ANNEX XV RESTRICTION REPORT

PROPOSAL FOR A RESTRICTION

SUBSTANCE NAMES:
Undecafluorohexanoic acid (PFHxA), its salts and related substances

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Abbreviations

AF	assessment factor
AFFF	aqueous film forming foams
ALP	Alkaline phosphatase
ALT	alanine aminotransferase
APFHx	ammonium salt of perfluorohexanoic acid
ASAT	aspartate aminotransferase
BAF	bioaccumulation factor
BCF	bioconcentration factor
BDD	boron doped diamond
BMF	biomagnification factor
CEA	cost effectiveness analysis
CEN	European Committee for Standardization
CMF	ceramic membrane filtration
decaBDE	decabromodiphenyl ether
diPAP	polyfluoroalkyl phosphoric acid diesters
DMEL	derived minimum effect level
DNEL	derived no-effect level
DOC	dissolved organic carbon
DWR	durable water repellent
ECF	edible part concentration factor
EEA	European Economic Area
ERC	environmental release category
EtOH	ethanol
FOD	frequency of detection
FT	fluorotelomer
FT(M)A	fluorotelomer (meth)acrylate
FTAL	fluorotelomer aldehyde
FTCA	fluorotelomer carboxylic acid
FTI	fluorotelomer iodide
FTO	fluorotelomer olefin
FTOH	fluorotelomer alcohol
FTS	fluorotelomersulfonic acid
FTTAoS	fluorotelomer thioether amido sulfonate
FTU	fluorotelomer urethane
FTUCA	fluorotelomer unsaturated carboxylic acid
FTUI	fluorotelomer unsaturated iodide
GAC	granular activated carbon
LC-PFCA	longchain-perfluoroalkyl carboxylic acid
LOAEL	lowest observed adverse effect level
LOD	limit of detection
LOEC	lowest observed effect concentration

LOQ	limit of quantification
MDL	method detection limit
monoPAP	polyfluoroalkyl phosphoric acid monoesters
NaPFHxA	sodium perfluorohexanoate
NOAEC	no observed adverse effect level
NOEC	no observed effect concentration
OCRA	ozofractionative catalysed reagent addition
PAC	powdered activated carbon
PBT	persistent, bioaccumulative and toxic (substance)
PEC	predicted environmental concentration
PFAA	perfluoroalkyl acid
PFAB	polyfluorinated alkyl betaine
PFAL	perfluoroalkyl aldehyde
PFAS	per- and polyfluoroalkyl substance
PFBA	perfluorobutanoic acid, C4-PFCA
PFBS	perfluorobutansulfonic acid
PFCA	perfluoroalkyl carboxylic acid/ perflouroalkyl carboxylate
PFDA	perfluorodecanoic acid, C10-PFCA
PFHpA	perfluoroheptanoic acid, C7-PFCA
PFHxA	perfluorohexanoic acid, C6-PFCA
PFHxS	perfluorohexasulfonic acid
PFNA	perfluorononanoic acid, C9-PFCA
PFOA	perfluorooctanoic acid, C8-PFCA
PFOS	perfluorooctansulfonic acid
PFPA	perfluoralkyl phosphonic acid
PFPeA	perfluoropentanoic acid, C5-PFCA
PFPiA	perfluoroalkyl phosphinic acids
PFPrA	Perfluoropropanoic acid, C3-PFCA
PFSA	perfluoroalkyl sulfonic acid
PFUnDA	Perfluoroundecanoic acid, C11-PFCA
PND	postnatal days
PNEC	predicted no effect concentration
PoD	point of departure
RCR	risk characterisation ratio
Related substance (to PFCAs)	Substances that may degrade to PFCAs (e.g. fluorotelomers and side-chain fluorinated polymers) …
SFP	side-chain fluorinated polymers
sFTOH	secondary fluorotelomer alcohol
SPAC	super-fine powder activated carbon
sRV	standard respiratory volume
TFA	Trifluoroacetic acid, C2-PFCA
TOF	total organic fluorine
TOP assay	total oxidisable precursor assay

vPvB	very persistent and very bioaccumulative (substance)
WWTP	waste water treatment plant
ZVO	German national metal plating assosciation

Annex A: Manufacture and uses

PFHxA itself is not manufactured or used in the EU. The ammonium salt APFHx is used as a processing aid in fluoropolymer manufacture and is imported into the EU. Mainly, precursors, like 6:2 FTOH or 6:2 FT(M)A that may degrade to PFHxA are manufactured and used in the EU in large quantities. These substances in a large part are used as monomers in fluorotelomer polymer manufacture. These polymers again are applied in an enormous number of uses.

Only known substances could be assessed regarding their manufacture and uses and the following possible release into the environment. There are many (per-)fluorinated substances that may degrade to PFHxA. These substances itself may already be produced by degradation of other substances. Therefore, there is a high uncertainty about these unknown substances.

Large amounts of articles and products, containing fluorochemicals are imported into the EU. The quality and the quantity of the containing substances often are unknown und bear high level of uncertainties.

A.1 Manufacture, import and export

A.1.1 REACH-Registrations

Table 1: Uses and tonnage bands of registered APFHx and registered related substances (ECHA dissemination site).

CAS number	Name	Tonnage band in t/a	Uses
21615-47-4	Ammonium perfluorohexanoate	10-100	at industrial sites
133331-77-8	1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorotetradecane	> 10	at industrial sites and in manufacturing
73609-36-6	dichloromethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane	1-10	at industrial sites and in manufacturing
2043-57-4	1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane		intermediate
647-42-7	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol		intermediate
27619-89-2	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonyl chloride		intermediate
96383-55-0	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-chloroacrylate	1-10	at industrial sites
17527-29-6	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (6:2 FTA)	100-1000	at industrial sites and in manufacturing
2144-53-8	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate (6:2 FTMA)	100-1000	at industrial sites and in manufacturing
27619-97-2	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanesulphonic acid (6:2 FTS)	10-100	in formulation or re-packing and at industrial sites

26650-09-9	thiocyanic acid, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester		intermediate
34455-22-6	N-[3-(dimethylamino)propyl]-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octane-1-sulfonamide		intermediate
1189052-95-6	sodium hydrogen (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphonate	1-10	perfumes, fragrances, cosmetics and personal care products
-	2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl N-[6-([[(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)oxy]carbonyl]amino)-3,3,5-trimethylhexyl]carbamate	1-10	e.g. building materials, electrical/electronic products, plastic articles
-	reaction mass of ammonium bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phosphate and diammonium 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl phosphate and diammonium P,P'-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) pyrophosphate	1-10	
85995-91-1	alkyl iodides, C8-14, γ-ω-perfluoro		intermediate
-	ammonium salts of mono- and bis[3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl and/or hydropoly(oxyethylene)] phosphate	1-10	coating products, non-metal-surface treatment products, inks and toners, polishes and waxes and washing & cleaning products
108196-44-7	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 3-dibutylaminopropionate	Conf.	notification of new substances (NONS)[1]

A.2 Uses

Detailed description of uses, emissions, exposure, alternatives and impacts of the planned restriction on uses are presented in Annex E. The following paragraphs give a brief overview over the different uses.

PFHxA, its salts and related substances are used for the production of (per-)fluorinated polymers, either as monomers or as processing aids to control the polymerisation process. Fluoropolymers are used for several applications as finishing agents or as repellents. Therefore, they are used in a wide range of sectors e.g. aqueous based products based on fluorinated polymer dispersions are used to impart functional oil and water repellency when applied to textile, leather, hard surfaces or paper fabrics (industrial and consumer

[1] Substance previous notificated under Directive 67/548/EEC

applications). A large quantity of the fluoropolymers is further processed into a variety of specialized articles such as fibers and tubes.

The semiconductor industry uses PFASs as processing agents for the photolithography process, etching process and furthermore in cleaning fluids. Besides surface activity, also purity and stability of PFASs are relevant properties for semiconductor industry. Furthermore, usage of PFASs in photo-acid generators (PAGs) allows the creation of strong acids and non-diffusive, highly soluble and non-agglomerating PAG molecules (Stakeholder Consultation, 2018).

Fire extinguishers based on foams are used for class B fires (flammable liquids) as well as in special cases for class A fires (combustible materials). The fluorinated surfactants contained in fire fighting foams lower the surface tension and allow the formation of an aqueous film between fuel and foam, thereby cooling the surface, acting as a vapor barrier, allowing a fast spreading of the foam on the fuel and preventing re-iginition. Furthermore, fuel shedding is prevented. Diverse areas of application can be found, e.g. aviation, petrochemical industry, defence applications, other industrial uses such as plant fire brigardes or other uses such as hand-held fire extinguishers.

Adding fluorinated surface active substances to inkjets improves the working of modern printers as well as enhancing picture quality with different media. The surface active fluorinated substance improves surface wetting during the printing process (UNEP, 2012b). During stakeholder consultation it was confirmed that C6 based short-chain fluorinated surfactants are used in some water based inkjet inks and latex inks. The main function is the reduction of the water surface tension, when applied on nonporous substrates.

6:2 FTS is used in hard chrome plating processes as well as decorative chrome plating processes as surfactant to lower the surface tension of the plating solution. The aim of hard chrome/ functional chrome plating is to provide e.g. hardness, corrosion and wear resistance, lubricity and high resistance against chemicals. Hard metal plated parts are used e.g. in automotive industry, aircraft construction, shipbuilding and engineering like hydraulic cylinders and rods, railroad wheel bearings and couplers, moulds for the plastic and rubber industry (Blepp et al., 2017; UNEP, 2018a). Decorative chrome plating is used for decorative surface finish e.g. for sanitary industry, kitchen appliances, car and truck pumpers or motorcycle parts (Blepp et al., 2017; UNEP, 2018a). A further electroplating process is the electroplating of plastics in combination with decorative chrome plating.

PFASs are used in different building materials. Fluorinated substances are for example added in paints to improve flow, wetting, and levelling. In coatings fluorinated substances are used to achieve water, oil or dirt repellent properties and protect building materials from weather influence. Fluorinated surfactants can yield in higher stability or resilience of foams for the formation of low-density concrete building blocks. Due to the good wetting property, fluorinated surfactants are also used as additives in adhesives and glues. PFHxA or related substances are used in oil and water repellents in special glass for construction as well as in the solar sector and were detected in treated floor waxes and stone/wood sealants and wood insulation materials.

C6-based fluorinated surfactants are used in small tonnages in photographic equipment or in coatings when manufacturing conventional photographic films (Stakeholder Consultation, 2018). These substances are applied for coating printing plates, coating of photographic layers

for various applications (e.g. for medical applications) and for production of conductive screen ink and coating formulations. In these applications the substances are used as surfactants, as static control agents, as dirt repellents during coating operations and as friction control agents.

Products made by PFHxA, its salts and related substances have properties that are essential for handling of fragrance and ordour componds in products and articles, such as they are surface-active and inert to different chemicals. However, the use of PFHxA, its salts and related substances in the field of fragrance and flavour is not clear so far.

PFASs occur in various mixtures intended for end-use by consumers. These include impregnating agents, ski or floor wax, cleaning products, car care and polishes (Jensen et al., 2008; KEMI, 2015; Knepper et al., 2014; Posner et al., 2013). Only limited information is available regarding the use of PFHxA related substances in these products.

Recent studies indicate that fluorinated substances are used in various cosmetic products such as foundations, concealer and sunscreen. PFASs serve as emulsifiers and surfactants and are added to cosmetic products for binding, bulking and skin/hair conditioning purposes.

The occurrence of fluorotelomer alcohols and PFCAs in textiles is (primarily) related to the durable water repellent (DWR) finishing that imparts water, oil and stain resistance to the textile. DWR finishing finds important application in functional clothing such as performance outdoor textiles, which provide weather protection and body moisture management to the wearer (Schellenberger et al., 2018).

Annex B: Information on hazard and risk

B.1 Identity of the substances and physical and chemical properties

This proposal for restriction covers the substances undecafluorohexanoic acid (PFHxA), its salts and related substances. Related substances mean any related substance (including its salts and polymers) having a linear or branched perfluoropentyl group with the formula C_5F_{11}- directly attached to another carbon atom, as one of the structural elements. In addition, related substances also cover any related substance (including its salts and polymers) having a linear or branched perfluorohexyl group with the formula C_6F_{13}- as one of the structural elements. However, the following substances are excluded from this proposal for restriction:

- — C_6F_{13}-X, where X = F;
- — C_6F_{13}-C(=O)OH, C_6F_{13}-C(=O)O-X’ or C_6F_{13}-CF2-X’ (where X’ = any group, including salts).

The perfluorinated substance with a fluorine atom attached to the C_6F_{13}-group is not degraded to the corresponding PFCA as the carbon fluorine bond is known to be very stable.

