentrations of 2125 to 3825 ng/L China **Dongzhulong River** Between 1750 and 2060 ng/L Pan et al. 2017 (2015)

limit (<0.14 ng/mL)

Quzhou 1.91 ng/L

Mediam value below detection

Huantai was 410 ng/L, Changsu

47.8 ng/L, Zhoushan 2.96 ng/L,

Table 43 Field data from different monitoring exercises carried out in China, compiled by the SVHC supporting
document for HPFO-DA ²⁶³

ADONA

China

(2018)

China

(2018)

48 residents from the city

Huantai, living close to a fluorochemical production

Water of rice paddy fields

near four cities

plant

The detection levels of ADONA in the environment are not as high as for GenX. Germany has useful documentation on the substance, as ADONA is produced in the country. Facilities using ADONA have been investing in structural improvements to minimize emissions to water and air as well and to maximize recovery of the substance. Despite these efforts, the substance has been found in wastewater streams, although in very small quantities²⁶⁴. According to the manufacturer, ADONA is not added to the products *intentionally.* The manufacturer also states that most of the substance used in fluoropolymer manufacturing is recaptured from waste stream and products for reuse or destroyed during the manufacturing process²⁶⁵. However, emerging evidence highlights the presence of the substance in the environment. As previously noted in the literature, ADONA was detected in River Alz in the downstream water from 3M/Dyneon factory, with concentrations ranging from 0.32 to 6,2 ng/L²⁶⁶. ADONA was found at very small concentrations (less than 2 ng/L) in Cape Fear River during the GenX monitoring²⁶⁷.

When it comes to possible migration of the substance into the final products and risks of exposure for consumers, there is very limited information. The safety evaluation of the substance conducted by ECHA has not found traces of ADONA in the sintered fluoropolymer materials above the threshold limit which was set at 0.02 mg/kg. Residual levels were detected in unsintered fluoropolymer powder at 3.3 mg/kg.

Pan et al. 2018

Cui et al., 2018

²⁶³ ECHA (2019), Support document for identification of 2,3,3,3-tetrafluoro-2(heptafluoropropoxy)propionic acid, its salts and its acyl halides (covering any of their individual isomers and combinations thereof) as substances of very high concern (article 57f).

²⁶⁴ Bavarian State Agency for the Environment, Einführung des PFOA-Ersatzstoffes ADONA (German).

²⁶⁵ Gordon S. for 3M Corporation, (2011) Toxicological evaluation of ammonium 4,8-dioxa-3H-perfluorononanoate, a new emulsifier to replace ammonium perfluorooctanoate in fluoropolymer manufacturing, Regulatory Toxicology and Pharmacology 59 (2011) 64–80.

²⁶⁶ As noted in Wang et al (2013), Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. Environment International, 60, pp.242-248.

²⁶⁷ Strynar et al, (2015), Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS), Environ. Sci. Technol. 2015, 49, 11622–11630.

Based on these findings, worst case migration scenarios were below 1 ng/kg for sintered materials and 31 ng/kg for unsintered materials²⁶⁸.

Another study detected limited quantities of ADONA in blood samples collected from the population living in the vicinity of the production plant, which was 14.4 mg/l in its highest value but remained under detection limit in most of the samples²⁶⁹. The highest measurement is thought to be due both to exposure through drinking water and occupational exposure but is not considered a likely health risk²⁷⁰.

C604 both its potassium and ammonium salts

Both ammonium difluoro{[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate (CAS RN 1190931-27-1) and potassium difluoro{[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy}acetate (CAS RN 1190931-39-5) are registered under REACH. The former was registered by Miteni in 2012 (now inactive) and again in 2018 by Solvay (active registrant)²⁷¹. The latter was registered by Solvay in 2011. The former is one of the new additions to the monitoring list of the Veneto Region as explained above. C604 was found in the river Bormida downstream from the Solvay factory²⁷². Furthermore, The Regional Agency for Prevention and Environmental Protection of Veneto (ARPAV) is reported to have detected C604 at concentrations of 42 ng/L at the Corbola sampling point in the Po River. The same substance was also detected in a smaller branch of Po, at San Basilo Ariano²⁷³. The table below provides an overview of concentrations of C604 from different sampling locations by ARPAV²⁷⁴.

Sample location	CAS NR. 1190931-27-1(ng/L)
Poscola stream	<50 ng/L for all samples
Incoming stream to Trissiono treatment facility	NA
Piezometer MW18	Lowest 1030 ng/L (August 2018) to highest 2100 ng/L (December 2018)
Piezometer MW25	Lowest <50 ng/L (December 2018) to highest 470 ng/L (November 2018)
Piezometer MW40	Lowest <50 ng/L (September 2018) to highest 74ng/L (November 2018)

Table 44 Concentrations detected by the monitoring carried out by ARPAV, between 2013-2018

C604 was also found in the blood samples collected from the factory workers in Miteni with the concentrations ranging from 0,5 ng/L to 60,77 ng/L²⁷⁵.

F53 and F53B

F53 and F53B are not produced in Europe but may be imported to be used in metal plating industries, or articles which have already undergone the process are imported from outside the EU. These substances

²⁶⁸ ECHA, (2011) Scientific Opinion on the safety evaluation of the substance, 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], ammonium salt, CAS RN 958445-44-8.

 ²⁶⁹ Fromme, H., et al., (2016) <u>ADONA and perfluoroalkylated substances in plasma samples of German blood donors living in South Germany</u>.
 Int. J. Hyg. Environ. Health, Volume 220, Issue 2, Part B, April 2017, Pages 455-460.

²⁷⁰ Ibid.

²⁷¹ ECHA, Registration Dossier for CAS RN 1190931-39-5.

²⁷² Consultation with public authority, November 2019.

²⁷³ Recycling Industry, <u>Riscontrata nel PO la presenza di cC604 PFAS di nuova generazione</u>.

²⁷⁴ ARPAV (2019), Contaminazione da PFAS Azioni ARPAV (Italian).

²⁷⁵ Girardi P, Rosina A and Merler E, (2018), La Concentrazione di sostanze perfluorurate nel sangue dei dipendenti ed ex dipendenti delle ditte RIMER et Miteni (Trissino, Vicenza) (Italian).

are used (mainly) in China²⁷⁶, F53 and F53B have been detected in the environment in several different places in the country. Examples include in Oujang River²⁷⁷ and in municipal sewage sludge in different places in the country.²⁷⁸

7.7 Key messages for Group 4 PFAEs

- Group 4 PFAEs are diverse and have a very wide range of applications in different industries, as a main ingredient in manufacturing PFPEs, as processing aids and as uses on consumer and industrial products. Some of these uses will be increasingly relevant in the future, such as fuel cells and solar panels.
- Nine Group 4 substances are registered under REACH. Among those, less than half have Information on aspects such as how much is produced and in which sectors they are used.
- Regulatory scrutiny and academic research focus on a handful of substances, especially those used as replacements to PFOA and PFOS.
- Information regarding human and environmental exposure is lacking for most of the Group 4 substances. Limited information comes from REACH registration files. Studies carried out by several environmental agencies contributed to some of the Group 4 substances being recognized as a concern and academic research focus.
- Available information suggests that release to the environment mainly occurs in the production stage, but also during industrial applications and use, depending on the substances.
- There is very limited information on exposure of workers to most of these substances, and even less information on the exposure of end-users.
- Information available on substances such as GenX shows that these chemicals are very mobile in the environment and are difficult to remove once they are released.
- It is therefore crucial to gain a more complete overview of these substances.

```
<sup>277</sup> <u>https://pubs.acs.org/doi/suppl/10.1021/es401525n/suppl_file/es401525n_si_001.pdf</u>
```

²⁷⁶ Ruan T et al, (2015) Identification of Novel Polyfluorinated Ether Sulfonates as PFOS Alternatives in Municipal Sewage Sludge in China, Environ. Sci. Technol. 2015, 49, 6519–6527.

²⁷⁸ Ruan T et al, (2015) Identification of Novel Polyfluorinated Ether Sulfonates as PFOS Alternatives in Municipal Sewage Sludge in China, Environ. Sci. Technol. 2015, 49, 6519–6527.

8 Group 5: Side-chain perfluoroether polymers

8.1 Overview of the substances in Group 5

8.1.1 Characteristics of Group 5 substances, including chemical structure

For the purposes of this study, side-chain perfluoroether polymers refer to polymers with non-fluorinated polymer backbones and perfluoroalkylether moieties on the side-chains, in line with the side-chain fluorinated polymers as referred in Buck et al²⁷⁹. As a general rule used in this study, the CnF2n+1-O-CmF2m- moiety connects to "Si" or an acrylic group, and usually has rather low molecular weights (e.g. <5000 Da/Amu or <20 carbons).

Seven CAS numbers were identified in this group. None of the CAS numbers are listed in any of the EEA databases (SPIN or ECHA), nor the USEPA CDR. Only two CAS numbers were found via Google search, and they appear in Japanese NITE (Chemical Risk Information Platform) (CAS RN 1005771-59-4 and 705291-24-3). The former is listed on the Existing Chemical Substances Database²⁸⁰ as "Addition products of 1-allyloxy-2,3-epoxypropane and 2,4,6,8-tetramethyl-2-(3-{2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]propoxy]propyl)cyclotetrasiloxane' and the latter is listed on the Newly Announced Chemical Substances document²⁸¹.

Databases searched	CAS numbers that appear in the database
ECHA registered substances database	0
ECHA pre-registered substances	0
C&L inventory	0
EU FCM	0
EU Cosing	0
SPIN Database	0
USFDA FCS	0
CDR 2012 (USA)	0
CDR 2016 (USA)	0
None of the above	7
Total ²⁸²	7

Table 45 Overview of CAS numbers in Group 5 and appearance in databases

There is no additional information available on the structures and formulas of the CAS numbers. The following structures were identified from the literature, without being linked to any CAS number. An example of the monomer which can be used a side-chain polymer within Group 5 is as follows:

²⁷⁹ Buck et al, (2011) Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins.

²⁸⁰ NITE CHRIP Database, registry for CAS RN 1005771-59-4.

²⁸¹ Japan CSCL: <u>Priority Assessment Chemical Substances List</u>, accessed September 2019.

Structure of a PFPE-trialkoxysilane.

(OR)3Si-(CH2)n-N(H)-C(O)-CF2O-(CF2CF2O)n-(CF2O)m-CF2C(O)-N(H)-(CH2)n-Si(OR)3

Source: Fluorinated Polymers: Applications: Volume 2.