B.1.1 Name and other identifiers of the substances

Table 2 summarizes chemical and regulative identifiers of the substance PFHxA.

PFHxA related substances follow a similar structural pattern: a perfluorinated carbon chain with 5-6 carbon atoms connected directly or indirectly (via a non-fluorinated molecular moiety) to a functional group (e.g. hydroxygroup). A nonexhaustive list of PFHxA salts and related substances, which are covered by this restriction proposal, is provided in Table 5.

Table 2: Substance identity of PFHxA.

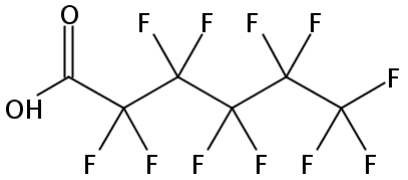
EC number:	206-196-6
EC name:	undecafluorohexanoic acid
CAS number (in the EC inventory):	307-24-4
CAS name:	hexanoic acid, 2,-2,-3,-3,-4,-4,-5,-5,-6,-6,-6-undecafluoro-
IUPAC name:	undecafluorohexanoic acid
Molecular formula:	$C_6HF_{11}O_2$
Molecular weight range:	314.05 g/mol
SMILES Code:	C(=O)(C(C(C(C(C(F)(F)F)(F)F)(F)F)(F)F)(F)F)O
Synonyms:	PFHxA perfluorohexanoic acid
Structural formula:	

Table 3: Substance identity of APFHx.

EC number:	244-479-6
EC name:	ammonium undecafluorohexanoate
CAS number (in the EC inventory):	21615-47-4
CAS name:	hexanoic acid, 2,-2,-3,-3,-4,-4,-5,-5,-6,-6,-6-undecafluoro-, ammonium salt (1:1)
IUPAC name:	ammonium undecafluorohexanoate
Molecular formula:	$C_6H_4F_{11}NO_2$
Molecular weight range:	331.08 g/mol
SMILES Code:	[NH4+].[O-]C(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
Synonyms:	APFHx ammonium perfluorohexanoate
Structural formula:	

Table 4: Substance identity of NaPFHx.

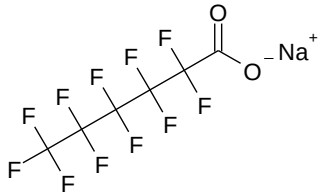
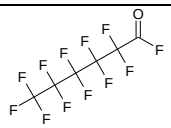
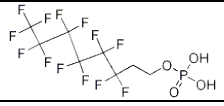
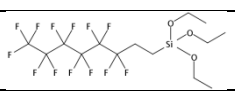
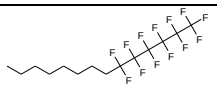
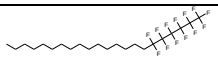
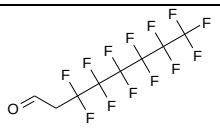
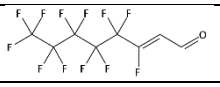
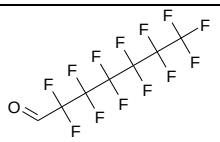
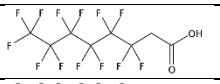
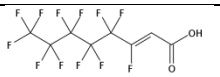
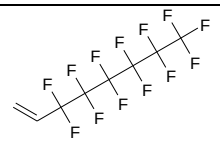
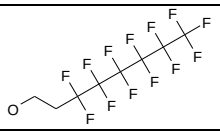
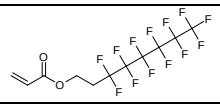
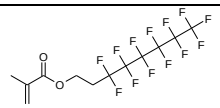
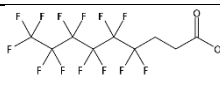
EC number:	220-881-7
EC name:	sodium undecafluorohexanoate
CAS number (in the EC inventory):	2923-26-4
CAS name:	hexanoic acid, 2,-2,-3,-3,-4,-4,-5,-5,-6,-6,-6-undecafluoro-, sodium salt (1:1)
IUPAC name:	sodium undecafluorohexanoate
Molecular formula:	$C_6F_{11}NaO_2$
Molecular weight range:	336.04 g/mol
SMILES Code:	[Na+].[O-]C(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F
Synonyms:	NaPFHx sodium perfluorohexanoate
Structural formula:	

Table 5: Nonexhaustive examples of PFHxA salts and related substances covered by the restriction proposal.

Name / Substance group	Structural formula	EC number	CAS number	REACH[2] (Pre-) Registration
perfluoroalkyl carboxylic acid halides				
perfluorohexanoyl fluoride		206-582-4	355-38-4	(X)
polyfluoroalkyl phosphoric acid mono/diesters				
6:2 fluorotelomer phosphate monoester			57678-01-0	(X)
polyfluoroalkyl silanes				
triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-		257-473-3	51851-37-7	X

[2] Registration status reviewed: 29.01.2019

tridecafluorooctyl)silane				
semifluorinated n-alkanes				
(perfluorohexyl)octane		432-570-5	133331-77-8	X
(perfluorohexyl)hexadecane			133310-71-1	
(n:2) fluorotelomer aldehydes				
6:2 fluorotelomer aldehyde			56734-81-7	
6:2 fluorotelomer unsaturated aldehyde			69534-12-9	
perfluoroalkyl aldehydes				
perfluoroheptanal			63967-41-9	
(n:2) fluorotelomer carboxylic acids				
6:2 fluorotelomer carboxylic acid			53826-12-3	
6:2 fluorotelomer unsaturated carboxylic acid			70887-88-6	
fluorotelomer olefins				
6:2 fluorotelomer olefin		246-791-8	25291-17-2	X
fluorotelomer alcohols				
6:2 fluorotelomer alcohol		211-477-1	647-42-7	X
fluorotelomer acrylates				
6:2 fluorotelomer acrylate		241-527-8	17527-29-6	X
fluorotelomer methacrylates				
6:2 fluorotelomer methacrylate		218-407-9	2144-53-8	X
other transformation products of n:2 Fluorotelomer alcohols				
4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoic acid			27854-30-4	

B.1.2 Physicochemical properties

The physicochemical properties of PFHxA are listed in Table 6. PFHxA has not been registered yet.[3] Thus, the physical-chemical data rely on publically available databases, which do neither provide detailed information on the software package nor on which form of the substance (dissociated vs. non-dissociated) or which relevant parameters were used for the calculation.

Table 7 summarizes the physicochemical properties of ammonium undecafluorohexanoate (APFHx), which are based on the registration[4] dossier.

[3] Registration status reviewed: 29.01.2019

[4] Registration reviewed: 29.01.2019

Table 6: Overview of physicochemical properties of PFHxA.

Property	Description of key information	Value [Unit]	Reference/source of information
Physical state at 20 °C and 101.3 kPa		liquid	
Melting/freezing point	experimental	12-14 °C	(Huang, 1987) Huang, Bing Nan; Journal of Fluorine Chemistry 1987, V36(1), P49-62
Boiling point	experimental	157 °C	(Savu, 2000)Savu PM; Fluorinated Higher Carboxylic Acids. Kirk-Othmer Encyclopedia of Chemical Technology (1999-2015). New York, NY: John Wiley & Sons. On-line Posting Date: 4 Dec 2000
Vapour pressure	estimated (no experimental value available, unknown reliability of estimated value)	1.98 mm Hg = 264 Pa at 25 °C	US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.11. Nov, 2012. Available from, as of Jan 11, 2015
Density	experimental	1.762 g/mL at 20 °C	(Kauck, 1951) Kauck, E. A.; Industrial and Engineering Chemistry 1951, V43, P2332-4
Water solubility	experimental	15.7 g/L (ambient temperature)	Zhao L et al; Chemosphere 114: 51-8 (2014) (Zhao et al., 2014)
Partition coefficient n-octanol/water	estimated	Log K_{OW} = 4.06	calc., COSMOtherm (temp. not specified) (Wang et al., 2011b)
Dissociation constant	comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluoro-carboxylic acids on three kinds of clay minerals.	pK_a = -0.16	Zhao L., Bian J., Zhang Y., Zhu L. and Liu Z.; Chemosphere 114, 51-58 (2014) (Zhao et al., 2014)

Table 7: Overview of physicochemical properties of Ammonium undecafluorohexanoate (APFHx).

Property	Description of key information	Value [Unit]	Reference/source of information
Physical state at 20 °C and 101.3 kPa		solid	
Melting/freezing point	experimental	decomposition at 135 °C	(Ota, 2017b) Ota, Y., (2017), Measurement of melting point for APFHx (C-1500N), Report No. 85024
Boiling point	experimental	decomposition at 135 °C	(Ota, 2017b) Ota, Y., (2017), Measurement of melting point for APFHx (C-1500N), Report No. 85024
Vapour pressure	experimental /calculated	0.005 Pa at 25 °C	(Ota, 2017c) Ota, Y., (2017), Measurement of vapor pressure for APFHx (C-1500N), Report No. 85027
Density	experimental	1.783 g/mL at 20 C	(Ota, 2017a) Ota, Y., (2017), Measurement of density for APFHx (C-1500N) Report No. 85026
Water solubility	experimental	57.61 g/L at 20 °C	(Takeda, 2017) Takeda, M. (2017), Measurement of Critical Micelle Concentration of APFHx (C-1500N), Report No. S414552
Partition coefficient n-octanol/water	calculated	Log K_{OW} = 2.06 (pH 4) 2.05 (pH 7) 2.05 (pH 9)	calc., ARChem SPARC. version 4.6, (2017)

The free undecafluorohexanoic acid (PFHxA) is in equilibrium with undecafluorohexanoate (PFHx), the conjugate base, in aqueous media in the environment as well as in the laboratory. The physico-chemical properties of PFHxA and PFHx are different. Therefore, the expected

environmental fate will depend on the environmental conditions, which influence the equilibrium between base and acid (pH and pKa).

The ammonium salt (APFHx), which is for example used in some animal experiments, is very soluble in water. In aqueous solution it is present as the anion PFHx and the ammonium cation. The dissolved anion PFHx remains in equilibrium with the corresponding acid in aqueous media. With currently available analytical methods it is not possible to distinguish between PFHx and PFHxA in samples. In the literature reporting human and environmental monitoring studies the concentrations are referred to as PFHxA or APFHx, but always both species (PFHx and PFHxA) are included in the given concentration.

In the following PFHxA refers to the acid (PFHxA) as well as to its conjugate base PFHx. Only in cases where it is important to distinguish between both species and where species specific knowledge is available it is clearly indicated that either the acid PFHxA or the conjugate base PFHx is meant.

B.1.3 Justification for grouping

PFHxA belongs to the substance category of perfluorinated carboxylic acids (PFCAs). The substances in this group have a highly similar chemical structure: a perfluorinated carbon chain and a carboxylic acid group. They differ only in the number of CF_2-groups whereas all other fragments are the same within the group. As a result of comparing the experimental and estimated data of the PFCAs, it can be concluded that with increasing chain length water solubility decreases and the sorption potential increases (see Table 5 Section B.1.1). It can be stated with sufficient reliability that the behaviour of the PFCAs follows a regular pattern.

B.2 Manufacture and uses (summary)

For detailed information on manufacture and uses please refer to chapter E.2.

B.3 Classification and labelling

B.3.1 Classification and labelling in Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)

PFHxA as well as their salts are not listed in Annex VI of CLP Regulation.

B.3.2 Classification and labelling in classification and labelling inventory/ Industry's self classification(s) and labelling

The following industry self-classifications and labelling for PFHxA, its ammonium salt and selected related substances are available in ECHA´s C&L Inventory (query from December 2018).

Table 8: Industry´s self classification and labelling (ECHA C&L Inventory).

Subsance	CAS No	Hazard Class and Category Code(s)	Hazard statement Code(s)	Number of Notfiers
PFHxA	307-24-4	Skin Corr. 1B	H314	29
		STOT SE 3	H335	3
		Met. Corr. 1	H290	1
		Eye Dam. 1	H318	1
		Acute Tox 3	H301	1
		Acute Tox 3	H311	1
		Acute Tox 2	H330	1
APFHx	21615-47-4	Skin Corr. 1B	H314	1
		Skin Sens. 1	H317	1
		Eye Dam. 1	H318	3
6:2 FTOH	647-42-7	Acute Tox 4	H302	79
		STOT RE 2	H373	3
		Skin Irrit. 2	H315	42
		Eye Irrit. 2	H319	42
		STOT SE 3	H335	42
		STOT RE 1	H372	1
		Aquatic Chronic 2	H411	19
		Not classified		6
6:2 FTA	17527-29-6	STOT RE 2	H373	4
		Skin Irrit. 2	H315	25
		Eye Irrit. 2	H319	25
		STOT SE 3	H335	40
		Not classified		78
6:2 FTMA	2144-53-8	STOT RE 2	H373	12
		Skin Irrit. 2	H315	28
		Eye Irrit. 2	H319	28
		STOT SE 3	H335	27
		Not classified		35

B.4 Environmental fate properties

B.4.1 Degradation

B.4.1.1 Degradation of PFHxA

For PFHxA itself there are no studies on its degradation potential known that follow a standardised and generally accepted study design, such as the OECD test guidelines. The ammonium salt of PFHxA, is registered but information on degradation behaviour is only available from screening tests on ready biodegradation. Therefore, a read-across to the structural similar substance PFOA is applied where necessary.

PFCAs, like PFHxA and PFOA, are synthetic compounds, which contain a common structural feature: a perfluorinated carbon chain combined with a carboxylic group. The chemical structure of these compounds differs only in the number of perfluorinated carbon atoms in the carbon chain. There are no hints available in the literature that the length of the perfluorinated carbon chain has an influence on the degradability /stability of these substances.

A number of studies for the longer chain homologue PFOA shows that this substance is very persistent and does not undergo abiotic or biotic degradation at all in studies under environmentally relevant conditions (European Chemicals Agency, 2013b). The persistence of PFOA (fulfilling P and vP) as well as its ammonium salts was already confirmed by the Member State Committee that identified the substances as SVHC i.a. based on its PBT properties (European Chemicals Agency, 2013a).

Also C9-C14 PFCAs as well as the ammonium and sodium salts of C_9-PFCA and C_{10}-PFCA were included on the Candidate List as substances of very high concern (SVHC). All substances meet the P and vP-criteria of REACH Annex XIII based on a weight of evidence approach (European Chemicals Agency, 2012a; European Chemicals Agency, 2012b; European Chemicals Agency, 2012c; European Chemicals Agency, 2012d; European Chemicals Agency, 2015b; European Chemicals Agency, 2016b).

The structurally related substance PFHxS also contains this type of a stable fluorinated carbon chain. The conclusion that PFHxS fulfils the criteria for being "very persistent" was adopted by the Member State Committee in 2017 (European Chemicals Agency, 2017).

Abiotic degradation

The degradation behaviour of PFHxA in the atmosphere was assessed by using the QSAR model AOPwin v1.92 (EPISuite). AOPwin predicts degradation rates and half lives for direct and indirect photolytic degradation in the atmosphere. For the common preset of the model – assuming indirect degradation via OH-radicals, 12h-day, 1.5 10^6 OH radicals per m^3 - the tool predicts a degradation rate constant of 0.52 10^{-12} $cm^3/(molec\ s)$ which is equal to an atmospheric half-life of 20.57 days. These results can be seen as an estimate only because perfluorinated substances are not fully covered by the EPISuite models.

A slow indirect photodegradation in air with an atmospheric lifetime of 130 days has been reported for PFOA (European Chemicals Agency, 2013b; OECD, 2006). Hurley et al. studied

the kinetics of the reactions of OH radicals with a homologous series of perfluorinated acids, $F(CF_2)_nCOOH$ (n = 1, 2, 3, 4), in 700 Torr of air at 296 ± 2 K. For n > 1, the length of the $F(CF_2)_n$ group had no discernible impact on the reactivity of the molecule. Atmospheric lifetimes of $F(CF_2)_nCOOH$ with respect to reaction with OH radicals are estimated to be approximately 230 days for n = 1 and 130 days for n > 1. Reaction with OH radicals is a minor atmospheric fate of $F(CF_2)_nCOOH$ (Hurley et al., 2004).

From the chemical structure it can be concluded that PFHxA will not undergo abiotic degradation via hydrolysis. The chain of fluorinated alkanes and the carboxylic acid are known to be stable against abiotic degradation via hydrolysis. This evaluation is backed-up by the registration dossier of APFHx where hydrolysis is not considered to be a relevant degradation pathway, too.

The analogue substance PFOA is hydrolytically stable under environmental conditions with a hydrolytic half-life greater than 92 years (European Chemicals Agency, 2013b).

No photodegradation in water of PFOA has been observed in studies conducted under relevant environmental conditions. The estimated DT_{50} for photolysis of the ammonium salt of PFOA in water is estimated to be greater than 349 days (European Chemicals Agency, 2013b). Because of the similar chemical structure it is assumed that PFHxA will not be subject to photolytic degradation in water in relevant order of magnitude under environmental relevant conditions.

Biotic degradation

For PFHxA itself no biotic degradation study is available.

For the ammonium salt of PFHxA the results from a screening test based on test method OECD 301D (Closed Bottle Test) with modifications was provided in the registration dossier. The data is obtained from Saez et al. (2008). In this study PFHxA was tested in a mixture with other PFAS substances (PFOA, perfluorononanoic acid (PFNA), and PFOS). The concentration of the mixture was 4 mg/L. The test only showed 15 percent decrease in PFHxA concentration within four weeks (based on test material analysis), even after a prolonged test period of 15 weeks only 45 percent decrease was observed. The registrant concludes that the substance has to be assessed as "not readily biodegradable". For interpretation of the measured degradation rates it has to be noted that the inoculum for the test was taken from a sewage treatment plant that is located in a highly industrialized area of the west harbour of Amsterdam. Therefore, it can be assumed that the sewage treatment plant is predominantly treating industrial waste water and that the inoculum was already subject to (low-level) preadaption to APFHx or structurally similar substances. Furthermore, according to Saez et al. (2008) there is no conclusive evidence for biodegradation of PFHxA in sludge under aerobic conditions. Although decreases in PFHxA concentrations were observed, the concentrations in the control bottles decreased to the same level, and it is therefore not possible to confirm that the decrease referred to biodegradation. The authors also stated that the concentration decrease could also be due to a non-biological degradation process, losses could occur not due to degradation or even due to incomplete sterilization of the control bottles (Saez et al., 2008).

In the study by Saez et al. (2008) also anaerobic tests were included. According to the authors, the anaerobic study did not show a significant decrease in the PFHxA concentration during 15 weeks. However, the presented figure shows a decrease of PFHxA-concentration of > 50% until week seven (both in experimental bottles and sterile control bottles).

For the structurally related substance PFOA ready biodegradability tests are available. In a 28-day ready biodegradability test according to test method OECD 301C using 100 mg/L PFOA, respectively, and 30 mg/L activated sludge non-biodegradability was demonstrated. Only 5 % (PFOA) and 7 % (ammonium salt of PFOA) degradation was observed by biochemical oxygen demand (BOD) within 28 days (MITI-List, 2002). In a further test of ready biodegradability according to test method OECD 301F no biodegradation of PFOA was observed in 28 days (Stasinakis et al., 2008). No toxicity control was done in this test.

For PFOA in the OECD SIDS Initial Assessment Report it was concluded that the substance is not expected to undergo biodegradation (OECD, 2006).

There are additional more complex studies available for degradation of PFOA in aquatic systems which are presented in the following. But these tests only provide information for dissipation of the substance from the test system, which does not necessarily represent biodegradation but for example might be the result of processes such as volatilization from open test systems, too. Therefore, it has to be considered that the half-life for biotic degradation may be higher than the dissipation half-life.

Hanson et al. performed a microcosm study in a water-sediment system. Microcosms were circulated for two weeks from a well-fed irrigation pond prior to the experiments. Nominal concentrations of 0.3, 1, 30, and 100 mg/L PFOA, as the sodium salt, plus controls were added to the microcosms. Over a 35-day field study PFOA showed no significant dissipation from the water column. However, at the highest concentration (100 mg/L) a partitioning from the water column into other compartments is suspected. In this field study only 32 % dissipation in 35 days was observed (Hanson et al., 2005). Since the documentation of the procedure was insufficient in the opinion of the dossier submitter the study is not reliable (reliability 3). A more detailed description of the study performed is available in the SVHC support document for PFOA (European Chemicals Agency, 2013b).

Liou et al. investigated the aerobic/anaerobic biodegradability of PFOA respectively its ammonium salt APFO in aqueous media by using a study design, which does not follow the stringent conditions of the OECD test guidelines for simulation tests in surface water or sediment (Liou et al., 2010). In a two-phase experiment (preliminary screening, hypothesis refinement) the use of PFOA as a physiological electron acceptor (electron donator: acetate, lactate, ethanol or hydrogen gas) was studied. Additionally, the possibility of co-metabolism of PFOA during reductive dechlorination of trichloroethene and during various physiological conditions (aerobic, nitrate-reducing, iron-reducing, sulfate-reducing, and methanogenic) was analysed. Five different inoculums were used (from a municipal waste-water treatment plant, industrial site sediment, an agricultural soil, and soils from two fire training areas). Soils and sludges were gathered from: the Ithaca sewage treatment plant; a water-saturated drainage ditch adjacent to the DuPont Chambers Works waste treatment facility in Salem County, New Jersey, previously shown to carry out reductive dechlorination; the Cornell agricultural field station (Collamer silt loam, Ithaca, NY), the Ithaca fire training facility, and

the Rochester, NY fire training facility. The latter two sites were chosen due to potential contamination with fluorinated fire retardant chemicals.

For the ^{14}C-PFOA experiments, Liou et al. utilized 15 mL serum bottles (50 % O_2-free N_2 headspace, 50 % inoculated anaerobic test medium) with non-radioactive PFOA and ^{14}C-PFOA (4.5 Ci/mL test medium) to give a final concentration of 100 mg/L PFOA. For establishing the various terminal electron-accepting processes, a standard anaerobic procedure was used. The samples taken were analysed for concentrations of PFOA, ^{14}C-PFOA, fluoride, nitrate, sulfate, and potential PFOA transformation products. Headspace gases were sampled with a gas-tight syringe (250 mL) and analysed for TCE, vinyl chloride and methane. PFOA quantification was performed by LC/MS/MS following a standard procedure. Potential PFOA metabolites were screened by applying LC/MS (Liou et al., 2010). For further description of the analytical approach please visit the SVHC support document for PFOA (European Chemicals Agency, 2013b).

In no combination of the inoculum source, electron donator or physiological conditions a significant percentage of the initial PFOA (100 ppm and 100 ppb, PFOA purity 96 %) was consumed (within test duration 259 days – phase 1). In addition the studies showed in the experiments for potential reductive defluorination, metabolism and cometabolism which the authors assign to "phase 2 considerations" that no significant concentration change compared to the initial PFOA concentration (100 ppm, 99.9 % PFOA purity, ^{14}C) occurred within a test period of 110 days. The authors found no indication of formation of radiolabeled transformation products. Part of these investigations was the biodegradation behaviour under aerobic conditions, too. In the aerobic test, at the end of the test period (110 days) no significant degradation was observed. Co-metabolism of PFOA during reductive dechlorination of trichloroethene was suggested by a drop in PFOA concentration in the 100 ppb treatment after a 65-day incubation. However, extensive analysis failed to determine corroborating transformation products (Liou et al., 2010).

The OECD SIDS Assessment Report also included studies for the soil compartment (OECD, 2006). Soils of various sites that were exposed to per- and polyfluorated substances – e.g. such as fire-training areas or industrial sites where applications of those substances occur – were analysed with regard to the concentration of PFOA in soil and groundwater. It was found that PFOA is still occurring in concentrations in the ppm-range in both environmental media.

Moody et al. investigated groundwater at a former fire-training area at Wurtsmith Air Force Base which was used between 1950s and 1993. Groundwater samples were collected from two types of monitoring wells. By using electron capture negative chemical ionisation (GC-MS) PFOA was found in ranges from 8 µg/L up to 105 µg/L, depending on the location of the sampling well. The authors estimated that perfluorinated surfactants had been in the groundwater for at least five years and possibly for as long as 15 years. This showed that degradation of PFOA was negligible under the environmental conditions at this site (for both soil and groundwater) (Moody et al., 2003). For further description of the analytical approach please visit the SVHC support document for PFOA (European Chemicals Agency, 2013b).

In conclusion, available studies on PFOA demonstrate the high persistence of the compound in various media, like sludge, soil, sediment and water. Due to the structural relationship between both substances it can be assumed that PFHxA will show high persistence in these environmental media, too.

Conclusion on degradation of PFHxA

The available information for PFHxA and the structurally related substance PFOA clearly show that PFHxA can be regarded as stable against abiotic degradation processes. Therefore, abiotic degradation is evaluated as a non-relevant pathway for removal of PFHxA from the compartments air, soil, waters and the related sediments.

A screening test with APFHx following test guideline OECD 301D, but with modifications showed only 15 percent decrease in PFHxA concentration in 4 weeks (Saez et al., 2008). This result is supported by available screening studies on ready biodegradation of the structurally similar substance PFOA. According to test guideline OECD 301C (MITI-List, 2002) and OECD 301F (Stasinakis et al., 2008) the degradation rate remained clearly below the threshold of 60 % within the standard test period of 28 days for concluding that the substance is "readily biodegradable".