Another example is the Fluorolink AD1700 and Fluorolink S10 product from Solvay, and Optool DSX produced by Daikin:

Table 46 Structures of two Fluorolink products developed by Solvay²⁸³

Product	Structure	Where X is
Fluorolink S10 (Solvay)	$XCF_2O-(CF_2CF_2O)_m(CF_2O)_n-CF_2X$	CONHR'Si(OR) ₃
Fluorolink AD1700 (Solvay)	$XCF_2O-(CF_2CF_2O)_m(CF_2O)_n-CF_2X$	CH ₂ OCOCH=CH ₂
Optool DSX (Daikin)	$CF_3CF_2CF_2O$ -($CF_2 CF_2 CF_2O$) _n - $CF_2 CF_2X$	CH ₂ CH ₂ Si(OR)3

Figure 3 Structures of side-chain fluorinated polymers

Side-chain-fluorinated polymers: Nonfluorinated polymer backbone with fluorinated side chains, ending in -C _n F _{2n+1}	Fluorinated acrylate and methacrylate polymers	$\label{eq:response} \begin{array}{l} Acrylate: \\ Backbone-CH-C(O)O-X-C_nF_{2n+1} \\ Methacrylate: \\ Backbone-C(CH_3)-C(O)O-X-C_nF_{2n+1} \\ -where X is -CH_2CH_2N(R')SO_2- \\ with R'=-C_nH_{2n+1} \ (n=0,1,2,4) \\ & \text{or} \\ -CH_2CH_2- \end{array}$
	Fluorinated urethane polymers	Backbone-NHC(O)O- X-C _n F _{2n+1} -where X is either -CH ₂ CH ₂ N(R')SO ₂ - with R' = -C _n H _{2n+1} (n = 0,1,2,4) or -CH ₂ CH ₂ -
	Fluorinated oxetane polymers	Backbone-CH ₂ OCH ₂ -R -where $R = -CF_3$, $-C_2F_5$ or $-CH_2C_4F_9$

Source: Buck et al, (2011), Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins.

Additionally, Solvay has other Fluorolink products than those listed in the table above, that are thought to contain Group 5 chemicals. These are Fluorolink MD700 and P56.

None of the CAS numbers that belong to Group 5 were listed in either the REACH Registered Substances nor the SPIN databases. It can be caused either by that these substances are manufactured/important under the 1 tonne/year threshold, or due to the exemptions granted to polymers under REACH. For instance, Fluorolink products are described as Perfluoropolyethers by their manufacturer²⁸⁴. They do not appear in any of the other databases included in this study.

 ²⁸³ Hoshino T, Morizava Y, Fluorinated Specialty Chemicals - Fluorinated Copolymers for Paints and Perfluoropolyethers for Coatings in Ameduri B. and Sawada H. (eds), (2016), Fluorinated Polymers: Applications: Volume 2. Blackwell's Publishing.
 ²⁸⁴ Solvay USA, <u>Fluorolink® PFPE</u>, accessed November 2019.

8.2 Group 5 substances used in mixtures

The research did not identify any uses directly linked to the CAS numbers in Group 5. Findings from literature indicate that side-chain perfluoroether polymers include silicone polymers and acrylate polymers. Some of these substances are also known as modified perfluoropolyethers (PFPEs)²⁸⁵. Their main use appears to be surface treatment agents, as indicated in the figure above or as ingredients in formulations²⁸⁶. Fluorolink AD1700 from Solvay, is an example of modified PFPEs. Fluorolink AD1700 is a *solution perfluoropolyether (PFPE)-urethane acrylate in a mixture of ethyl acetate and butyl acetate*²⁸⁷. As such, it is commercialized as an additive to be blended with other chemicals such as acrylic monomers for UV-curable coatings²⁸⁸.

CAS RN	Company	Mixture	Used as/function
NA	Solvay	Fluorolink AD1700	Additive for coating applications ²⁸⁹ , used in battery systems in automotive sector, used in smart devices to enhance design and connectivity ²⁹⁰ .
NA	Solvay	Fluorolink MD700	Surface modifier additive in UV curable coating, used in cladding of optical cables ²⁹¹
NA	Solvay	Fluorolink F56	Additive for paint and varnish to improve water/oil repellent, production of food packaging plastics ²⁹²
NA	Solvay	Fluorolink S10	Enhancing water and oil repellency of ceramic, glass or other siliceous surfaces ²⁹³
NA		Polyether Silanes	Application for siliceous surfaces ²⁹⁴
NA	Daikin	Optool DSX	Anti-smudge/anti-fingerpring coating

Table 47 Side-chain perfluoroether polymers used in mixtures

8.3 Group 5 substances used in articles

Group 5 substances are mainly used for coating applications, which make them directly relevant for several consumer articles. Important characteristics include providing very low surface energy, water and oil repellence, and easy-to-clean properties and durability against abrasive chemicals to the surfaces to which they are applied²⁹⁵.

²⁸⁵ Ameduri B. and Sawada H. (eds), (2016), Fluorinated Polymers: Applications: Volume 2. Blackwell's Publishing.

²⁸⁶ Acota Website, <u>Solvey Fluorolink specialty polymers</u>, accessed October 2019.

²⁸⁷ Solvay, <u>Provisional Product Data Sheet for Fluorolink AD1700</u>, accessed October 2019.

²⁸⁸ Ibid.

²⁸⁹ Solvay, <u>Provisional Product Data Sheet for Fluorolink AD1700</u> accessed November 2019.

²⁹⁰ Solvay, <u>Fluorolink AD1700</u>, accessed November 2019.

²⁹¹ Solvay Fluorolink MD700, accessed November 2019.

²⁹² Solvay Fluorolink p56. accessed November 2019.

²⁹³ Coatings World (2017), <u>Solvay Features Extensive Portfolio of Specialty Polymers for Functional Coatings at ABRAFATI</u>, accessed November 2019.

²⁹⁴ Ameduri B. and Sawada H. (eds), (2016), Fluorinated Polymers: Applications: Volume 2. Blackwell's Publishing.

²⁹⁵ Ameduri B. and Sawada H. (eds), (2016), Fluorinated Polymers: Applications: Volume 2. Blackwell's Publishing.

As mentioned above, no specific CAS numbers were identified for any of the articles/applications, but the mixtures identified in the previous section are used in the manufacturing of articles as well as information found from literature. The products mentioned above (Fluorolink AD1700, MD700, P56 and S10 from Solvay and Optool DSX from Daikin) generally refer to surface treatment applications such as stain release for textiles²⁹⁶, wall coverings, furnishings and hard surfaces such as tiles, glass, wood and metal²⁹⁷. Furthermore, the products are used as surface modifiers for paints (water and oil repellence)²⁹⁸, surface treatment for glass, anti-graffiti as well as anti-fingerprint coating additives²⁹⁹. This indicates a wide area of application for downstream users. These are presented in table 48 below.

CAS	Company	Related Article	Used as/function
NA	NA	Shower panels and bathroom ceramics	Surface coating ³⁰⁰ .
NA	NA	Outdoor fabrics	Surface treatment for water-repellence ³⁰¹
NA	Solvay (Fluorolink AD1700)	Smart devices, battery systems in automotive industry	Additive for coating applications ³⁰² , improvements to design and connectivity ³⁰³ . Treatment for metal, glass, plastic and wooden surfaces ³⁰⁴
NA	Solvay (Fluorolink MD700)	Photovoltaic panels	Photocurable formulation and surface modifying additive in acrylic UV-curable systems ³⁰⁵ , Treatment for metal, glass, plastic and wooden surfaces ³⁰⁶
NA	Solvay (Fluorolink P56)	Food packaging plastics, paint and varnish, textiles	Surface treatment for oil and water-repellency and easy- cleanability ³⁰⁷ , water/oil repellent and soil release additive for paint and varnish ³⁰⁸ , Treatment for metal, glass, plastic and textile ³⁰⁹
NA	Solvay (Fluorolink S10)	Food industry equipment	Treatment of metal surfaces in food industry ³¹⁰ , treatment of glass and ceramic surfaces ³¹¹

Table 48 Side-chain	perfluoroether polymers,	identified use in re	elation to articles
	perfluoroether polymers,	inclution ase in the	

²⁹⁶ UNEP, (2018) Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF).

²⁹⁷ Solvay, <u>Fluorolink</u>. accessed November 2019.

²⁹⁸ Solvay, Fluorolink <u>PFPE Surface Coating Modifiers</u>, accessed November 2019.

²⁹⁹ Acota Website, <u>Solvey Fluorolink specialty polymers</u>, accessed November 2019.

³⁰⁰ Ameduri B. and Sawada H. (eds), (2016), Fluorinated Polymers: Applications: Volume 2. Blackwell's Publishing.

³⁰¹ Buck et. al, (2011), Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and

Origins, Integrated Environmental Assessment and Management — Volume 7, Number 4—pp. 513–541.

³⁰² Solvay, Provisional Product Data Sheet for Fluorolink AD1700, accessed November 2019.

³⁰³ Solvay, <u>Fluorolink AD1700</u>, accessed November 2019.

³⁰⁴ Solvay, <u>Fluorolink PFPE Product Range</u>, accessed October 2019

³⁰⁵ Solvay <u>Fluorolink MD700</u>, accessed October 2019

³⁰⁶ Solvay, <u>Fluorolink PFPE Product Range</u>, accessed October 2019.

³⁰⁷ Solvay <u>Fluorolink p56</u>, accessed November 2019.

³⁰⁸ Solvay, <u>Fluorolink PFPE</u>, accessed October 2019.

³⁰⁹ Solvay, <u>Fluorolink PFPE Product Range</u>, accessed October 2019.

³¹⁰ Huo J. et al. (2019), Effects of Fluorolink[®] S10 surface coating on WPC fouling of stainless steel surfaces and subsequent

cleaning, Food and Bioproducts Processing, Volume 118, November 2019, p: 130-138.

³¹¹ Solvay, <u>Fluorolink PFPE Product Range</u> accessed October 2019.

CAS	Company	Related Article	Used as/function
NA	Daikin (Optool DSX)	Glasses of camera lenses, touch screens,	Anti-smudge and anti-fingerprint coating ³¹²
	2011	smart phones, tablets	

Fluorolink AD1700 listed in the table above is used as an additive in acrylic UV-curable systems. This is one type of UV curing coatings technology, with a very wide range of application. An industry report from 2016 indicates that UV curing technology is still in development has an overall penetration of 5% across all industries and novel uses are added to the spectrum. The uses already include 3D printing additives, inkjets, fingernail finishing, food packaging, industrial metals, industrial coatings, adhesives. Each of these uses can be applied to different articles. For example, the report lists parquets, furniture, door skins, dash boards, decorative panels as applications of the industrial wood finishing industry, one of the most important areas of application. Another very important area of application is consumer electronics in which UV coatings are used as protective coating on plastic parts, in the electronic devices display screens and on the printed circuit boards as etch resists³¹³.

8.4 Key producers and suppliers

The research did not identify links between the CAS numbers included in Group 5 and specific producers. Apart from Solvay, other producers may also have substances which have similar characteristics.