No simulation studies according to standard test guidelines are known to be available for PFHxA. Hence, there are no relevant half-lives for biotic degradation under relevant environmental conditions available for the comparison with the persistence criteria of REACH Annex XIII. For the structurally similar PFOA the information from simulation and field data shows that the degradation rates for this substance under relevant environmental conditions will be negligible or very slow.

The stability of organic fluorine compounds has been described in detail by Siegemund et al. (Siegemund et al., 2000): "When all valences of a carbon chain are satisfied by fluorine, the zig-zag-shaped carbon skeleton is twisted out of its plane in the form of a helix. This situation allows the electronegative fluorine substituents to envelope the carbon skeleton completely and shield it from chemical attack. Several other properties of the carbon-fluorine bond contribute to the fact that highly fluorinated alkanes are one of the most stable organic compounds. These include polarisability and high bond energies, which increase with increasing substitution by fluorine. The influence of fluorine is greatest in highly fluorinated and perfluorinated compounds. Properties that are exploited commercially include high thermal and chemical stability".

Based on their molecular properties perfluorinated compounds can be expected to be poorly degradable. In accordance with this, in the studies considered for the SVHC identification of PFOA no degradation of PFOA was observed. PFOA was already assessed to fulfil the P and vP criteria (European Chemicals Agency, 2013a). Considering the organic chemistry of the substance group of perfluorinated carboxylic acids, it seems to be very likely that PFHxA is as resistant to degradation as it has been shown for PFOA and as it has been concluded on the basis of the data from PFOA for the C9-C14 PFCAs (European Chemicals Agency, 2012a; European Chemicals Agency, 2012b; European Chemicals Agency, 2012c; European Chemicals Agency, 2012d; European Chemicals Agency, 2015b; European Chemicals Agency, 2016b).

In summary, PFHxA is very persistent according to the criteria of Annex XIII to REACH. Moreover, its rate of abiotic or biotic degradation under relevant environmental conditions is expected to be slow. The degradation half-life is expected to clearly exceed the triggers for vP.

B.4.1.2 Degradation of PFHxA-related substances

PFHxA-related substances degrade to PFHxA under environmentally relevant conditions. Besides degradation studies for PFHxA-related substances, also degradation studies for PFOA-related substances and PFBA-related substances are shown. In general, the polyfluorinated substances are degraded to perfluorinated acids. It can be assumed that the degradation mechanism for PFHxA-related substances is similar to the homologues containing a carbon chain of eight carbon atoms. Using the weight of evidence approach it seems very likely that also similar substances may degrade in a similar way in the environment. At the end of a number of degradation steps PFCAs like PFHxA may most probably be the end product and persist in the environment.

In the following sub-chapters the degradation pathways of polyfluorinated substances (PFCA-related substances) are described.

Most of the following text was copied from the background documents of the restriction proposals on PFOA and the long-chain PFCAs (European Chemicals Agency, 2015a; European Chemicals Agency, 2018a).

B.4.1.2.1 Fluorotelomer alcohols (FTOHs)

Table 9: Summary of formed PFCAs during degradation of FTOHs and intmediate products (5:3 acid, fluorotelomer carboxylic acid and fluorotelomer unsaturated carboxylic acid (FTUCA).

Substance	Compartment	Study duration	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	Reference
6:2 FTOH	atmosphere		+	+	+	+				(Ellis et al., 2004)
	atmosphere			+	+	+				(Styler et al., 2013)
	soil (flow through)	84 d	0.8 %	4.2 %	4.5 %	-				(Liu et al., 2010a)
	soil (closed system)	180 d	1.8 %	30 %	8.1 %	-				(Liu et al., 2010b)
	mixed bacterial culture	90 d	< 0.5 %	< 0.5 %	5 %	-				(Liu et al., 2010b)
	WWTP-activated sludge	60 d	-	4.4 mol%	11 mol%	-				(Zhao et al., 2013b)
	aerobic river sediment system	100 d	1.5 mol%	10.4 mol%	8.4 mol%	-				(Zhao et al., 2013a)
	anaerobic digester sludge	90 d		-	0.2 mol%	-				(Zhang et al., 2013b)
		176 d		-	0.4 mol%	-				
	anaerobic sediment	100 d	-	-	0.6 mol%					(Zhang et al., 2016b)
8:2 FTOH	atmosphere		0.1 %	0.1 %	0.24 %	0.32 %	1.5 %	1.6 %		(Ellis et al., 2004)
	aqueous photolysis – H_2O_2 solution	10 h					40 %	+		(Gauthier and Mabury, 2005)
	aqueous photolysis – synthetic field water	140-146 h					1-8 %	+		
	aqueous photolysis – Lake Ontario						3	+ (but below LOQ)		

	mixed microbial system (sediment and groundwater	81 d				-	3 %	-		(Dinglasan et al., 2004)
	mixed bacterial culture	90 d			1 %	not evaluated	6 %	-		(Wang et al., 2005a)
	activated sludge	28 d				not evaluated	2.1 %	-		(Wang et al., 2005b)
	soil	197 d			1-4 %	-	10-40 % (average 25 %)			(Wang et al., 2009)
	anaerobic digester sludge	181 d			-	-	0.3 mol%			(Zhang et al., 2013b)
	anaerobic activated sludge	150 d	1.9 %	1.2 %	5.4 %	8.9 %	17 %			(Li et al., 2018)
8:2 FTCA	sediment-water system	50 d					21 mol% (water) 9.3 mol% (sed.)			(Myers and Mabury, 2010)
8:2 FTUCA	sediment-water system	35 d				12 mol% (water, at day 22)	27 mol% (water) 9 mol% (sed.)	< 1 mol%	< 1 mol%	(Myers and Mabury, 2010)

[+] detected, but not quantified; [-] not detected; [ ] not evaluated

Ellis and co-workers studied the kinetics of the reactions of Cl atoms and OH radicals with a series of fluorotelomer alcohols with differing chain lengths (4:2; 6:2, 8:2 FTOH) in 700 Torr of N_2 or air, diluent at 296 ± 2 K. Interestingly, the length of the perfluorinated carbon chain residue had no discernible impact on the reactivity of the molecules. The authors conclude atmospheric life-time of the FTOHs of 20 days by reaction with OH radicals (Ellis et al., 2003).

6:2-FTOH

The photooxidation of 6:2 FTOH was investigated at the surface of TiO_2, SiO_2, Fe_2O_3, Mauritanian sand, and Icelandic volcanic ash (Styler et al., 2013). At all surfaces the photooxidation resulted in the production of surface-sorbed PFCAs (PFHpA, PFHxA and PFPeA). These results provide evidence that the heterogeneous photooxidation of FTOHs at metal-rich atmospheric surface may provide a significant loss mechanism for FTOHs and also act as a source of aerosol-phase PFCAs close to source regions. The long-range transport of these aerosols is a possible source of PFCAs to remote areas.

The aerobic biodegradation of 6:2 FTOH was performed in a flow through soil incubation system (Liu et al., 2010a). After 1.3 days, 50 % of ^{14}C labelled 6:2 FTOH disappeared from soil, because of microbial degradation and volatilisation. The overall mass balance during the 84-day incubation averaged 77 % and 87 % for the live and sterile treatments, respectively. 16 % [^{14}C] 5:2 secondary fluorotelomer alcohol (sFTOH), 14 % [^{14}C] 6:2 FTOH and 6 % [^{14}C] CO_2 were measured in the airflow after 84 days. In soil the following stable transformation products were detected after 84 days: 5:3 acid (12 %), PFHxA (4.5 %), PFPeA (4.2 %), and PFBA (0.8 %). In soil-bound residues, the major transformation product was 5:3 acid, which may not be available for further biodegradation in soil. In a further study, the authors investigated the aerobic biodegradation of 6:2 FTOH (without ^{14}C-labelling) in soil (closed system) (Liu et al., 2010b). 6:2 FTOH primary degradation half-life was 1.6 days. The overall mass balance in aerobic soil was ~67 % after 180 days (e.g. due to irreversible bond to soil). After 180 days the following substances were accounted: 30 % PFPeA, 8.1 % PFHxA, 1.8 % PFBA, 15 % 5:3 acid, 1 % 4:3 acid, 3 % 6:2 FTOH, and 7.1 % 5:2 sFTOH. 5:2 sFTOH, 5:3 acid and the intermediate 5:2 fluorotelomer (FT) ketone were incubated with soil to elucidate the biodegradation pathway. 5:2 FT ketone yielded 5:2 sFTOH (78 %), PFHxA (4 %) and PFPeA (18 %) after 90 days. Incubation with 5:2 sFTOH for 60 days yielded PFHxA (12 %), PFPeA (85 %) and small amounts of 5:2 FT ketone (< 0.5 %). Incubating with 5:3 acid 4:3 acid (2.3 ± 0.4 %) was the only metabolite after 60 days. The concentration of the initial 5:3 acid concentration decreased to 63 %, this is likely due to the strong adsorption to soil (5:3 acid is becoming non-extractable).

Liu et al. also investigated the biodegradation of 6:2 FTOH in mixed bacterial culture (Liu et al., 2010b). Activated sludge was collected from an industrial wastewater treatment plant and was mixed with a nutrient medium. The sludge was pre-exposed to fluorinated chemicals. The bacterial culture itself was not pre-exposed to fluorinated chemicals. The primary degradation of 6:2 FTOH was rapid with an estimated half-life of 1.3 days. After 90 days, the overall mass balance was 60 % (low mass balance can be attributed to unidentified or unquantified metabolites). PFHxA (5 %), 6:2 FTCA (6 %), 6:2 FTUCA (23 %), 5:2 sFTOH (16 %) and 5-3 acid (6 %) were observed at the end of the study.

Zhao et al. investigated the aerobic biotransformation of 6:2 FTOH in activated sludge of two domestic WWTP (Zhao et al., 2013b). Primary biotransformation was rapid. More than 97 mol% converted within 3 days to at least nine transformation products. The most abundant

transformation product was the volatile 5:2s FTOH. After two months 40 mol% 5:2sFTOH (30 mol% in the headspace) was detected. Further major biotransformation products were 5:3 acid (14 mol%), PFHxA (11 mol%), and PFPeA (4.4 mol%). PFBA and PFHpA were not observed within two months.

In an aerobic river sediment system similar biotransformation products as in soil and activated sludge were detected (Zhao et al., 2013a). The recovery of 6:2 FTOH and quantifiable transformation products ranged 71-88 mol% of initially applied 6:2 FTOH. The lower mass balance compared to sterile control (86-98 mol%) could be explained by formation of bound residues. After 100 days 22.4 mol% 5:3 acid, 10.4 mol% PFPeA, 8.4 mol% PFHxA, and 1.5 mol% PFBA were detected. PFHpA was not observed. Most of the 5:3 acid formed bound residues with sediment organic components, which can only be recovered by sodium hydroxide and ENVI-Carb™ carbon. In addition, 5:3 acid can be further degraded to 4:3 acid (2.7 mol%). Major intermediates during biotransformation of 6:2 FTOH were 6:2 FTCA, 6:2 FTUCA, 5:2 ketone, and 5:2 sFTOH. The 6:2 FTOH primary degradation half-life in sediment system was estimated to be 1.8 days. Figure 1 illustrates the proposed biodegradation pathway of 6:2 FTOH in aerobic sediment systems.

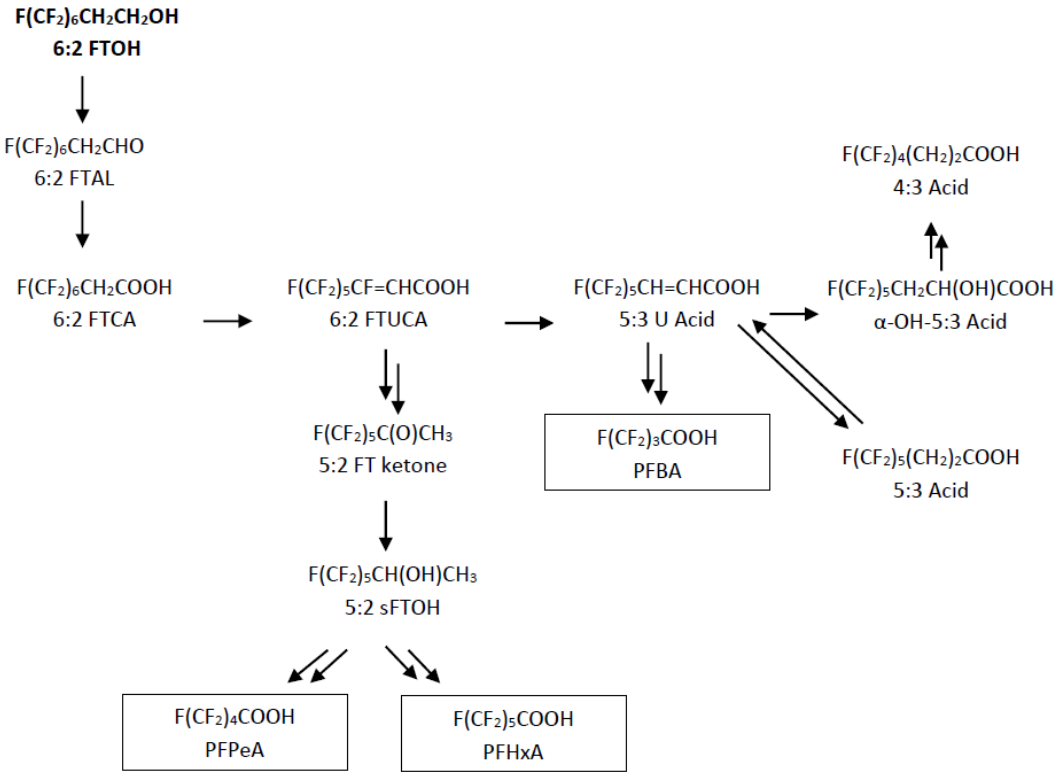


Figure 1: *Proposed 6:2 FTOH biotransformation pathways in aerobic sediment system. The single arrows indicate transformation steps based on observed transformation product and the double arrows indicate multiple transformation steps (based on (Zhao et al., 2013a)).*

Anaerobic degradation of 6:2 FTOH under methanogenic conditions has been analysed by Zhang et al., (Zhang et al., 2013b). Anaerobic digester sludge was incubated dosed with 6:2

FTOH in two studies one for 90 and the other for 176 days. The half-life of 6:2 FTOH (primary degradation) was about 30 days. PFHxA formation was much lower compared with the results of the aerobic sludge and soil studies (0.2 mol% in the 90d-study, 0.4 mol% in the 176d-study). Approximately 30 mol% and 6 mol% of the added 100 mol% 6:2 FTOH still remained at day 90 and day 176, respectively. An average of 43 mol% of intermediate transformation products (sum of 6:2 FTCA and 6:2 FTUCA) were detected in both studies. 5:3 acid was detected as a stable degradation product (average 21 mol%). The results on anaerobic degradation obtained by Zhang et al. may be relevant for conditions such as landfill leachate and anaerobic WTTP sludge.

8:2-FTOH

8:2 FTOH metabolism universally shows the formation of PFOA and, to a smaller fraction, PFNA and lower-chain-length PFCAs (Butt et al., 2014).

Dinglasan et al. investigated biodegradation of 8:2 FTOH using a mixed microbial system (Dinglasan et al., 2004). The enrichtment culture was obtained from sediment and groundwater from a contaminated site. By day 81, PFOA was detected at 3 % of the total mass of added 8:2 FTOH. 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA) was identified as the major metabolite at day 81 (~50 % of the total mass). Further degradation of 8:2 FTUCA may lead to an increase of PFOA concentration (see Figure 2). By day 81 only 55 % of products could be accounted. There may be a number of reasons for the loss: Volatile metabolits may have been lost during routine sampling (loss of initial 8:2 FTOH ~20 % in sterile control), volatile metabolites that were left unidentified or unsaturated metabolites, which are covalently bound to biological macromoldecules.

Biodegradation of ^{14}C-labelled 8:2 FTOH has been investigated in mixed bacterial culture and in activated sludge (Wang et al., 2005a; Wang et al., 2005b). The mixed bacterial culture was obtained from sludge from an industrial wastewater treatment plant (WWTP). Meanwhile, the second study was performed with inoculums from a domestic WWTP (200-fold diluted). The results showed that 8:2 FTOH is adsorbed to sludge and degraded subsequently. A significant portion of the ^{14}C 8:2 FTOH had volatilized from the solid/aqueous matrix and deposited onto the PTFE septa of the experimental vessels. 36 % of ^{14}C 8:2 FTOH remained in the mixed bacterial culture at day 90 (Wang et al., 2005a) and 57 % of the parent still remained in the activated sludge system after 28 days (Wang et al., 2005b). In the mixed bacterial culture system, the concentration of PFOA increased over 56 days and levelled off to 6 % of the ^{14}C mass balance until day 90. Approximately 25 % of the sum of 8:2 fluorotelomer carboxylic acid (8:2 FTCA), 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA) and 7:2 fluorotelomer secondary alcohol (7:2 sFTOH) were detected at day 90. These substances are degradation intermediates and can be further degraded to PFOA (see Figure 2) (Wang et al., 2005a). In the activated sludge system 2.1 % PFOA and 33 % sum of 8:2 FTUCA and 8:2 FTCA of the initial ^{14}C mass have been identified after 28 days (Wang et al., 2005b). Similar degradation pathways were observed in aerobic soil, whereby formation of PFOA was higher in the soil compared to mixed bacterial cultures and activated sludge. 10 – 40 % (average 25 %) of ^{14}C- 8:2 FTOH (half-life (primary degradation) < 7 days) was degraded to form PFOA (steady state after 7 – 56 days; test duration 197 days) (Wang et al., 2009). 10-35 % of total ^{14}C was irreversibly bound to soil, whereby PFOA was not irreversibly bound to soils.

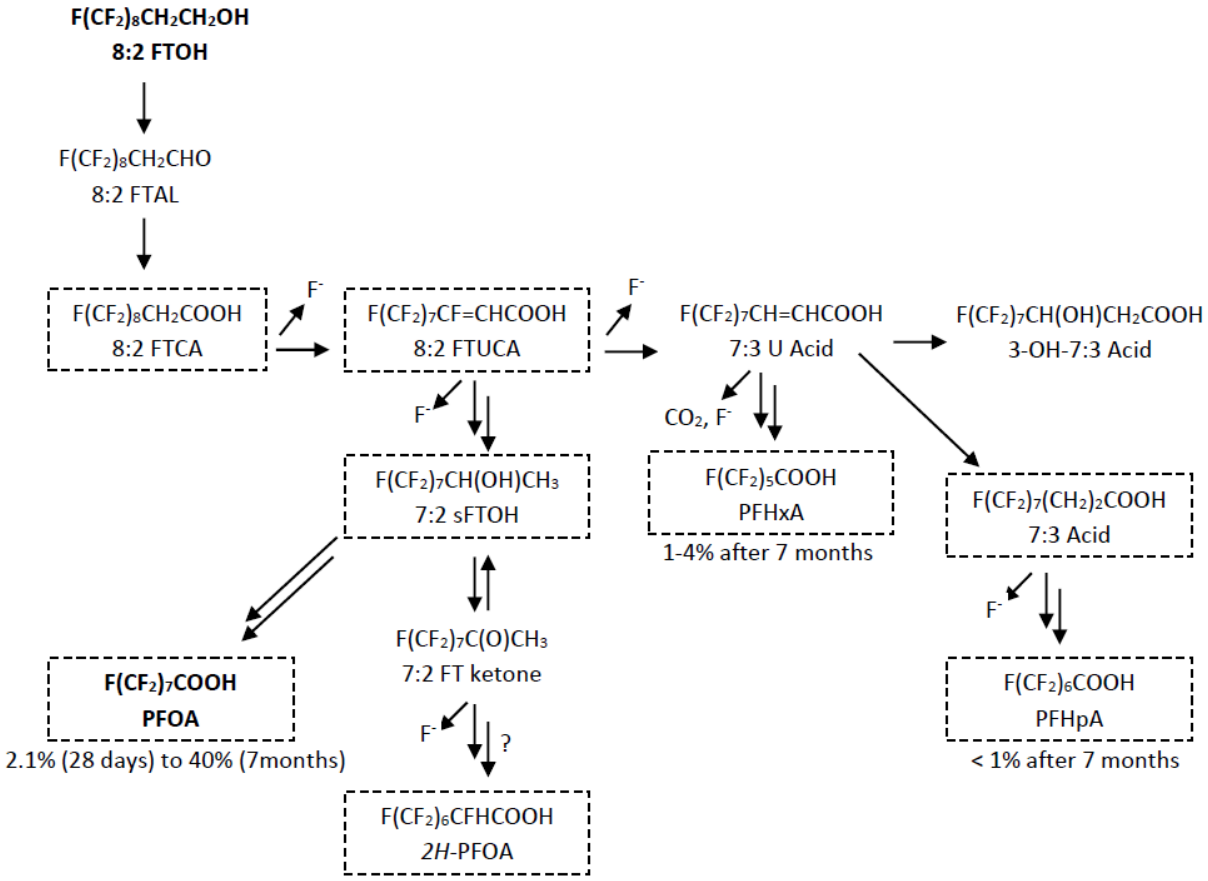


Figure 2: *Aerobic degradation pathways of 8:2 FTOH in soil and activated sludge (Figure based on (Liu and Mejia Avendaño, 2013). The double arrows indicate multiple transformation steps. Defluorination reactions are indicated by release of fluoride ions (F^-). Stable and semi-stable compounds are shown inside dashed boxes. 2H-PFOA has been proposed, but it has not been successfully validated as a PFOA degradation product. The percentages of the degradation products refer to studies by (Dinglasan et al., 2004; Wang et al., 2005a; Wang et al., 2009; Wang et al., 2005b)).*

Anaerobic degradation of 8:2 FTOH under methanogenic conditions has been analysed by Zhang et al., (Zhang et al., 2013b). Anaerobic digester sludge was incubated dosed with [3-^{14}C] 8:2 FTOH for 181 days. The half-life of 8:2 FTOH (primary degradation) is about 145 days. PFOA formation was much lower compared with the results of the aerobic sludge and soil studies (0.3 mol% of initially applied [3-^{14}C] 8:2 FTOH within 181 days). Approximately 39 mol% of the added 100 mol% [3-^{14}C] 8:2 FTOH still remained by day 181. 23 mol% of intermediate transformation products (sum of 8:2 FTCA and 8:2 FTUCA) were detected at day 181 2H, 2H, 3H, 3H-Perfluordecanic acid (7:3 acid) was detected as a stable degradation product (27 mol%). The results on anaerobic degradation obtained by Zhang may be relevant for conditions such as landfill leachate and anaerobic WTTP sludge.

Li et al. investigated the anaerobic biodegradability and metabolic pathways of 8:2 FTOH in anaerobic activated sludge (Li et al., 2018). In the influent of the sampled WWTP fluorine containing organic compounds (e.g. FTOHs or PFCAs) were detected at ppb level. Beside the anaerobic biodegradation of 8:2 FTOH the authors also studied the metabolic pathway of

known metabolites (8:2 FTUCA, 8:2 FTCA, 7:3 acid, 7:2 sFTOH). After 150 days the following metabolites were detected during anaerobic biodegradation of 8:2 FTOH: 17 % PFOA, 8.9 % PFHpA, 5.4 % PFHxA, 1.9 % PFBA, 1.2 % PFPeA, 10 % 7:3 acid, 4.2 % 8:2 FTUCA, 1.4 % 8:2 FTCA, 1.2 % 7:2 sFTOH. The observed metabolites accounted for 57 % of initial 8:2 FTOH at the end of the study. The authors mentioned that neither conjugation nor volatilization losses could be contributed to the decline of the total molar recovery. Hence, unknown metabolites could be formed during the biodegradation process. The studies with 8:2 FTUCA, 8:2 FTCA, 7:3 acid, 7:2 sFTOH show that these substances are intermediates during the 8:2 FTOH anaerobic biodegradation as they were further transformed to the PFCAs.

Atmospheric degradation was further studied in a smog chamber (Ellis et al., 2004). Experiments were performed in 750 Torr of air at 296 K. Reaction mixtures were subject to 0.5 to 15 min UV radiation leading to a consumption of FTOH in the range of 66 to > 98 %. It was shown that 8:2 FTOH is oxidized, initiated by Cl atoms which represent OH radicals, and forms PFNA, PFOA (1.5 % C mass balance of 8:2 FTOH) and PFCAs containing a carbon chain of less than eight carbon atoms. The formation of PFOA is expected to be greater, because intermediate transformation products were still observed (e.g. 26 % 8:2 FTCA, 6 % 8:2 fluorotelomer aldehyde (8:2 FTAL)). The authors stress that the formation of PFOA is small but significant and postulate that FTOH degradation is likely an important source of PFOA and other PFCAs in remote areas.