8.5 Volumes of Group 5 substances

8.5.1 Within the EEA

An overview of the production volumes of the Group 5 chemicals is not available. Furthermore, it is difficult to establish to what extent the substances are used in different industries since different technologies are used for the same processes, because of the complexity of supply chains of the industries which are using these chemicals.

One illustrative example can be the information on the coating industry. Consumption of UV/EB coatings was between 150,000 and 200,000 metric tonnes for the EMEA region in 2016, most of which can be attributed to the EEA³¹⁴. However, this number remains very general, as it is not clear to what extent these coating applications use Group 5 substances. It is necessary to look at each of these sectors in detail in order to establish an understanding regarding the use of PFAEs.

8.5.2 Globally

Information regarding the global manufacture and use of the Group 5 substances is not available. Following from the example above, UV curable coatings world consumption is reported to be around 600.000 metric tonnes³¹⁵. But as also explained about this gives a general idea of the whole market only, without the specific information on the Group 5 substances.

³¹² Daikin, <u>Optool anti-smudge coating</u>, accessed December 2019.

³¹³ European Association for UV/EB Curing Technology, (2018) UV/EB Brochure.

³¹⁴ European Association for UV/EB Curing Technology, (2018) UV/EB Brochure.

³¹⁵ European Association for UV/EB Curing Technology, (2018) <u>UV/EB Brochure</u>.

8.6 The potential for exposure

The study identified no information specifically focusing on substances in Group 5. Buck et al. notes that fluorinated side-chains attached to the non-fluorinated backbones can detach from the latter, resulting in PFAS releases into the environment³¹⁶.

8.7 Key messages for Group 5 PFAEs

- Very little is known about Group 5 substances, and they do not appear in any of the EEA databases.
- They seem to be used mainly as additives in mixtures which are in turn used to treat a variety of surfaces (glass, wood, metal, ceramics) as modifiers and treatment agents.
- These uses suggest a wide variety of applications in the industry, but data are not available on how much these substances may be emitted into the environment, nor on human exposure.
- As suggested by the limited information, there might be risks related to the fluorinated sidechains detaching from the non-fluorinated backbones. As there is limited knowledge on this topic, it should be further investigated.
- It is necessary to gather more information on the different uses of these substances, which requires a sectoral approach since their applications vary greatly.

³¹⁶ Buck et. Al, (2011) Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins, Integrated Environmental Assessment and Management — Volume 7, Number 4—pp. 513–541.

9 Discussion on findings and challenges

The following lessons have emerged during the course of the project.

9.1 A general lack of information on PFAEs as a group

Information from the manufacturing phase is difficult to obtain, due to the complexities of the chemicals and the industry.

This study confirms what has already been documented in the literature: only limited information on the production and use of most PFASs, including PFAEs, is available in the public domain. Several factors contribute to this situation. First, the large family of PFASs is very diverse, and their naming convention is not entirely harmonised across different actors. This diversity is also present within the group of PFAEs. In particular, products under the same brand name can still be quite diverse (e.g. Fluorolink, Nafion). Secondly, communicating chemical information throughout the supply chain and to the public is a continuous challenge. CAS registry numbers, as unique identifiers, are a very important tool for linking the chemicals, their uses and in some cases specific products and articles. However, using CAS numbers as the starting point created its own challenges. For most of the products identified, manufacturers have Safety Data Sheets (SDS), which provide important information. However, CAS numbers are rarely included in the SDS and in other cases, access to SDS is limited.

Providing an exhaustive overview of downstream uses is also difficult.

The lack of information on the production volumes of PFAEs is compounded by a limited understanding of downstream applications of these substances. The research found a wide range of applications for all five sub-groups of PFAEs. They are used as building blocks for manufacturing of other chemical substances, as coating applications for food-contact materials, as ingredients in beauty products or as embedding liquids in biomedical MRI research, to give just a few examples. Furthermore, the supply chains are very complex, making it difficult to map the relations between different actors. Because of this complexity, along with the lack of information from manufacturers, it was not possible for the project to arrive at sound estimates of the quantities of PFAEs used across the numerous sectors.

Information on exposure of humans and the environment to PFAEs is limited and when available, very fragmented.

The information available on environmental releases and human exposure to PFAEs is also limited. The diversity of applications underlined above contributes to this situation. The information relies on two main sources: the manufacturers of the substances, and research and monitoring by academics and regulatory authorities following a discovery of contamination. Companies frequently withhold key information on characteristics of substances, despite it potentially being fundamental for determining the behaviour of the substances in the environment. Information gathered for regulatory purposes, for instance under REACH, is scattered and can be difficult to use, especially for non-specialists. Research and monitoring after an instance of contamination has occurred may bring a more in-depth understanding, but it usually comes too late and at a high price.

Nevertheless, most of the available information suggest that there is a bigger risk for exposure for workers than end-consumers, and that releases to the environment occur during the manufacturing phase.

However, this does not exclude the potential exposure of the general population to these substances via diffuse pollution since environmental releases during the manufacturing phase can also lead to the contamination of different environmental media such as drinking water or agricultural land. Therefore, these findings remain highly general and approximative since they are based on regulations and generic scenarios and not actual screening of individual substances in the environment.

9.2 Gaps in regulatory frameworks contribute to this lack of information

Industry provides little information on a voluntary basis and the regulatory framework does not provide enough coverage for all substances.

Several manufacturers and suppliers were contacted as part of this study to obtain more information on the volumes and uses of PFAEs. This did not result in any additional information for the study.

A more reliable and standardised way of obtaining information on the chemical substances is through regulation. However, the European regulatory framework does not cover all PFAEs. For instance, the REACH Regulation does not require polymers to be registered, which leads to major information gaps on important sub-groups of PFAEs such as PFPEs. Furthermore, even when the substances are covered under REACH, companies can withhold information if they consider it sensitive or confidential for trade purposes. The widespread use of a 'confidential business information' approach by the industry undermines the efforts of public institutions which rely on the information provided by the producers. In the same vein, legislation on chemical substances mainly focus on industrial uses, where information is largely missing on articles due to the registration requirements concerning substances in articles³¹⁷.

9.3 Impact of emerging technologies

Emerging technologies are expected to affect the quantities used and produced of certain PFAEs.

Some PFAEs are coming to be used in emerging technologies such as fuel cells and advance consumer electronics. These chemicals are expected to be used in increasing amounts in the future. Though some of these technologies are still in the process of consolidation, with competing approaches that may or may not use PFAEs, they are expected to converge at some point, creating lock-in effects which will then be very difficult to change. Therefore, early intervention could be encouraged. For instance, a discussion on how essential it is to use specific fluoropolymer technology in fuel cells could be beneficial. This could enable the companies to invest in other technologies while the market is still in development. However, a lack of transparency within the industries means that regulators and other interested stakeholders cannot take necessary steps to create a long-term sustainable strategy for society when it comes to the sound management of these substances, including substitution with non-chemical solutions.

³¹⁷ ECHA, <u>Requirements for substances in articles</u>, accessed January 2020.

10 Annexes

10.1 Overview of Chemical Groups and the number of CAS numbers that appear in databases included in the study

Databases searched	Group 1 (Perfluoropoly- ethers (PFPE))	Group 2 (Fluoro- polymers)	Group 3 Perfluoroether non-polymers with unsaturated bonds	Group 4 (Perfluoro- ether non- polymers with saturated bonds	Group 5 (Side- chain perfluoroether polymers)	Total
ECHA registered substances database	0	NA	9	9	0	18
ECHA pre- registered substances	60	NA	27	32	0	119
C&L inventory	9	2	6	32	0	49
EU FCM	1	NA	2	3	0	6
EU Cosing	2	0	0	0	0	2
SPIN Database	9	4	0	9	0	22
USFDA FCS	3	6	6	0	0	15
CDR 2012 (USA)	0	0	5	10	0	15
CDR 2016 (USA)	1	2	4	8	0	15
None of the above	63	45	20	90	7	225
Total ³¹⁸	128	57	51	152	7	394

Table 49 Overview of CAS numbers, groups and appearance in databases

10.2 Overview of CAS numbers

CAS numbers, in ascending order, grouped into 5 different groups. The CAS number on which there was no information are highlighted in dark grey.

Group 1: Perfluoropo	lyethers, 128 CAS nu	umbers in total					
37382-64-2	161075-00-9	161212-13-1	161212-29-9	162492-17-3	274917-93-0	620963-42-0	1260733-08-1
51798-33-5	161075-01-0	161212-14-2	161308-16-3	162492-18-4	274917-94-1	721399-20-8	1378309-01-3
60164-51-4	161075-02-1	161212-15-3	161308-17-4	162492-22-0	274917-95-2	721399-22-0	1422364-27-9
69991-61-3	161075-03-2	161212-16-4	161308-18-5	162567-73-9	274917-96-3	769967-14-8	1423039-10-4
69991-62-4	161075-04-3	161212-17-5	161308-19-6	162567-74-0	274917-97-4	844491-91-4	1431551-16-4
69991-67-9	161075-05-4	161212-18-6	161308-20-9	162567-75-1	274918-01-3	851085-64-8	1538576-70-3
75888-49-2	161075-06-5	161212-19-7	161308-21-0	162567-76-2	274918-02-4	925918-64-5	1564254-27-8
76415-97-9	161075-07-6	161212-20-0	161308-22-1	175449-31-7	274918-03-5	933999-90-7	1627515-87-0
83606-67-1	161075-08-7	161212-21-1	161308-23-2	200013-65-6	274918-09-1	1031300-27-2	1638852-32-0
88645-29-8	161075-09-8	161212-22-2	161308-24-3	202200-80-4	274918-10-4	1033385-42-0	1638852-33-1
90317-75-2	161075-10-1	161212-23-3	161308-25-4	211697-45-9	274918-12-6	1198429-17-2	1638956-40-7
101316-90-9	161075-11-2	161212-24-4	162492-11-7	220864-25-5	370097-12-4	1207376-64-4	1638956-41-8
126066-30-6	161075-12-3	161212-25-5	162492-12-8	220864-26-6	370097-18-0	1214752-85-8	1644456-24-5
130030-19-2	161075-13-4	161212-26-6	162492-13-9	223557-70-8	374931-83-6	1214752-86-9	1644456-27-8
134035-61-3	161075-14-5	161212-27-7	162492-14-0	233676-28-3	502164-17-2	1214752-87-0	1646599-55-4
156559-18-1	161075-15-6	161212-28-8	162492-15-1	264142-24-7	588699-63-2	1259853-34-3	1664368-38-0