The aqueous phase photo-oxidation of 8:2 FTOH in aqueous hydrogen peroxide solution, synthetic field water, and water from Lake Ontario (Canada) was investigated by Gauthier and Mabury (Gauthier and Mabury, 2005). The half-lives of 8:2 FTOH were 0.83 ± 0.20 hours (10 mM H_2O_2), 38.0 ± 6.0 hours (100 µM H_2O_2), 30.5 ± 8.0 to 163.1 ± 3.0 hours (synthetic field water), and 93.2 ± 10.0 hours (Lake Ontario). The major products detected in the H_2O_2 study after 10 hours were 8:2 FTCA (~60 %) and PFOA (~40 %). During the experiment 8:2 FTAL was observed as a short-lived intermediate that underwent further photo-oxidation to -PFOA. 8:2 FTCA was shown to undergo aqueous phase photo-oxidation leading to PFOA as the major product. It therefore appears that aqueous phase photo-oxidation of 8:2 FTOH will result in 75-100 % PFOA with time. In the other test systems 1-8 % (after 140-146 hours; synthetic field water) and 18 % PFOA (duration not specified; Lake Ontario), respectively, were formed. Although the study is only of qualitative nature (no rate coefficients reported), it shows that fluorotelomer alcohols and other related compounds will undergo photo-oxidation in aqueous surface layers and in the atmospheric aqueous phases (cloud droplets and deliquescent particles). Since the PFOA yield from 8:2 FTOH photo-oxidation is 75-100 % in the aqueous phase (compared to 3-6 % in the gas phase), aqueous phase photo-oxidation may turn out to be very important in spite of the low solubility. Any quantitative statements will require multiphase modelling.

Kudo et al. (2005) investigated the biotransformation of 8:2 FTOH in male mice dosed via intraperitoneal injection and the diet. The PFOA levels in the animals continued to rise throughout the experiment. In the experiment where the male mice where exposed to 8:2 FTOH via the diet, the PFOA levels increased in a dose- and time dependent manner. The formation of PFOA was around ten times higher than that of PFNA (Kudo et al., 2005). Similar results were observed in a study by Martin et al. (2005) where the formation of PFOA was ten times higher than that of PFNA when measured plasma from rats after 8:2 FTOH injection (Martin et al., 2005).

Nabb et al. (2007) investigated the in vitro metabolism of ^{14}C labelled 8:2 FTOH in rat, mouse, trout and human hepatocytes, and in rat, mouse and human liver microsomes and cytosol fractions. The 8:2 FTOH clearance rates were highest in rat, followed by mouse, humans and lowest in trout. The yield of PFOA was low. However, the author found that the 8:2 FTOH volatilized from the aqueous fraction and into the headspace of the experimental set up and was not available for biotransformation (Nabb et al., 2007).

In a study by Himmelstein et al. (2012) biotransformation of 8:2 FTOH in rats exposed via inhalation was investigated. The most abundant metabolites were 7:3 FTCA > PFOA > 8:2 FTCA (Himmelstein et al., 2012).

Timed-pregnant CD-1 mice received a single dose of 8:2 FTOH (30 mg/kg bw) or vehicle by gavage on gestation day 8 (GD8). During gestation (GD9 to GD18), maternal serum and liver concentration of PFOA decreased from 789 ± 41 to 668 ± 23 ng/mL and from 673 ± 23 to 587 ± 55 ng/g, respectively. PFOA was transferred to the developing foetuses as early as 24 h post-treatment with increasing concentration from 45 ± 9 ng/g (GD10) to 140 ± 32 ng/g (GD18). The group of pups only exposed via lactation had a PFOA concentration of 57 ± 11 ng/mL at PND3 and 58 ± 3 ng/mL at PND15. 8:2 FTOH-intermediates were not assessed in this study (Henderson and Smith, 2007).

In a study by D'Eon and Mabury (2007) rats exposed to two doses of 8:2 FTOH (200 mg/kg bw) had increased concentrations of PFOA in blood with a peak of 34± 4 ng/g (D'eon and Mabury, 2007). Nilsson et al. (2013) measured the different metabolites FTCAs and FTUCAs of 8:2 FTOH in serum from professional skiwaxers during the skiing season in addition to summer season without skiwaxing. Several different polyfluorinated metabolites were detected in the serum, with PFOA (median of eleven skiwaxers: 110 ng/mL) being the most abundant. Due to the findings of FTCs and FTUCAs in skiwaxers blood after exposure to high levels of 8:2 FTOH via air suggest metabolism of FTOH to PFOA (Nilsson et al., 2013a). The downside with this study is the lack of a control group showing possible background levels of FTOH-metabolites.

Conclusion: Based on the available data it can be confirmed that n:2 FTOH will be degraded and transformed into C_x-PFCA (with x= n-2, n-1, n, n+1) in individual amounts greater than 0.1 % per year. For example, 6:2 FTOH will be degraded to PFHxA.

B.4.1.2.2 Fluorotelomer derivates

Table 10: Summary of formed PFCAs during degradation of fluorotelomer derivates.

Substance	Compartment	Study duration	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Reference
fluorotelomer iodide (FTI)									
6:2 FTI	soil	91 d	-	20 mol%	3.8 mol%	16 mol%			(Ruan et al., 2013)
4:2 FTI	atmosphere		+	+					(Young et al., 2008; Young and Mabury, 2010)
FTI	hydrolysis (modelling)		corresponding FTOHs and PFCAs						(Nielsen, 2014; Rayne and Forest, 2010)
fluorotelomer stearate monoester/fluorotelomer citrate triester									
8:2 fluorotelomer stearate monoester	agricultural soil	80 d			0.16 mol%	0.38 mol%	1.7 mol%	0.009 mol%	(Dasu et al., 2012)
8:2 fluorotelomer stearate monoester	forest soil	94 d			0.2 mol%	0.9 mol%	4 mol%		(Dasu et al., 2013)
8:2 fluorotelomer citrate triester	forest soil	218 d			0.2 mol%	0.8 mol%	4 mol%		(Dasu et al., 2013)
polyfluorinated olefins									
polyfluorinated olefins	atmosphere		corresponding FTOHs and PFCAs						(Nielsen, 2014; Sulbaek Andersen et al., 2005)
fluorotelomer (meth)acrylates (FT(M)A)									
n:2 FT(M)A (n=2-12)	hydrolysis (modelling)		corresponding FTOHs and PFCAs						(Nielsen, 2014; Rayne and Forest, 2010)
4:2 FTA	atmosphere		corresponding PFCAs						(Butt et al., 2009)
8:2 FTA	soil	105 d			< 0.4 mol%	1.3 mol%	8 mol%		(Royer et al., 2015)
8:2 FTMA	soil	105 d			< 0.4 mol%	3.4 mol%	10.3 mol%		(Royer et al., 2015)
polyfluoroalkyl phosphoric acid mono-/diesters (monoPAP/diPAP)									
n:2 diPAPs (n=4,6,8,10)	rats		Corresponding FTOHs and PFCAs						(D'eon and Mabury, 2011)

Substance	Compartment	Study duration	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Reference
6:2 monoPAP	wastewater and sewage sludge	92 d		0.7 mol%	2.1 mol%	8.4 mol%			(Lee et al., 2010)
6:2 diPAP	wastewater and sewage sludge	92 d		1.5 mol%	6.2 mol%	7.3 mol%			
n:2 monoPAPs (n=4,6,8,10)	wastewater and sewage sludge	92 d	corresponding FTOHs (1-2% after 92 days) and PFCAs						
6:2 diPAP	soil and plant	5.5 months	+	+	+	+			(Lee et al., 2014)
6:2 PAPs	activated sludge	30 d		0.47 mol%	2 mol%	0.04 mol%			(Lewis et al., 2016)
6:2 diPAP	soil	112 d	0.73 %	6.4 %	6 %				(Liu and Liu, 2016)
8:2 diPAP	soil	112 d			0.34 %	0.25 %	2.1 %		
6:2 diPAP	carp	14 d uptake; 14 d depuration			+	+			(Chen et al., 2019)
8:2 diPAP	carp	14 d uptake; 14 d depuration				+	+	+	
8:2 diPAP	gilt-head bream	7 d					+		(Zabaleta et al., 2017a)
8:2 diPAP	compost amended soil 2.4	108 d			+	+	10 %		(Bizkarguenaga et al., 2016)
	compost amended substrate				+	+	62 %		
	in presence of crops (carrot)	3 month	+	+	+	+	+	+	
	in presence of crops (lettuce)	1 month					+		

Substance	Compartment	Study duration	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Reference
8:2 monoPAP and diPAP	hydrolysis	14 d					8:2 FTOH		(D'eon and Mabury, 2007; Nielsen, 2014; Rayne and Forest, 2010)
8:2 monoPAP and diPAP	rats	15 d			-	+	+	-	(D'eon and Mabury, 2007)
polyfluorinated silanes									
Polyfluorinated silanes	atmosphere		corresponding PFCAs						(Nielsen, 2014)
perfluorinated amides/perfluoroalkane sulfonamides/perfluoroalkane sulfonamidoethanols									
N-ethyl-perfluoro-butyramide (N-EtFBA)	atmosphere		16 %						(Jackson et al., 2013)
perfluorobutane sulfonamidoethanol (N-MeFBSE)	atmosphere		+						(D'eon et al., 2006)
N-ethyl-N-(2-hydroxyethyl)perfluorooctaneamide (N-EtFOA)	hydrolysis pH14 pH 8.5	 24 h 8 d					 98 % -		(Jackson and Mabury, 2013)
N-ethyl perfluorobutanesulfonamide (N-EtFBSA)	atmosphere		0.33 %						(Martin et al., 2006)
fluorotelomer urethane (monomers)									
toluene-2,4-di(8:2 fluorotleomer urethane) (FTU)	agricultural soil	180 d					+ (from residual 8:2 FTOH)		(Dasu and Lee, 2016)
	forest soil	117 d			0.07 mol%	0.11 mol%	0.84 mol%		
hexamethylene-1,6-di(8:2 fluorotleomer urethane) (HMU)	forest soil	180 d			0.06 mol%	0.14 mol%	0.94 mol%		

Substance	Compartment	Study duration	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	Reference
fluorotelomer ethoxylates (FTEO)									
(FTEO) with perfluorinated chain lengths between 4 and 12 and a degree of ethoxylation between 0 and 18	WWTP effluent	48 d	-	-	2.5 mol% (could have been formed from FTOH-residues)	-	0.3 mol% (could have been formed from FTOH-residues)	-	(Frömel and Knepper, 2010)
fluorotelomer sulfonate (FTS)									
6:2 FTS	WWTP-activated suldge	90 d	0.14 %	1.5 %	1.1 %	-			(Wang et al., 2011a)
6:2 FTS	aerobic sediment	90 d	-	21 mol%	20 mol%	0.55 mol%			(Zhang et al., 2016b)
	anaerobic sediment	100 d	-	-	-	-			
fluorotelomer thioether amido sulfonate (FTTAoS)									
n:2 FTTAoS (n=4,6,8)	soil amended with an AFFF solution	60 d	+	+	+	+			(Harding-Marjanovic et al., 2015)
perfluoroalkyl phosphinic acids (PFPiAs)									
PFPiAs			hydrolyse to PFPAs and $C_nF_{2n+1}H$ (further oxidation to PFCAs, when heated or alkalized)						(Wang et al., 2016)

[+] detected, but not quantified; [-] not detected; [ ] not evaluated

Fluorotelomer iodide (FTI)

The hydrolysis of fluorotelomer iodides was modelled with HYDROWIN module of EPI Suite software program (Nielsen, 2014; Rayne and Forest, 2010). At 20 °C the hydrolytic half-life is expected to remain constant at 126 days between pH 0 and 9 and then decrease to < 7 hours at pH 14. In marine system (pH = 8.1) the hydrolytic half-life decreased from about 8 years at 0 °C to about 130 days at 20 °C. The hydrolysis of fluorotelomer iodides may be contributing to substantial FTOH and PFCA inputs in aquatic systems.

The atmospheric fate of 4:2 fluorotelomer iodides was investigated in a smog chamber experiment by Young et al. (Young et al., 2008; Young and Mabury, 2010). Atmospheric lifetime of fluorotelomer iodides is expected to range from about 1 to 7 days (limited by photolysis), depending on time of year and latitude. Photolysis of fluorotelomer iodides occurs via elimination of the iodine atome leading to the formation of the fluorotelomer aldehyde. The fluorotelomer aldehyde will be further degraded (atmospheric lifetime ~4 days) to perfluoroaldehyde. Perfluoroaldehyde has an atmospheric lifetime of approximately one day with respect to photolysis and approximaltey 20 days with respect to reaction with OH-radicals. The oxidation of perfluoroaldehyde leads to the formation of PFCAs (e.g. for 4:2 FTI to perfluoropropanoic acid (PFPrA), PFBA and PFPeA). Because of their long-range potential fluorotelomer iodides contribute to the occurence of PFCAs in remote areas.

Gas phase photolysis and hydrolysis of 8:2 FTI will lead to the release of 8:2 FTOH and thus PFOA (Rayne and Forest, 2010; Young et al., 2008; Young and Mabury, 2010).

Ruan et al. investigated the aerobic biotransformation of 6:2 FTI in soil (Ruan et al., 2013). Primary biotransformation was rapid with an estimated dissipation half-life of 4.5 days. The study showed that 6:2 FTI underwent biotransformation processes via 6:2 FTOH pathway to form PFPeA (20 mol%), PFHxA (3.8 mol%), 5:3 acid (16 mol%), and 4:3 acid (3 mol%). Furthermore, a significant level of PFHpA (16 mol%) was formed, perhaps via the intermediate 6:2 fluorotelomer unsaturated iodide (FTUI). Nevertheless, because of the lack of standard the authors could not verify their hypothesis.

Conclusion: Based on the available data it can be expected that n:2 FTI will be degraded and transformed into C_x-PFCA (with x= n-1, n, n+1) in individual amounts greater than 0.1 % per year. For example, 6:2 FTI will be degraded to PFHxA.

Fluorotelomer stearate monoester/fluorotelomer citrate trimester

The biodegradation of 8:2 fluorotelomer stearate monoester was studied by Dasu et al., in agricultural loam soil using laboratory microcosms within 80 days (Dasu et al., 2012). Although the microcosms were closed, the oxygen concentrations were comparable to aerobic conditions. The 8:2 fluorotelomer stearate monoester was degraded with a half-life (primary degradation) of 10.3 days (first-order kinetic model fit well up to day 20). At the end of the experiment 22 % of the initial 8:2 fluorotelomer stearate monoester was detected. The ester bond was hydrolysed and 8:2 FTOH was rapidly formed with a half-life of two days. Subsequent degradation was monitored. Similar reaction products as shown in Figure 2 were found. PFOA, which was the major terminal product, consistently increased over time reaching 1.7 mol% by day 80. PFOA concentration has not reached a plateau

until day 80. Furthermore, PFHpA (0.38 mol%) and PFHxA (0.16 mol%) were detected as terminal product. PFNA was also observed and increased over time (0.009 mol% on day 80). PFNA is suspected to be from low residuals of 10:2 FTOH in the fluorotelomer stearate monoester. Approximately 14 mol% of intermediate transformation products (sum of 8:2 FTCA, 8:2 FTUCA and 7:2s FTOH) were detected at day 80. Therefore, further increase of PFOA concentration with time is possible. Total mass balance decreased over time to about 38 mol% by day 80. Reasons could be irreversible sorption and decreasing extraction efficiencies of degradation products over time and formation of unidentified products.

A similar study was performed with forest soil (Dasu et al., 2013). 8:2 fluorotelomer stearate was degraded with a half-life (primary degradation) of 28.4 days (first-order kinetic model fit well up to day 46), which was slower than in the previous experiment based on agricultural soil. The major terminal metabolite was PFOA (4 mol% at 94 days). Further terminal metabolites were PFHpA (0.9 mol%) and PFHxA (0.2 mol%). PFOA concentration has not reached plateau until day 94. Approximately 25 mol% of inital fluorotelomer stearate monoester remained at day 94. 13 mol% of intermediate transformation products (sum of 8:2 FTCA, 8:2 FTUCA, and 7:2 sFTOH) were detected at day 94. Total mass balance decreased over time to about 44 mol% by day 94.

Dasu and co-workers also studied the biodegradation of 8:2 fluorotelomer citrate in a similar experimental setup (Dasu et al., 2013). The citrate was degraded slower. Approximately 56 mol% of the initial fluorotelomer citrate remained by the end of the study (218 days). Formation of 8:2 FTOH and secondary metabolites were identical to those shown in Figure 2. 4 mol% PFOA, 0.2 mol% PFHxA, and 0.8 mol% PFHpA were detected at day 218 (sum of 8:2 FTOH, 8:2 FTUCA, 8:2 FTCA, 7:2sFTOH ~6 mol%).

Conclusion: Based on the available data it can be expected that n:2 fluorotelomer stearate monoester /fluorotelomer citrate trimester will be degraded and transformed into C_x-PFCA (with x= n-2, n-1, n) in individual amounts greater than 0.1 % per year. For example, 6:2 fluorotelomer stearate monoester/fluorotelomer citrate trimester will be degraded to PFHxA.

Polyfluorinated olefins

The atmospheric lifetimes of polyfluorinated olefins are around 8 days with 90 % removal via reaction with OH radicals and 10 % removal via reaction with ozone (O_3) (smog chamber experiment) (Sulbaek Andersen et al., 2005). The major product (~ 90 %) in the atmospheric photo-oxidation is the corresponding perfluoroalkyl aldehyde (PFAL). The atmospheric lifetimes of PFALs are estimated to be around 90 days with respect to reaction with OH. It is therefore likely that PFALs in part will partition to the atmospheric aqueous phase and undergo photo-oxidation there to form the corresponding PFCA (Nielsen, 2014).

Fluorotelomer olefins (FTO, $F(CF_2)_nCH=CH_2$), a sub-class of polyfluorinated olefins, can therefore be considered as a class of substances leading to release of PFCAs.

Conclusion: Based on the available data it can be expected that polyfluorinated olefins will be abiotic degraded and transformed into corresponding PFCAs.

Fluorotelomer (meth)acrylates (FT(M)A)

In general, carboxylic acid esters will undergo hydrolysis resulting in the corresponding alcohols and carboxylic acids. It is reported that hydrolysis of perfluorinated telomer acrylates (and methacrylates) may be fast in landfills (half-lives < 4 days; 40-50 °C and pH 4-9), but that they have half-lives in the range of years in marine systems (half-lifes = 3-5 years; 15 °C and pH 8.1) (using SPARC software program). Hydrolysis of monomeric perfluorinated telomer acrylates may be a significant source to current environmental loadings of FTOHs and the corresponding PFCA. Under some saturated landfill conditions abiotic hydrolytic degradation of fluorotelomer acrylates could be occur resulting in significant fluxes of FTOHs and their degradation products into ground water and surface water (Nielsen, 2014; Rayne and Forest, 2010).

Butt el al. investigated the atmospheric chemistry of 4:2 fluorotelomer acrylate (4:2 FTA) (Butt et al., 2009). The atmospheric lifetime of 4:2 FTA is determined by its reaction with OH radicals and is approximately one day. The OH-radical-initiated oxidation in 700 Torr of air in the presence of NO gives HCHO with 4:2 fluorotelomer glyoxylate as the expected coproduct. The atmospheric fate of 4:2 fluorotelomer glyoxylate wil be photolysis and reaction with OH radicals, which will lead to formation of 4:2 fluorotelomer aldehyde and ultimately perfluorocarboxylic acids. Hence, the atmospheric oxidation of FTA is expected to lead to the formation of perfluorocarboxylic acids (1-10 % molar yield) in approximately 10 days. Therefore, the atmospheric oxidation of FTA is a potential source of perfluorocarboxylic acids in remote areas.

Microbial transformation (microbially mediated hydrolysis) of 8:2 fluorotelomer acrylate (8:2 FTA) and 8:2 fluorotelomer methylacrylate (8:2 FTMA) in aerobic soils was investigated by Royer et al. (Royer et al., 2015). 8:2 FTA and 8:2 FTMA were rapidly degraded with half-lives of 3-5 days and 15 days, respectively. Both substances were hydrolysed at the ester linkage as evidenced by the formation of 8:2 FTOH. 8:2 FTOH was further degraded via the known biotransformation pathway (see Figure 2). 8 mol% PFOA was formed in FTA-amended soil, and 10.3 mol% PFOA was formed in FTMA-amended soil after 105 days, respectively. Besides the stable metabolites like PFOA, PFHpA (1.3-3.4 mol%), PFHxA (< 0.4mol%), and 7:3 acid (2.3-3.4 mol%), 38-47 mol% of intermediate metabolites (8:2 FTUCA, 8:2 FTCA, 7:2 sFTOH) were observed at day 105. Total mass balance decreased with incubation time with 50-75 % recovery at the end of 105 day incubation. Reasons for loss of mass balance could be: reduced extractability, increased irreversibly bound metabolites over time, or additional metabolites that were not quantified or identified.

Conclusion: Based on the available data it can be expected that n:2 FT(M)A will be degraded and transformed into C_x-PFCA (with x = n-2, n-1, n) in individual amounts greater than 0.1 %per year. For example, 6:2 FT(M)A will be degraded to PFHxA.

Polyfluoroalkyl phosphoric acid mono-/diesters (monoPAP/diPAP)

Degradation of polyfluoroalkyl phosphates (6:2 monoPAP and diPAP) was studied by Lee and co-workers (2010) using raw wastewater and sewage sludge. It was shown that the ester bonds were cleaved (microbial hydrolysis) by the formation of monoPAP and thereafter 6:2 FTOH. In the end, the degradation of 6:2 monoPAP and 6:2 diPAP resulted

in PFHpA (8.4 mol% and 7.3 mol% expressed as percent PAP present in the aqueous phase at the start of the experiment), PFHxA (2.1 mol% and 6.2 mol%), PFPeA (0.7 mol% and 1.5 mol%), and 5:3 acid (0.12-0.38 mol% and 1.5mol%). It should be noted, that only approximately 10 % of the initial 6:2 monoPAP and approximately 33 % of the intial 6:2 diPAP could be detected in the aqueous phase at the start of the experiment. The authors also performed a chain length study with n:2 monoPAP (n = 2,4,6,8). The production of FTOHs in the headspace and the production of FTCAs, FTUCAs and PFCAs in the aqueous phase of the bottles suggest that the monoPAPs were microbially transformed. Although the monoPAP congeners were observed to produce the corresponding FTOHs in relatively similar order (1-2 % after 92 days; conservative estimates), the rate of production was observed to decrease significantly as the chain length of the monoPAP increased. The short-chain monoPAPs fully degrade to the corresponding PFCAs, whereas the long-chain monoPAPs only partially degraded to the intermediates (FTCA and FTUCA). This difference may be explained by the steric constraint of the longer chain lengths to microbial attack and that the long-chain monoPAPs maybe preferentially associated with the various surfaces present in the experimental system (Lee et al., 2010).

D'eon and Mabury demonstrated in a study with rats that metabolism of 8:2 mono and diPAP in mammals leads to the formation of 8:2 FTOH, which is then available for oxidation to PFOA. The authors suggest that exposure in rats to either 8:2 monoPAPs or 8:2 diPAPs will result in increased PFOA blood levels (D'eon and Mabury, 2007). A later study by the same authors confirms these results and suggest that biotransformation of diPAP even with low exposure could over time result in significant exposure to PFOA (D'eon and Mabury, 2011).

Biodegradation pathways and plant uptake were elucidated in a greenhouse microcosm supplemented with high concentration of 6:2 diPAP (Lee et al., 2014). WWTP biosolids-amended soil sown with plant seeds (*Medicago truncatula*) and premixed with 100 mg of 6:2 diPAP from an ethanol-based standard were used for this study. The authors estimated a disappearance half-life in soil of ~2 months for 6:2 diPAP. The dissipation of the diPAPs in soil may occur through multiple pathways. The majority of 6:2 diPAP resided in the soil (99 %), with minor uptake observed in plants (1 %), leaching corresponded to < 0.1 %. Analyses of volatile substances like FTOH were not performed, as the vessels were open to the greenhouse atmosphere. For the same reason no mass balance calculation was performed. The following metabolites were observed after 5.5 months in soil: PFHxA > 5:3 acid > PFPeA > 6:2 FTUCA = 6:2 FTCA > PFBA > 5:3 Uacid = PFHpA. PFBA was the PFCA with the highest concentration in the plants after 5.5 months followed by PFHxA, PFPeA and PFHpA.

Lewis et al. investigated the biotransformation of 6:2 PAPs (mixture of 6:2 monoPAP, diPAP, triPAP, monopyro PAP and monopoly PAP = 11.5 % of 6:2 FTOH equivalent active ingredients) by three known FTOH-degrading *Pseudomonas* strains under different co-substrate conditions and compared the results with biotransformation by activated sludge (Lewis et al., 2016). The *Pseudomonas* strains (*P. butanovora*, *P. oleovorans*, and *P. fluorescens*) transformed 6:2 PAP to following transformation products after 30 days: 6:2 FTOH, 6:2 FTCA, 6:2 FTUCA, 5:2 ketone, 5:2 sFTOH, PFHxA, 5:3 acid and 5:2 Uacid. In the biotransformation study with activated sludge PFHpA (0.04 mol%/g cells basis at day 30) and PFPeA (0.47 mol%/g cells basis at day 30) were detected as additional

transformation products. PFHxA was present with 2 mol%/g cells basis at day 30 in the activated sludge study.