Table 50 Group 1 substances

Table 51 Group 2 substances

Group 2: Fluoropolymer	'S					
26425-79-6	56357-87-0	66796-30-3	71832-66-1	106108-23-0	190062-24-9	878545-84-7
26654-97-7	60917-27-3	68182-34-3	74499-68-6	107810-71-9	192575-94-3	1378928-76-7
26655-00-5	63391-86-6	68805-70-9	74499-71-1	108144-05-4	252846-11-0	1380335-29-4
26658-70-8	63654-41-1	69068-23-1	85177-88-4	111173-25-2	25170811	
29087-71-6	63863-44-5	69087-47-4	85600-80-2	116018-07-6	709666-21-7	
31175-20-9	64346-91-4	69462-70-0	86414-61-1	149935-01-3	754191-93-0	
31176-88-2	65059-79-2	69531-49-3	86999-93-1	163336-49-0	852533-63-2	
31784-04-0	65086-49-9	70776-76-0	93611-23-5	165178-32-5	870707-45-2	
35397-13-8	65104-43-0	70788-53-3	105656-63-1	177484-43-4	874288-99-0	

Table 52 Group 3 substances

Group 3: Perfluoroether non-polymers with unsaturated bonds										
1187-93-5	13782-76-8	27009-57-0	69087-46-3	86883-85-4	174082-81-6	77706-02-06				
1644-11-7	13845-92-6	29514-94-1	69804-18-8	96250-49-6	204270-10-0	912841-29-03				
1998-53-4	13846-22-5	40573-09-9	69804-19-9	100016-68-0	346662-93-9	700874-87-09				
2599-84-0	16090-14-5	61097-79-8	73928-40-2	106108-22-9	369371-47-1					
6037-91-8	1623-05-08	63863-43-4	80962-91-0	122857-45-8	402570-09-6					
10372-98-2	19190-61-5	64080-43-9	83877-85-4	174080-50-3	62361-02-08					
10493-43-3	24520-19-2	64346-90-3	84145-18-6	174082-79-2	69818-05-09					
13269-86-8	26953-98-0	67635-63-6	85737-06-0	174082-80-5	77545-07-04					

Group 4: Perfluoroet	her non-polymers w	vith saturated bor	nds				
308-48-5	3330-15-2	26131-32-8	65150-88-1	97571-69-2	144938-16-9	510774-77-3	1198297-33-4
335-35-3	3330-16-3	26537-88-2	67118-55-2	106394-03-0	145510-89-0	61098-01-09	1198297-65-2
335-36-4	4089-57-0	26738-51-2	67118-57-4	106394-04-1	147492-57-7	646029-82-5	1198297-66-3
356-47-8	4089-58-1	27120-63-4	67963-76-2	106394-05-2	160228-75-1	646029-84-7	1198297-67-4
378-03-0	13071-65-3	27617-34-1	67963-77-3	112820-37-8	167631-99-4	646029-85-8	1198297-83-4
382-28-5	13140-22-2	27639-98-1	68155-54-4	119511-16-9	174082-83-8	65566-03-02	1643445-09-3
424-20-4	13140-24-4	34761-47-2	69116-72-9	119511-19-2	174082-84-9	717825-76-8	1643489-49-9
425-38-7	13140-25-5	37486-69-4	69116-73-0	119511-20-5	174082-85-0	753446-03-6	1643531-45-6
646-85-5	13140-26-6	39187-47-8	69661-30-9	122075-99-4	17559-01-02	773148-75-7	1643531-85-4
801-26-3	13140-29-9	55154-18-2	71302-72-2	122076-00-0	283593-02-2	89965-07-01	1428-40-6
1600-71-1	13140-34-6	55716-11-5	79754-25-9	122734-47-8	330562-41-9	903523-21-7	144728-59-6
1644-10-6	13252-13-6	58194-00-6	80153-82-8	125034-27-7	330562-44-2	921204-31-1	147224-18-8
1682-78-6	13252-14-7	58979-41-2	84041-66-7	127003-77-4	369371-42-6	921204-32-2	874288-98-9
2062-98-8	13252-15-8	59852-65-2	84100-11-8	13043-05-05	369371-43-7	957209-18-6	919005-14-4
2479-73-4	14548-74-4	60632-00-0	85720-80-5	133080-89-4	402570-10-9	1132933-86-8	93200-92-1
2479-75-6	14620-81-6	61097-96-9	85720-81-6	133609-46-8	402570-11-0	1173199-13-7	73606-19-6
2641-34-1	16835-51-1	61097-98-1	85720-82-7	133881-46-6	413570-89-5	1190931-27-1	754925-54-7
2927-83-5	2501-01-01	61098-00-8	85720-83-8	137780-68-8	426264-19-9	1190931-39-5	756426-58-1
3330-14-1	25711-77-7	62037-80-3	87000-86-0	141977-66-4	446312-61-4	1198296-49-9	

Table 53 Group 4 substances

Table 54 Group 5 substances

Group 5: Side-chain perfluoroether polymers							
705291-24-3	1005771-59-4	1202381-95-0	1380516-78-8	1382351-49-6	1382351-52-1	1443502-50-8	

69991-61-3	161075-08-7	161212-18-6	161308-17-4	162492-15-1	274917-95-2	588699-63-2	1422364-27-9
69991-62-4	161075-09-8	161212-19-7	161308-18-5	162492-17-3	274917-96-3	620963-42-0	1423039-10-4
88645-29-8	161075-10-1	161212-20-0	161308-19-6	162492-18-4	274917-97-4	721399-20-8	1431551-16-4
101316-90-9	161075-11-2	161212-21-1	161308-20-9	162492-22-0	274918-01-3	721399-22-0	1538576-70-3
156559-18-1	161075-12-3	161212-22-2	161308-21-0	162567-73-9	274918-02-4	844491-91-4	1564254-27-8
161075-00-9	161075-13-4	161212-23-3	161308-22-1	162567-74-0	274918-03-5	925918-64-5	1627515-87-0
161075-01-0	161075-14-5	161212-24-4	161308-23-2	162567-75-1	274918-09-1	933999-90-7	1638852-32-0
161075-02-1	161075-15-6	161212-25-5	161308-24-3	162567-76-2	274918-10-4	1214752-85-8	1638852-33-1
161075-03-2	161212-13-1	161212-26-6	161308-25-4	175449-31-7	274918-12-6	1214752-86-9	1638956-40-7
161075-04-3	161212-14-2	161212-27-7	162492-11-7	200013-65-6	370097-12-4	1214752-87-0	1638956-41-8
161075-05-4	161212-15-3	161212-28-8	162492-12-8	223557-70-8	370097-18-0	1259853-34-3	1644456-24-5
161075-06-5	161212-16-4	161212-29-9	162492-13-9	274917-93-0	374931-83-6	1260733-08-1	1644456-27-8
161075-07-6	161212-17-5	161308-16-3	162492-14-0	274917-94-1	502164-17-2	1378309-01-3	1664368-38-0

10.3 CAS numbers registered using process-based naming conventions

Table 55 List of CAS numbers registered using process-based naming conventions

10.4 Background information on ERCs Provided by REACH³¹⁹

Note	No	ERC Default worst-case release ERC resulting from the condition use described in the ERCs.			
			to air	to water (before STP)	to soil
1,7	1	Manufacture of the substance	5%	6%	0.01%
2,7	2	Formulation into a mixture	2.5%	2%	0.01%
2,7	3	Formulation into a solid matrix	30%	0.2%	0.1%
3, 7	4	Use of non-reactive processing aid at industrial site (no inclusion into or onto article)	100%	100%	5%
4,7	5	Use at industrial site leading to inclusion into/onto article	50%	50%	1%.
5,7	6A	Use of intermediate	5%	2%	0.1%
5,7	6B	Use of reactive processing aid at industrial site (no inclusion into or onto article)	0.10%	5%	0.025 %
5,7	6C	Use of monomer in polymerisation processes at industrial site (inclusion or not into/onto article)	5%	5%	0%
5,7	6D	Use of reactive process regulators in polymerisation processes at industrial site; (inclusion or not into/onto article)	35%	0.005%	0.025 %
6,7	7	Use of functional fluid at industrial site	5%	5%	5%
3,7	8A	Widespread use of non-reactive processing aid (no inclusion into or onto article, indoor)	100%	100%	n.a.
5,7	8B	Widespread use of reactive processing aid (no inclusion into or onto article indoor)	0.10%	2%	n.a.
4,7	8C	Widespread use leading to inclusion into/onto article (indoor)	15%	30% 42	n.a.
3,7,8	8D	Widespread use of non-reactive processing aid (no inclusion into or onto article, outdoor)	100%	100%	20%
4,7	8E	Widespread use of reactive processing aid (no inclusion into or onto article outdoor)	0.10%	2%	1%
4,7	8F	Widespread use leading to inclusion into/onto article (outdoor)	15%	5%	0.5%
6,7	9A	Widespread use of functional fluid (indoor)	5%	5%	n.a.
6,7	9B	Widespread use of functional fluid (outdoor)	5%	5%	5%
8	10A	Widespread use of articles with low release (outdoor)	0.05%	3.2.%	3.2%
9,10	10B	Widespread use of articles with high or intended release (outdoor)	100%	100%	100%
8	11A	Widespread use of articles with low release (indoor)	0.05%	0.05%	n.a.
9,10	11B	Widespread use of articles with high or intended release (indoor)	100%	100%	n.a.
10	12A	Processing of articles at industrial with low release	2.5%	2.5%	2.5%
10	12B	Processing of articles at industrial processing with high release	20%	20%	20%
8	12C	Use of articles at industrial sites with low release	0.05%	0.05%	n.a.

10.5 Exposure information from the SPIN database (Exposure toolbox)

The **exposure** is classified as follows³²⁰:

- One or several product uses indicate a very probable exposure 5
- One or several product uses indicate a probable exposure 4
- One or several product uses indicate a potential exposure 3
- The registered product use do not indicate direct exposure 0, 1 or 2

³¹⁹ ECHA, <u>Guidance Document</u>, p.75

³²⁰ See <u>http://spin2000.net/?p=302</u> for more information

The range is classified as follows:

- Very wide range of applications (more than 100 applications) 5
- Wide range of applications (33 100)
- Intermediate range of applications (11 32)
- Narrow range of applications (4 10)
- Very narrow range of applications (1 3)

With regard to **quantity**, the total amounts of a substance in all registered products shows:

4

3

2

1

high volume use	5		
medium high volume use	4		
medium volume use	3		
medium low volume use	2		
low volume use	1		
With regard to Article, one or several uses indicate a:			
 very probable use in article productions 	3		
 probable use in article productions 	2		
 potential use in article productions 	1		

10.6 Substances found in Cape Fear River, North Carolina

The following substances from Groups 3 and 4 were identified using high resolution mass spectrometry on samples of water from the Cape Fear River in North Carolina, downstream from the Fayetteville Chemours chemical manufacturing plant.³²¹

CAS RN	Name	Group	
1187-93-5	Trifluoro(trifluoromethoxy)ethylene		
10493-43-3	Trifluoro(pentafluoroethoxy)ethylene	3	
	1,1,2,2-tetrafluoro-2-[1,2,2-trifluoro-1-(trifluoromethyl)-2-		
16090-14-5	[(trifluorovinyl)oxy]ethoxy]ethanesulphonyl fluoride	3	
1623-05-08	1,1,1,2,2,3,3-heptafluoro-3-[(trifluorovinyl)oxy]propane	3	
1682-78-6	Propanoyl fluoride, 2,3,3,3-tetrafluoro-2-(1,1,2,2,2-p entafluoroethoxy)-	4	
2062-98-8	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionyl fluoride	4	
2927-83-5	2,3,3,3-tetrafluoro-2-(trifluoromethoxy)propionyl fluoride	4	
	Propane, 1-1-difluoro(1,2,2,2-tetrafluoroethoxy)methyl -1,2,2,2-		
3330-14-1	tetrafluoroethoxy -1,1,2,2,3,3,3-heptafluoro-	4	
3330-15-2	1,1,1,2,2,3,3-heptafluoro-3-(1,2,2,2-tetrafluoroethoxy)propane	4	

Table 56 List of substances found in Cape River

³²¹ Strynar et al. (2015), Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS), Environ. Sci. Technol. 2015, 49, 19, 11622-11630

CAS RN	Name	Group
	2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-[1,1,2,2-tetrafluoro-2-	
4089-58-1	(fluorosulphonyl)ethoxy]propoxy]propionyl fluoride	4
13140-29-9	2,3,3,3-Tetrafluoro-2-(trifluoromethoxy)propanoic acid	4
13252-13-6	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid	4
62037-80-3	Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate	4
137780-68-8	Not available	4
1132933-86-8	1,1,2,2-Tetrafluoro-2-(1,2,2,2-tetrafluoroethoxy)ethanesulfonic acid	4

10.7 Glossary of frequently used terms

Mixture³²²

A mixture or solution composed of two or more substances.

Compound³²³

A chemical that combines two or more elements.

Substance³²⁴

A chemical element and its compounds in the natural state or obtained by any manufacturing process, including any additive necessary to preserve its stability and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition.

Article³²⁵

An object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition

Downstream user³²⁶

Any natural or legal person established within the Community, other than the manufacturer or the importer, who uses a substance, either on its own or in a M3 mixture, in the course of his industrial or professional activities. A distributor or a consumer is not a downstream user. A re-importer exempted pursuant to Article 2(7)(c) shall be regarded as a downstream user;

Intermediate³²⁷

A substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance.

Moiety³²⁸

Any part of a molecule. Does not have to be a complete functional group.

Functional group³²⁹

A group of atoms whose bonding is the same from molecule to molecule. A functional group has similar behavior regardless of the molecule that contains it, so molecules with identical functional groups tend to have similar chemical and physical properties. In addition, functional groups with similar structures tend to impart similar chemical and physical properties to the molecules which contain them.

³²² REACH Regulation, Article 3.

³²³ https://dictionary.cambridge.org/dictionary/english/compound

³²⁴ <u>REACH Regulation, Article 3.</u>

³²⁵ <u>REACH Regulation, Article 3.</u>

³²⁶ <u>REACH Regulation, Article 3.</u>

³²⁷ REACH Regulation, Article 3.

³²⁸ http://www.chem.ucla.edu/~harding/IGOC/M/moiety.html

³²⁹ http://www.chem.ucla.edu/~harding/IGOC/F/functional_group.html

Surfactant³³⁰

A surfactant is a surface-active agent, i.e. a substance that, because of its design, seeks out the interface between two distinguished phases, thereby altering significantly the physical properties of those interfaces through the modification of some superficial or interfacial activity. The interfaces can independently be liquid, solid or gaseous immiscible liquids, a solid and a liquid. One example of a surfactant is an emulsifier, i.e. a substance that lowers the interfacial tension between immiscible liquids (e.g. oil and water) thereby allowing them to mix.

Lubricant³³¹

A lubricant is a substance applied between two moving surfaces to reduce the friction and wear between them. A lubricant provides a protective thin film which allows two surfaces to be separated while performing a certain functionality by reducing the friction between them. Some lubricants contain reactive functional groups, with the purpose of creating a boundary layer to the surface(s) to be lubricated. Any substance thus generated is exempted from the registration provisions unless manufactured or placed on the market themselves. An example of this could be a lubricant that reacts with the surface of a metal to provide a physically attached 'oil' layer.

Fire retardants³³²

A fire retardant is a substance used to protect a combustible material, for instance certain plastics or wood, against fire. The flame retardants mechanism of action generally involves chemical reactions with the flame retardants under the conditions of a fire. While the flame retardant itself is subject to registration, the substances formed during the exposure of the treated material to heat / fire are not.

10.8 List of stakeholders contacted

Company/Organisation	Country	Completed	Remarks
ECHA (PFAS working group)	EU / FI	Yes	NA
Swedish Chemical Agency (KEMI)	SE	Yes	NA
ANSES	FR	Refused	
RIVM	NL	Yes	NA
Irsa CNR	IT	Yes	NA
Food Contact Forum	СН	No	Asked questions to be sent by mail, but no questions were sent.
German Environmental Agency	DE	Yes	NA
International Aerospace Environmental Group (Boeing/Airbus)	US(?)		No response
Apollo Scientific	UK		No response
Avantor	NL		No response
Asahi Glass	BE		No reponse

Table 57 List of interviews conducted

³³⁰ <u>https://ec.europa.eu/environment/chemicals/reach/pdf/8_draft_guidance_5.pdf</u>

³³¹ https://ec.europa.eu/environment/chemicals/reach/pdf/8 draft guidance 5.pdf

³³² <u>https://ec.europa.eu/environment/chemicals/reach/pdf/8 draft guidance 5.pdf</u>

Arkema	FR	No	Arkema said they do not produce the substance in question
Chemours Netherlands	NL		No response
Merck (Sigma Aldrich)	UK		Refused
Solvay	FR		Solvay said the main industry association is working on a collective response form the industry.
Thermo Scientific	UK		No response
Unimatec Chemicals	UK		No response
3M	BE		No response

10.9 Bibliography

10.9.1 Reports, academic articles, newspaper articles, other documents

Abo, Grote gevolgen (tijdelijk) handelingskader PFAS (en GenX), (No date), Available at: <u>https://www.abo-milieuconsult.nl/grote-gevolgen-tijdelijk-handelingskader-pfas-en-genx/</u>

ARPAV, Contaminazione da PFAS Azioni ARPAV Regione Veneto, 2019, Available at: https://www.arpa.veneto.it/arpav/paginegeneriche/allegati-pagine-generiche/pfas-relazioniattivitaarpav/AGGIORNAMENTO%20RELAZIONE%20PFAS%2 0 ARPAV%202019 05 13.pdf

Ameduri B. and Sawada H. (eds), *Fluorinated Polymers: Applications*, 2016, Volume 2. Blackwell's Publishing.

Bao, Yixiang et al., *Degradation of PFOA Substitute -GenX (HFPO-DA ammonium salt): Oxidation with UV/Persulfate or Reduction with UV/Sulfite?*, 2018, Environmental Science & Technology. 52. 10.1021/acs.est.8b02172, Available at: https://pubs.acs.org/doi/10.1021/acs.est.8b02172

Bavarian State Agency for the Environment, Einführung des PFOA-Ersatzstoffes ADONA. (No date), Available at: <u>https://www.lfu.bayern.de/altlasten/pfoa_gendorf/</u> adona/index.htm

BACO Adviesbureau, Onderzoek naar biociden in efflienten van rwzi's najaar 2017 (deel 1), 2017, Available at: <u>https://docplayer.nl/105992001-</u> <u>Onderzoek-naar-biociden-in-effluenten-van-rwzi-s-</u> najaar-2017-deel-1-opgesteld-door.html

Brandsma, S.H., Koekkoek, J.C., van Velzen, M.J.M., de Boer, J., *The PFOA substitute GenX detected in the environment near a fluoropolymer manufacturing plant in the Netherlands*, Chemosphere, Volume 220, April 2019, Pages 493-500, Available at: <u>https://doi.org/10.1016/j.chemosphere.2018.12.135</u>

Buck et al, for E.I du Pont de Nemours & Co, Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins, Integr Environ Assess Manag. 2011 Oct;7(4):513-41, Available at: https://www.ncbi.nlm.nih.gov/pubmed/21793199

Bulluck et al. United States Patent: wash-out resistant underwater Grease, 2016, Available at: <u>https://patentimages.storage.googleapis.com/85/a8</u> /c4/b59e520579a196/US9441183.pdf, Accessed December 2019.

Centers for Disease Control and Prevention, Notes from the Field: Targeted Biomonitoring for GenX and Other Per- and Polyfluoroalkyl Substances Following Detection of Drinking Water Contamination — North Carolina, 2018, Available at:

https://www.cdc.gov/mmwr/volumes/68/wr/mm68 29a4.htm

Dutch SVHC Action against GenX is 'first of kind', *Chemical Watch*, (Date not available), Available at : <u>https://chemicalwatch.com/75464/dutch-svhc-action-against-genx-is-first-of-kind#overlay-strip</u> Accessed November 2019.

'Solvay Features Extensive Portfolio of Specialty Polymers for Functional Coatings at ABRAFATI', *Coatings World*, 24 April 2017, Available at: <u>https://www.coatingsworld.com/contents/view_vid</u> <u>eos/2017-04-24/solvay-features-extensive-portfolioof-specialty-polymers-for-functional-coatings-atabrafati/, Accessed November 2019.</u>

The Danish Environmental Protection Agency, More environmentally friendly alternatives to PFOScompounds and PFOA, 2005, Available at: https://mst.dk/service/publikationer/publikationsark iv/2005/jun/more-environmentally-friendlyalternatives-to-pfos-compounds-and-pfoa/

The Dutch Ministry of Infrastructure and Water, *Afvalstromen van Chemours*, 2018. Available at:

https://www.google.be/url?sa=t&rct=j&q=&esrc=s& source=web&cd=1&ved=2ahUKEwjsINLKx7rmAhXTT 8AKHUZRCVoQFjAAegQIARAC&url=https%3A%2F%2 Fwww.rijksoverheid.nl%2Fbinaries%2Frijksoverheid %2Fdocumenten%2Frapporten%2F2018%2F06%2F2 6%2Fafvalstromen-van-chemours%2Fafvalstromen<u>van-</u>

chemours.pdf&usg=AOvVaw0aoLrNiP1cIn6IOIQLPJjX

The Dutch Ministry of Infrastructure and Water, *Vervolgonderzoek afvalstromen Chemours*, 2019, Available at:

https://www.rijksoverheid.nl/documenten/rapporte n/2019/09/25/ilt-rapport-vervolgonderzoekafvalstromen-chemours

The Dutch Ministry of Infrastructure and Water, (2019), *Vervolgonderzoek afvalstromen*, 2019, Available at:

https://www.rijksoverheid.nl/documenten/rapporte n/2019/09/25/ilt-rapport-vervolgonderzoekafvalstromen-chemours

Eurofins, Chain of Custody Record, (Date not readable), Available at <u>https://cfpua.org/DocumentCenter/View/9275/Swe</u> <u>eney-Raw--Post-GenX-Report-July-18?bidId=</u>, Accessed November 2019.

European Association for UV/EB Curing Technology, UV/EB Brochure, 2018, Available at: <u>https://www.radtech-</u> europe.com/sites/default/files/rte_uveb_brochure

<u>2018_0.pdf</u>

EU Regulation 10/2011 on Plastic Materials and Articles Intended to Come into Contact with Food, Available at:

https://ec.europa.eu/food/sites/food/files/safety/d ocs/cs_fcm_plastic-guidance_201110_reg_en.pdf

European Chemicals Agency, Scientific Opinion on the safety evaluation of the substance, 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], ammonium salt, CAS RN 958445-44-8 for use in food contact materials, 2011, Available at:

https://www.efsa.europa.eu/en/efsajournal/pub/21 82

European Chemicals Agency, Guidance on Information Requirements and Chemical Safety Assessment Chapter R.12: Use description, 2015, Available at:

https://echa.europa.eu/documents/10162/13632/in formation requirements r12 en.pdf

European Chemicals Agency, Guidance on Information requirements and Chemical Safety Assessment Chapter 16, 2015, Available at : https://echa.europa.eu/documents/10162/13632/in formation_requirements_r16_en.pdf

European Chemicals Agency, Justification for the selection of a substance for CoRAP inclusion (Ammonium 2,2,3 trifluor-3-(1,1,2,2,3,3-hexafluoro-3-trifluormethoxypropoxy)propionate), 2015, Available at:

https://echa.europa.eu/documents/10162/e33aeff8 -0210-488c-98ac-d8993af21e8a

European Chemicals Agency, What is an infocard? 2018, Available at:

https://echa.europa.eu/documents/10162/2217769 3/what is an infocard en.pdf

European Chemicals Agency, Agreement of the Member State Committee on the Identification of 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid, its salts and its acyl halides (covering any of their individual isomers and combinations thereof) as substances of very high concern, 2019, Available at:

https://echa.europa.eu/documents/10162/d062b53 d-8d56-f07b-f44f-e90c0b2838d3

European Chemicals Agency, Member State Committee Support Document for Identification Of 2,3,3,3-Tetrafluoro-2 (Heptafluoropropoxy)Propionic Acid, Its Salts and Its Acyl Halides (Covering Any of Their Individual Isomers And Combinations Thereof) As Substances Of Very High Concern, 2019, Available at:

https://echa.europa.eu/documents/10162/8da8ceca -2e2e-d999-3276-b83c5fbca009

European Commission, Draft Guidance for REACH Annex V (no date), Available at:

https://ec.europa.eu/environment/chemicals/reach/ pdf/8 draft guidance 5.pdf

European Food Safety Authority, Scientific Opinion, Scientific Opinion on the safety evaluation of the substance, 2H-perfluoro-[(5,8,11,14-tetramethyl)tetraethyleneglycol ethyl propyl ether] CAS RN 37486-69-4 for use in food contact materials, 2012, Available at:

https://efsa.onlinelibrary.wiley.com/doi/abs/10.290 3/j.efsa.2012.2978 European Food Safety Authority, Scientific Opinion on the safety assessment of the substance, Perfluoro {acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt, CAS RN 1190931-27-1, for use in food contact materials, Journal 2014;12(6):3718, Available at:

https://www.efsa.europa.eu/en/efsajournal/pub/37 18

ECOTOC, Addendum to ECOTOC Targeted Risk Assessment, Report No. 93, 2009, Available at: http://www.ecetoc.org/wpcontent/uploads/2014/08/ECETOC-TR-093.pdf

Expertisecentrum PFAS, Aanwezigheid van PFAS in Nederland: Deelrapport B - Onderzoek van PFAS op potentiële risicolocaties, 2018, Available at: https://www.expertisecentrumpfas.nl/images/Hand elingskader/DDT219-1-18-008.228-rapd-Voorkomen_PFAS_in_Nederland_deelrapport_B_Verdachte_locaties_-_definitief.pdf

Fromme, H., et al., ADONA and perfluoroalkylated substances in plasma samples of German blood donors living in South Germany. Int. J. Hyg. Environ. Health. 2016, Available at:

http://dx.doi.org/10.1016/j.ijheh.2016.12.014

Global Market Insights, Perfluoropolyether Market By Product (PFPE-K, PFPE-M, PFPE-Z, PFPE-Y, PFPE-D), By Type (Grease, Oil), By End-Use, Industry Outlook Report, Regional Analysis, Application Potential, Price Trends, Competitive Market Share & Forecast, 2019 – 2025, available at: <u>https://www.gminsights.com/industry-</u> <u>analysis/perfluoropolyether-market</u>

Gordon S. for 3M Corporation, Toxicological evaluation of ammonium 4,8-dioxa-3Hperfluorononanoate, a new emulsifier to replace ammonium perfluorooctanoate in fluoropolymer manufacturing, Regulatory Toxicology and Pharmacology 59 (2011) 64–80, Available at: https://www.ncbi.nlm.nih.gov/pubmed/20875479

Girardi P, Rosina A and Merler E, *La Concentrazione di sostanze perfluorurate nel sangue dei dipendenti ed ex dipendenti delle ditte RIMER et Miteni* (*Trissino, Vicenza*), 2018, Available at: <u>http://www.google.be/url?sa=t&rct=j&q=&esrc=s&s</u> <u>ource=web&cd=13&cad=rja&uact=8&ved=2ahUKEwi</u>

<u>|-</u>

azwwLrmAhWUT8AKHZFxBLcQFjAMegQIARAC&url= http%3A%2F%2Frepository.regione.veneto.it%2Fpub lic%2Fd2ec9f70f6cbc96bd4b3467dec922de7.php%3 Flang%3Dit%26dl%3Dtrue&usg=AOvVaw32lCLF9tvP usl4teeUsOGX

Google Patents, Korrosionsschutzgel und Korrosionsschutzbeschichtung für elektronische und/oder mikromechanische Bauteile, 2008, Available at:

https://patents.google.com/patent/DE10200801289 5A1/da, Accessed November 2019.

Greenpeace, Sette scomode verità sul GenX, 2018. Available at :

https://storage.googleapis.com/planet4-italystateless/2018/11/a81718bc-a81718bcsette scomode verità sul genx.pdf

Hoshino T, Morizava Y, Fluorinated Specialty Chemicals - Fluorinated Copolymers for Paints and Perfluoropolyethers for Coatings in Ameduri B. and Sawada H. (eds), 2016, Fluorinated Polymers: Applications: Volume 2. Blackwell's Publishing. Available at:

https://www.researchgate.net/publication/3120605 25 Chapter_5_Fluorinated_Specialty_Chemicals -__Fluorinated_Copolymers_for_Paints_and_Perfluoro polyethers_for_Coatings

Huo J. et al., *Effects of Fluorolink® S10 surface coating on WPC fouling of stainless steel surfaces and subsequent cleaning, Food and Bioproducts Processing*, Volume 118, November 2019, p: 130-138. Available at:

https://doi.org/10.1016/j.fbp.2019.09.005

"Klüber Lubrication acquires PFPE grease business from Solvay", *Kluber*, January 18 2013, Available at: <u>https://www.klueber.com/en/news/news-</u> <u>detail/2472/</u>, Accessed November 2019

National Industrial Chemicals Notification And Assessment Scheme, (2012), <u>Public Report for</u> <u>Polymer in Intersleek</u> 970, available at: <u>Public Report</u> <u>for Polymer in Intersleek.</u> New consumer exposure example helps companies to comply with REACH, *The European Chemicals Agency Press Release*, May 11 2015. Available at: <u>https://echa.europa.eu/view-article/-</u>

/journal content/title/new-consumer-exposureexample-helps-companies-to-comply-with-reach, Accessed November 2019

New Dyneon Emulsifier Eliminates APFO from Production of Fluoropolymers, *3M-Dyneon*, 2008. Available at:

http://multimedia.3m.com/mws/media/5416240/e mulsifier-eliminates-apfo-from-production-offluoropolymers.pdf, Accessed October 2019.

The Netherlands National Institute for Public Health and the Environment (RIVM), *Risk Management Option Analysis Conclusion Document*, November 2018. Available at:

https://echa.europa.eu/documents/10162/a69d536 b-4274-ff51-800a-65e6af17d0fa

The Netherlands National Institute for Public Health and the Environment (RIVM), *Verspreiding van GenX-stoffen in het milieu: Metingen in Nederland -*2013-2018, 2019. Available at:

https://www.rivm.nl/publicaties/verspreiding-vangenx-stoffen-in-milieu-metingen-in-nederland-2013-2018

The Netherlands National Institute of Public Health, *Evaluation of substances used in the GenX technology by Chemours, Dordrecht*. RIVM Letter report 2016-0174. 2016. Available at: <u>https://www.rivm.nl/bibliotheek/rapporten/2016-0174.pdf</u>

The Netherlands National Institute for Public Health and the Environment (RIVM), *Risicobeoordeling van GenX en PFOA in moestuingewassen in Dordrecht, Papendrecht en Sliedrecht*, 2018. Available at: <u>https://www.rivm.nl/publicaties/risicobeoordelingvan-genx-en-pfoa-in-moestuingewassen-indordrecht-papendrecht-en</u>

The Nordic Council of Ministers, the cost of inaction: A socioeconomic analysis of environmental and health impacts linked to exposure to PFAS, 2018, Available at: <u>http://norden.diva-</u> portal.org/smash/record.jsf?pid=diva2%3A1295959 &dswid=-4202 The Nordic Council of Ministers, *PFAS in paper and board for food contact*, TemaNord 2017:573. Available at:

https://backend.orbit.dtu.dk/ws/portalfiles/portal/1 49769110/Rapport PFAS in paper and board for food contact Options for risk management of po ly and perfluorina.pdf

North Carolina State, Consent Order 17 CVS 580, Accessed December 2019, Available at: https://files.nc.gov/ncdeg/GenX/2019-02-20-Final-

Revised-Proposed-Consent-Order-with-attachmentsand-signatures.pdf, Accessed November 2019.

Sorg, L, Chemours says it's been "re-importing" GenX waste from Netherlands to Fayetteville plant for five years, *NC Policy Watch*, January 25 2019. Available at:

http://www.ncpolicywatch.com/2019/01/25/chemo urs-says-its-been-re-importing-genx-waste-fromnetherlands-to-fayetteville-plant-for-five-years/, Accessed December 2019.

OECD, Working Towards a Global Emission inventory of PFAS: Focus on PFCAS - Status Quo and The Way Forward, 2015. Available at:

http://www.oecd.org/chemicalsafety/Working%20T owards%20a%20Global%20Emission%20Inventory% 20of%20PFASS.pdf

'Chemours ontstemd over ministersbrief over 'illegale PFAS-export' naar België', *Process Control*, November 19 2019. Available at:

https://www.processcontrol.nl/chemours-ontstemdover-ministersbrief-over-illegale-pfas-export-naarbelgie/, Accessed December 2019.

Riscontrata nel PO la presenza di cC604 PFAS di nuova generazione, *Recycling Industry*, 17 April 2019, Available at:

https://www.recyclind.it/ita/2712/riscontratanelpol apresenzadicc6o4pfasdinuovagenerazione/, Accessed November 2019.

Chemours exporteerde illegaal GenX, *RTV Dordrect*, November 14 2019, Available at : <u>http://www.rtvdordrecht.nl/%E2%80%9Cchemours-</u> <u>exporteerde-illegaal-genx%E2%80%9D/nieuws-uit-</u> <u>dordrecht/nieuws/item?1147240, Accessed</u> <u>December 2019.</u> Ruan T et al, *Identification of Novel Polyfluorinated Ether Sulfonates as PFOS Alternatives in Municipal Sewage Sludge in China*, Environ. Sci. Technol. 2015, 49, 6519–6527, Available at:

https://pubs.acs.org/doi/full/10.1021/acs.est.5b010 10?src=recsys

Sianesi et al, *Perfluoropolyethers (PFPEs) from Perfluoroolefin Photooxidation,* 1994. Available at: <u>https://www.semanticscholar.org/paper/Perfluorop</u> <u>olyethers-(PFPEs)-from-Perfluoroolefin-Sianesi-</u> <u>Marchionni/048b75721329cf0636860d1bc28d0d93f</u> <u>373afb4</u>

SPIN Database, <u>Companies liable for declaration</u>, Accessed November 2019.

Strynar et al., Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)', Environ. Sci. Technol. 2015, 49, 19, 11622-11630. Available at:

https://www.ncbi.nlm.nih.gov/pubmed/26392038

Swedish Chemical Agency, *Occurrence and use of highly fluorinated substances and alternatives*, 2015. Available at:

https://www.kemi.se/en/global/rapporter/2015/rep ort-7-15-occurrence-and-use-of-highly-fluorinatedsubstances-and-alternatives.pdf

Trier, X., Taxvig, C., Rosenmai, A. K., & Pedersen, G. A., *PFAS in paper and board for food contact: Options for risk management of poly-and perfluorinated substances. Nordic Council of Ministers*, 2018, Available at:

https://backend.orbit.dtu.dk/ws/portalfiles/portal/1 49769110/Rapport_PFAS in_paper and board_for_ food contact Options for risk management of po ly and perfluorina.pdf

UNEP, Report on the assessment of alternatives to perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), 2018, Available at:

http://www.pops.int/Implementation/IndustrialPOP s/PFOS/Guidance/tabid/5225/Default.aspx

University of North Carolina, Report to the Environmental Review Commission from The University of North Carolina at Wilmington Regarding the Implementation of Section 20.(a)(2) of House Bill 56 (S.L. 2017-2019). Available at : https://www.ncleg.gov/documentsites/committees/ ERC/ERC%20Reports%20Received/2018/CFPUA%20a nd%20UNC-W/2018-April%20HB%2056%20UNCW%20Rpt.pdf

US Environmental Protection Agency, (2018). Notice of Temporary Objection, Available at:

https://cswab.org/wpcontent/uploads/2019/02/EPA-Notice-of-Objection-PFAS-Shipment-from-Chemours-Netherlands-Dec-2018.pdf, Accessed November 2019.

United States International Trade Commission, 2006, Memorandum On Proposed Tariff Legislation of the 109th Congress, 2006., Available at:

https://www.usitc.gov/tariff_affairs/documents/bill reports/109c/hr2543.pdf

United States International Trade Commission, Memorandum on Proposed Tariff Legislation of the 112th Congress, 2012. Available at:

https://www.usitc.gov/tariff_affairs/documents/bill reports/112c/hr4989.pdf

US Environment Protection Agency, Human Health Toxicity Values for Hexafluoropropylene Oxide (HFPO) Dimer Acid and Its Ammonium Salt (CAS RN 13252-13-6 and CAS RN 62037-80-3), 2018, Available at:

https://www.epa.gov/sites/production/files/2018-11/documents/genx_public_comment_draft_toxicity assessment_nov2018-508.pdf

US Environmental Protection Agency, Chemical Data Reporting, The Basics, Available at:

https://www.epa.gov/chemical-datareporting/2016-chemical-data-reportingresults#basics, Accessed October 2019.

Wang, S. et al, First report of a Chinese PFOS alternative overlooked for 30 years, its toxicity, persistence and presence in the environment, 2013, Available at:

https://pubs.acs.org/doi/suppl/10.1021/es401525n/ suppl_file/es401525n_si_001.pdf

Wang et al., Hazard assessment of fluorinated alternatives to long-chain perfluoroalkyl acids (PFAAs) and their precursors: Status quo, ongoing challenges and possible solutions, Environment International Volume 75, February 2015, Pages 172-179, Available at: https://doi.org/10.1016/j.envint.2014.11.013

Wang, Z., Cousins, I., Scheringer, M. and Hungerbühler, K., *Fluorinated alternatives to longchain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors*. Environment International, 60, 2013, pp.242-248, Available at: <u>https://greensciencepolicy.org/wp-</u> <u>content/uploads/2014/10/Wang-et-al.-2013.pdf</u>

World Health Organization, *Keeping our water clean: the case of water contamination in the Veneto Region, Italy*, 2016, Available at: <u>http://www.euro.who.int/en/publications/abstracts</u> <u>/keeping-our-water-clean-the-case-of-water-</u> <u>contamination-in-the-veneto-region,-italy-2017</u>

Winkel V, 'GenX: What Is Nafion', And Why Is It In The Water?, *WHQR Public Media*, August 31 2017, Available at: <u>https://www.whqr.org/post/genx-</u> <u>what-nafion-and-why-it-water#stream/0</u>, Accessed November 2019.

Young, Cora & Hurley, Michael & Wallington, Timothy & Mabury, Scott., *Atmospheric Lifetime and Global Warming Potential of a Perfuoropolyether*. Environmental science & technology, 2006. 40. 2242-6. 10.1021/es052077z, Available at: <u>https://www.researchgate.net/publication/7135736</u> <u>Atmospheric_Lifetime_and_Global_Warming_Pote</u> <u>ntial_of_a_Perfuoropolyether</u>.

10.9.2 Databases and lists European Chemicals Agency, Classification and Labelling Inventory, available at: <u>https://echa.europa.eu/information-on-</u> <u>chemicals/cl-inventory-database</u>

European Chemicals Agency, Pre-registered substances database, Available at: <u>https://echa.europa.eu/information-on-</u> <u>chemicals/pre-registered-substances</u>

European Chemicals Agency, Registered substances, available at: <u>https://echa.europa.eu/information-on-chemicals/registered-substances</u>

European Commission, Cosing Database (Cosmetics), available at: <u>https://ec.europa.eu/growth/tools-</u> <u>databases/cosing/index.cfm?fuseaction=search.simp</u> le

European Commission, EURL for Food Contact Materials, Available at: <u>https://ec.europa.eu/jrc/en/eurl/food-contact-</u> materials/reference-substance-database

Substances in preparations in Nordic Countries (SPIN) Database, available at: <u>http://spin2000.net/</u>

Substances in preparations in Nordic Countries (SPIN) Exposure Toolbox, Available at: <u>http://www.spin2020.com/2015/09/10/8-1-spin-exposure-toolbox/</u>

US Environmental Protection Agency, 2012 Chemical Data Reporting, <u>https://www.epa.gov/chemical-</u> <u>data-reporting</u> (direct link not available)

US Environmental Protection Agency, 2016 Chemical Data Reporting, <u>https://www.epa.gov/chemical-</u> <u>data-reporting/2016-chemical-data-reporting-results</u>

US Food and Drug Administration, Inventory of Effective Food Contact Substance (FCS) Notifications, Available at: <u>https://www.fda.gov/food/packaging-</u> <u>food-contact-substances-fcs/inventory-effective-</u> <u>food-contact-substance-fcs-notifications</u>

Trade Navi, Listado de ingredientes permitidos en productos cosméticos, accessed November 2019, available at :

http://www.tradenavi.or.kr/CmsWeb/resource/atta ch/cntl/[481]List%20of%20permitted%20ingredients %20in%20cosmetics.pdf

Japanese National Institute of Technology and Evaluation Chemical Risk Information Platform (NITE CHRIP) Database, available at:

https://www.nite.go.jp/en/chem/chrip/chrip_search /systemTop

Japanese National Institute of Technology and Evaluation, Priority Assessment Chemical Substances List, Available at:

https://www.nite.go.jp/chem/jcheck/list7.action?cat egory=230&request_locale=en

H&M Group, 2018, H&M Group Chemical Restrictions 2018: Restricted Substances List (RSL),

Cosmetic Products, Available at:

https://sustainability.hm.com/content/dam/hm/abo ut/documents/masterlanguage/CSR/Policies/HM%2 0Chemical%20Restrictions%20Manufacturing%20Re stricted%20Substances%20List%202018.pdf

10.9.3 Product pages and safety datasheets 3M, 3M[™] Dyneon[™] Peroxide Cure Perfluoroelastomer PFE 80Z, Available at: https://www.3m.com/3M/en_US/company-us/all-3m-products/~/3M-Dyneon-Peroxide-Cure-Perfluoroelastomer-PFE-80Z/?N=5002385+3292678322&rt=rud, Accessed December 2019.

3M, Safety Data Sheet for 3M[™] CCM105-GRN-246, Available at:

http://multimedia.3m.com/mws/mediawebserver?S SSSSuUn_zu8l00x4829n82UMv70k17zHvu9lxtD7SSSS SS--, Accessed December 2019.

3M[™] Fluorinert[™] Electronic Liquid FC-3284, Available at:

https://www.3m.com/3M/en_US/company-us/all-3m-products/~/3M-Fluorinert-Electronic-Liquid-FC-3284/?N=5002385+3290667346&rt=rud, Accessed December 2019.

3M, Safety Sheet for 3M™PF-5052 Fluide Performance, Available at: <u>https://multimedia.3m.com/mws/mediawebserver?</u>

<u>mwsId=SSSSSuUn_zu8lzgvl8_elxmxMv7bM17zHvu9l</u> <u>xUb7SSSSSS--</u>, Accessed November 2019.

3M, Safety Datasheet for Performance Fluid 5052, Available at: <u>https://www.acota.co.uk/wp-</u> <u>content/uploads/2018/11/3M-Performance-Fluid-</u> <u>PF-5052.pdf</u>, Accessed November 2019.

3M France, Product Range for Performance Fluids for Consumers, Available at:

https://www.3mfrance.fr/3M/fr FR/notre-societefr/tous-les-produits-3M/~/Tous-les-produits-3M/Électronique/Électronique-grandpublic/Produits-chimiques-et-matériaux-depointe/FUZE-Chemicals/Performance-Fluid/?N=5002385+8709318+8709341+8710650+87 10710+8711017+8734660&rt=r3, Accessed November 2019.

3M, Safety Datasheet for 3M[™] Novec[™] 7700 Engineered Fluid, Available at: https://multimedia.3m.com/mws/mediawebserver? mwsId=SSSSSuUn_zu8l00xmx2xmYtUNv70k17zHvu9l xtD7SSSSSS-- ,Accessed November 2019.

Acota Website, Solvey Fluorolink specialty polymers, Available at:

https://www.acota.co.uk/products/specialtypolymers/solvay-fluorolink-specialty-polymers/, Accessed November 2019.

AGC, Fluon PTFE, Available at: <u>https://www.agcce.com/fluon-ptfe/</u>, Accessed December 2019.

Alfa Aesar, 44626 Nafion® R-1100 resin, sulfonyl fluoride form, Available at: <u>https://www.alfa.com/en/catalog/044626/</u>, Accessed December 2019.

Alfa Chemistry, Product Page for CAS RN 73606-19-6, Accessed October 2019, Available at: <u>https://www.alfa-chemistry.com/2-6-chloro-1-1-2-2-</u> <u>3-3-4-4-5-5-6-6-dodecafluorohexyl-oxyl-1-1-2-2-</u> <u>tetrafluoroethanesulfonic-acid-potassium-cas-</u> <u>73606-19-6-item-10494.htm</u>, Accessed October 2019.

Akzon Nobel, Safety Data Sheet for INTERSLEEK 1100SR PART C, Available at:

https://marinecoatings.brand.akzonobel.com/m/74e cfb666023703a/original/FXA994_0010eu_KR_EN_20 170503_1.pdf

American Chemicals, Brayco 815Z, Available at: http://www.american-

<u>chemicals.com/productshow/888803.html</u>, accessed November 2019

Cadre inc. RFHC [®] Surface Treatment Series, accessed November 2019, Available at: <u>http://www.ironhorseadv.com/images/4173a.pdf</u>, Accessed November 2019.

Chemours, Dordrecht, Available at : https://www.chemours.com/en/About%20Chemour s/Global%20Reach/Dordrecht

Chemours, Nafion™ Membranes, available at: <u>https://www.nafion.com/en/applications/chemical-processing</u>, accessed December 2019.

Chemours, Kyrtox: <u>https://www.krytox.com/en</u>

Chemours, Nafion : https://www.nafion.com/en

Chemours Safety Datasheet for Kyrtox 157FSH: SAFETY DATA SHEET Krytox[™] 157FSH

Chemours 2019, Nafion™ Membranes, Dispersions, and Resins in Chemical Processing, Available at: <u>https://www.nafion.com/en/applications/chemicalprocessing</u>, Accessed December 2019.

CHEManager, (2016), IMCD Distributes Solvay Fluorinated Lubricants, accessed November 2019

Chemours 2019, Nafion[™] Sulfonic Membranes, Available at: https://www.nafion.com/en/products/sulfonic-

membranes, Accessed December 2019.

Cymit Quimica, Product Page for CAS RN. 330562-41-9, Available at: https://cymitquimica.com/search/330562-41-9/, Accessed November 2019.

Daikin, Optool anti-smudge coating, Available at: https://www.daikinchemicals.com/solutions/produc ts/optool-anti-smudgecoating.html?gclid=EAlaIQobChMI9JSX6OK55gIVSbD tCh1p8AapEAAYASAAEgKrKPD_BwE

Dow Corning-Automotive Solutions, Smart Lubrication Solutions. Available at http://msdssearch.dow.com/PublishedLiteratureDO WCOM/dh 09b2/0901b803809b22bd.pdf?filepath= consumer/pdfs/noreg/80-8059-01.pdf?filepath=consumer/pdfs/noreg/80-8059-01.pdf&fromPage=GetDoc

DuPont, (2015), Safety Data Sheet for Krytox[®] Sodium Nitrite Inhibited PFPE/PTFE Greases, Available at:

https://www.google.be/url?sa=t&rct=j&q=&esrc=s& source=web&cd=1&ved=2ahUKEwjSrt3jL3mAhXDvqQKHd-

PCxUQFjAAegQIBBAC&url=https%3A%2F%2Fwww.c hempoint.com%2Fproducts%2Fdownload%3Fgrade %3D29211%26type%3Dsds&usg=AOvVaw2gZiz5BjU Gfef2i_IUdVoL, Accessed November 2019.

Edwards, Material safety data sheet for Grease – Fomblinæ CR 861, Available at:

http://www.premierpumps.com.au/uploadedFiles/R esource/MSDS/P120-03040%20Fomblin%20CR861%20issue%20C.pdf, Accessed November 2019

Edwards, Material safety data sheet for Grease -Fomblinæ CR 862, Available at http://www.premierpumps.com.au/uploadedFiles/R esource/MSDS/P120-03-055%20Fomblin%20CR862%20issue%20A.pdf, Accessed November 2019

Edwards, MATERIAL SAFETY DATA SHEET for Gearbox Lubricant - Drynert 25/6, Available at: http://www.premierpumps.com.au/uploadedFiles/R esource/MSDS/P120-01-030E%20Drynert%2025-6%20.pdf, Accessed November 2019.

Fluorochem Ltd, Safety Data Sheet for Galden HT-90 (Solvay), Available at: <u>Safety Data Sheet</u> accessed November 2019

Fuchs, Safety Data Sheet according to Regulation (EC) No. 1907/ 2006 (REACH): CARBAFLO XTR S5 F80. Available at:

http://sds.chemtel.net/docs/Fuchs%20Lubricants%2

0002505/Fuchs%20Lubritech%20GmbH_CARBAFLO %20XTR%205F%2080 A01-07343 04-15-2015_English.pdf

Howei Pharm, Product Page for CAS RN 73606-19-6, Accessed November 2019, Available at: <u>https://www.howeipharm.com/g/LD1256603</u>, Accessed November 2019.

Klueber, Solutions for high performance and safety, Available at:

https://www.klueber.com/ecomaXL/files/PFPE_prod ucts_for_the_chemical_industry.pdf

Matrix Scientific, Product Page for CAS RN 97571-69-2, Available at: http://www.matrixscientific.com/001399.html,

Accessed September 2019.

Matweb, Technical Datasheets of all Fomblin (Solvay) products: <u>http://www.matweb.com/search/GetMatlsByTraden</u> <u>ame.aspx?navletter=F&tn=FOMBLIN%C2%AE</u>+

ParChem, Polyperfluoroethoxymethoxy peg-2 phosphate, Available at: https://www.parchem.com/chemical-supplierdistributor/polyperfluoroethoxymethoxy-peg-2phosphate-167161.aspx

Quadrant 2007, SYMALIT PFA-HP 1000, Available at: https://www.mcam.com/fileadmin/quadrant/docum ents/QEPP/EU/Product_Data_Sheets_PDF/Symalit/P RODUCT_DATA_SHEET-SYMALIT_PFA_HP_1000.pdf, Accessed December 2019.

Solvay, Fluorolink PFPE Surface Coating Modifiers, Available at:

https://www.solvay.jp/ja/binaries/Fluorolink-PFPE-Surface-Modifiers-for-Coatings_EN-220531.pdf, Accessed November 2019.

Solvay Fluorolink MD700, Available at: https://www.solvay.com/en/product/fluorolinkmd700, Accessed November 2019.

Solvay Fluorolink P56, Available at: <u>https://www.solvay.com/en/product/fluorolink-p56</u>, Accessed November 2019.

Solvay, Provisional Product Data Sheet for Fluorolink AD1700, Available at: <u>https://www.acota.co.uk/wpcontent/uploads/2018/11/AD1700.pdf</u>, Accessed November 2019.

Solvay, Fluorolink PFPE Product Range. Available at: https://www.solvay.com/en/brands/pfpefunctional-fluids/fluorolink-pfpe, Accessed October 2019

Solvay, Galden PFPE FAQ, Available at: https://www.solvay.com/en/brands/galdenpfpe/faq Accessed November 2019.

Solvay USA, Fluorolink® PFPE, Available at https://www.solvay.us/en/markets-andproducts/featured-products/Fluorolink.html, accessed November 2019.

Solvay 2015, Technical Data Sheet: Aquivion P87S-SO2F perfluorosulfonyl fluoride, Available at: <u>http://catalog.ides.com/Datasheet.aspx?I=92041&F</u> <u>MT=PDF&U=0&CULTURE=en-US&E=238476</u>, Accessed December 2019.

Solvay, Safety data sheet for solkatherm [®] SES 36, Available at :

https://www.solvay.us/en/binaries/P19486-USA-237825.pdf, Accessed November 2019. Solvay Specialty Polymers Usa, LLC, 2015, Safety Data Sheet: FOMBLIN® Y LVAC, Available at: <u>https://www.sisweb.com/referenc/msds/fomblin-y-sds.pdf</u>, Accessed November 2019

Solvay Solexis, Fomblin HC Classic, Available at: https://cdn.thomasnet.com/ccp/01092357/132599. pdf Accessed November 2019.

Solvay, Fluorolink® E10H, Available at: https://www.solvay.com/en/product/fluorolinke10h, Accessed November 2019.

Solvay, Fomblin® PFPE Lubricants: https://www.solvay.com/en/brands/fomblin-pfpelubricants

Synquest Laboratoires, Fomblin Z60 (Average MW = 13000) Safety Data Sheet 2108260, Available at: http://www.synquestlabs.com/msds/2100/2108-2-60.pdf, Accessed November 2019.

Synquest Laboratoires, Fomblin Z-15, Available at : Fomblin Z-15, Accessed November 2019

Tikkurila Safety Data Sheet for Tikkurila, Hardener 008 7067, Available at:

https://new.tikkurila.com/industry/products/harden er-008-7067, Accessed November 2019.

ThermoFisher Scientific 2018, Safety Data Sheet Ethanesulfonyl fluoride, 2-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2tetrafluoroethoxy]-1,1,2,2-tetrafluoro-, polymer with tetrafluoroethene,_Available at: <u>https://www.alfa.com/en/msds/?language=EE&subf</u> <u>ormat=CLP1&sku=44626,</u> Accessed December 2019

Unimatec product range, Available at: <u>http://www.unimatec-</u> <u>europe.com/index.php?id=87</u>, Accessed November 2019.

Unimatec product range for Cosmetic Additives, Available at: <u>http://www.unimatec-</u> <u>chemicals.de/index.php?id=135</u>, Accessed October 2019.

Zeiss, Safety Data Sheet Immersol W, Available at: https://www.zeiss.com/content/dam/Microscopy/D ownloads/Pdf/MSDS/immersol w en.pdf