Within 30 days more 6:2 PAPs were transformed by activated sludge (22 mol%/g cells basis) than by the FTOH-degrading *Pseudomonas* strains (*P. butanovora*: 1.5 mol%/ g cells basis, *P. oleovorans*: 1.1 mol%/ g cells basis, and *P. fluorescens*: 8.6 mol%/ g cells basis*)*. Co-substrates (citrate and lactate) affected the amount of metabolites but did not have a major impact on total biotransformation yields.

The biotransformation of 6:2 and 8:2 diPAPs in aerobic soil was investigated in semidynamics reactors (Liu and Liu, 2016). To investigate the phenomenon of solvent-enhanced hydrolysis, six different extraction solvents were compared. None of the six solvents was able to extract 6:2 and 8:2 monoPAPs with satisfactory recoveries and without causing solvent-enhanced hydrolysis. 6:2 and 8:2 diPAPs have exhibited higher stability and lower tendency to undergo solvent-enhanced hydrolysis. Acetic acid, which lowers the pH of the solution, seemed to play a more important role than the type of the solvents in achieving satisfactory recoveries and minimizing undesirable solvent-enhanced hydrolysis of diPAPs. The estimated half-lives for 6:2 diPAP were 12 days using a double first-order in parallel model and 15 days using single first-order model. After 112 days, 6 % PFHxA, 6.4 % PFPeA, 0.73 % PFBA and 9.3 % 5:3 acid were detected as stable transformation products. The biotransformation of 8:2 diPAP in soil proceeded much slower than the biotransformation of 6:2 diPAP. The estimated half-lives for 8:2 diPAP were > 1000 days using a double first-order in parallel model and 114 days using single first-order model. After 112 days, 2.1 % PFOA, 0.25 % PFHpA, 0.34 % PFHxA and 0.29 % 5:3 acid were detected as stable transformation products. The declining mass balances over 112 days (108 % to 40 % for 6:2 diPAP, 124 % to 69 % for 8:2 diPAP) could be attributed to the formation of soil bound residues.

Chen et al. investigated the biotransformation of 6:2 diPAP and 8:2 diPAP in common carp liver (*Cyprinus carpio*) (Chen et al., 2019). The carp was exposed to 6:2 diPAP or 8:2 diPAP at 8 nM in water during a 14-day uptake period. The uptake period was followed by a 14-day depuration period. No diPAPs were detected in the background water and control fish samples. DiPAPs could be quickly taken up by carp from water as these substances were detected in the fish liver on the first day of exposure and continuously increased with exposure time (no steady state during uptake period). During exposure period in the 6:2 diPAP study increasing concentration of several metabolites like 6:2 FTUCA, 5:3 FTCA, PFHxA (93.0 pmol/g ww on day 14) and PFHpA (2.01 pmol/g ww on day 14) were observed in fish livers (not detected in control fish). 6:2 monoPAP, 6:2 FTOH or PFPeA were not identified due to faster biotransformation or extremely low concentrations. During the depuration phase concentrations of PFHxA and PFHpA still increase, whereas concentrations of 6:2 diPAP, 6:2 FTUCA and 5:3 FTCA decrease. This suggests that biotransformation of the accumulated parent compound or intermediate metabolites continued. In the 8:2 diPAP biotransformation study 8:2 FTUCA, 8:2 FTCA, 7:3 FTCA as well as PFHpA, PFOA and PFNA were detected with increasing concentration during uptake period. PFOA and PFNA were detected in the control fish at relatively low concentrations, therefore concentrations in the exposed fish liver were corrected. After 14 days exposure, 7.39 pmol PFOA/g ww, 5.13 pmol PFNA/g ww and 3.96 pmol PFHpA/g ww were observed. The concentrations of the PFCAs further increased, whereas concentrations of the parent compound as well as the other metabolites decreased.

In the total, a higher transformation rate was observed for 8:2 diPAP (6.78 – 14.6 mol%) compared to 6:2 diPAP (0.49 – 0.66 mol%). According to the authors, a possible reason is that 8:2 diPAP contains more electron-withdrawing fluorine atoms, which makes it subject of stronger hydrolysis (Chen et al., 2019).

Zabaleta et al. studied biotransformation of 8:2 diPAP in gilt-head bream (*Sparus Aurata*) via dietary exposure (29 µg 8:2 diPAP/g) over seven days (Zabaleta et al., 2017a). 8:2 diPAP and potential transformation products were monitored in plasma, liver, muscle, gills, bile and brain. With the exceptions of 8:2 diPAP in the dosed feed, no PFASs were detected in blanks or feed. In control fish PFOA was observed in bile, brain (both with negligible concentrations compared to exposed animals) and liver. This observation was surprising, as PFOA concentration in water was below LOD. Nevertheless, the liver data for PFOA in this study were control-corrected. 8:2 FTCA, 8:2 FTUCA, 7:3 FTCA and PFOA were observed as intermediate or terminal metabolites. After seven days, 8:2 FTCA was the major metabolite in all tissues and biofluids, except for bile and brain, where PFOA concentration was the highest. No PFOA was detected in muscle and liver. In all other tissues/biofluids the PFOA concentrations at the end of the study were 0.12 ng/mL (plasma), 0.6 ng/g (gills), 3.7 ng/g (brain), and 1.32 ng/mL (bile), respectively.

The degradation of 8:2 diPAP in two amended soils (soil 2.4 and substrate) was investigated by Bizkarguenag and co-authors. A compost, fortified with 8:2 diPAP (500 ng/g), were mixed with the soils. Within the first six hours concentration of 8:2 diPAP decreased and remained almost constant until the end of the study (108 days). 8:2 mono PAP, 8:2 FTUCA, 8:2 FCA, 7:3 FTCA as well as PFHxA, PFHpA and PFOA were detected as degradation products. The major degradation product was PFOA. 10 % and 62 % PFOA were observed in compost-amended soil 2.4 and compost-amended substrate, respectively. All other degradation products were present at < 10 %. In the presence of crops (carrot and lettuce) different degradation products were observed. Whereas in the experiment with carrot PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA and 7:3 FTCA were detected in the soils, in experiment with lettuce PFOA was the only degradation product (Bizkarguenaga et al., 2016).

8:2 mono- and diPAPs are reported to-undergo slow hydrolysis (lifetime of several years) at environmental conditions. D'eon and Mabury investigated the hydrolytic stability of 8:2 mono- and diPAPs under aggressive conditions (pH 9 and 50 °C) (D'eon and Mabury, 2007). Lifetimes of > 26 years were estimated. The reaction results in 8:2 FTOH and phosphoric acid (Nielsen, 2014). It is explicitly noted that the experimental hydrolysis rates cannot be reproduced by existing models (Rayne and Forest, 2010). Mono- and diPAPs of 8:2 FTOHs, including their polymers, can therefore be considered as a class of substances leading to release of PFOA by abiotic degradation processes.

Conclusion: Based on the available data it can be expected that n:2 monoPAP and n:2 diPAP will be degraded and transformed into C_x-PFCA (with x = n-2, n-1, n, n+1) in individual amounts greater than 0.1 % per year. For example, 6:2 monoPAP/diPAP will be degraded to PFHxA.

Polyfluorinated silanes

No relevant information concerning hydrolytic lifetimes of condensed or polymerized polyfluorinated silanes was found in the open literature.

Silanes have appreciable vapour pressures and may in principle evaporate and undergo photo-oxidation in the atmosphere. It is also conceivable that small siloxanes may partition to the atmosphere and undergo photo-oxidation there. As reaction product PFCA will be formed (Nielsen, 2014).

Conclusion: Based on the available data it can be expected that polylfuorinated silanes will be abiotic degraded and transformed into corresponding PFCAs.

Perfluorinated amides /perfluoroalkane sulfonamides /perfluoroalkane sulfonamidoethanols

Jackson and Mabury investigated the hydrolysis of the polyfluorinated amides *N*-ethyl-N-(2-hydroxyethyl)perfluorooctaneamide (NEtFOA) in 1 M NaOH solution (pH 14), in 5 mM tris buffer (pH 8.5), and in 50 mM borate buffer (pH 8.5) (Jackson and Mabury, 2013). No hydrolysis to PFOA was observed after eight days at pH 8.5. Rapid degradation was observed in the borate buffer, but not to PFOA. At pH 14 and at room temperature a quantitative (98 %) conversion of EtFOA to PFOA was observed after 24 hours. Hydrolysis from NEtFOA to PFOA under environmental conditions will be negligible. The environmental fate of polyfluorinated amides is suggested to be volatilized to the atmosphere followed by oxidation by hydroxyl radicals with a predicted lifetime of 3 – 20 days.

Jackson et al. studied the atmospheric photo-oxidation (smog chamber experiment) of N-ethyl-perfluoro-butyramide (NEtFBA, $C_3F_7C(O)NHCH_2CH_3$) as a more volatile surrogate for longer chained polyfluorinated amides and identified $C_3F_7C(O)NH_2$ as intermediate, and PFCAs and HNCO (isocyanic acid) as products (Jackson et al., 2013). They presented a general mechanism based on the observed product distribution. Atmospheric lifetime of NEtFBA, with respect to reaction with OH, was estimated to be 4.4 days. Primary oxidation products reacted further to PFCAs (16 % PFBA, 0.3 % PFPrA and 0.3 % trifluoroacetic acid (TFA)). The authors predict similar reaction kinetics for N-ethyl-perfluorooctanamide (NEtFOA) and NEtFBA since the length of a perfluorinated chain does not affect the reaction rate with OH. The primary oxidation products of NEtFOA are expected to have much longer lifetimes and could be capable of contaminating Arctic air. The primary oxidation products are expected to react further to form PFOA.

Martin et al. studied OH radical and Cl atom initiated atmospheric photo-oxidation (smog chamber experiment) of N-ethyl perfluorobutanesulfonamide (NEtFBSA, $C_4F_9S(O)_2NHCH_2CH_3$) (Martin et al., 2006). The atmospheric lifetime of NEtFBSA in the gas-phase (reaction with OH radicals) is estimated to be 20-50 days. The authors observed that Cl atoms are 23 times more reactive toward NEtFBSA than OH radicals. Therefore, Cl atoms were used in place of OH radicals for product experiments. Product formation experiments with OH radicals would be proceeded too slowly to produce secondary products in the experimental system. Nevertheless, Cl atoms and OH radicals are expected to react with NEtFBSA via hydrogen abstraction to give the same products (although not necessarily in the same field). Based on chlorine atom initiated oxidation, $C_4F_9S(O)_2NHC(O)CH_3$, $C_4F_9S(O)_2NHCH_2CHO$and $C_4F_9S(O)_2NHCHO$ were identified as intermediates, and SO_2, COF_2 and PFCAs as stable products. Three PFCAs were detected above the level of the blank: 0.33 % PFBA, 0.11 % PFPrA, and 0.09 % TFA of the molar balance, respectively. At the same time only 0.65 % COF_2 of the starting material had unzipped. Extrapolation of these results suggests that 45 % of the carbon in the

perfluoroalkane chain will ultimately be incorporated into PFCAs upon complete oxidation, while the remaining fraction is expected to go to COF_2 (timeframe not given). PFBS was not detected in any sample. The authors suggest that it is evident that analogous perfluorooctane sulfonamide is a potential source for PFOA. They presented a general mechanism based on the observed product distribution.

D'eon et al. measured the gas-phase reaction of N-methyl perfluorobutane sulfonamidoethanol (N-MeFBSE) with OH radicals (D'eon et al., 2006). Experiments were performed in 750 Torr of air diluent at 296 K. An atmospheric lifetime of approximately two days was determined. The following products were identified by in situ FTIR spectroscopy and offline GC-MS and LC –MS/MS analysis: N-methyl perfluorobutane sulfonamide (NMeFBSA), COF_2, PFBA, PFPrA, TFA and PFBS. The concentration of PFBA and PFPrA increased with proceeding reaction. For quantification of PFCAs and PFBS a mass balance was carried out. After 50 % consumption of N-MeFBSE, the cumulative concentration of PFCAs and PFBS accounted for approximately 10 and 1 %, respectively. In addition, the authors performed Cl-atom initiated oxidation. The products of this oxidation were similar to those observed in the OH-radical initiated oxidation experiments. PFCAs and PFBS were detected with similar concentration profiles.

Conclusion: Based on the available data it can be expected that perfluorinated amides, perfluoroalkane sulphonamides and perfluoroalkane sulfonamidoethanols will be abiotic degraded and transformed into corresponding PFCAs in individual amounts greater than 0.1 % per year.

Fluorotelomer urethane (monomers)

Dasu and Lee studied the biodegradation of two 8:2 fluorotelomer urethane monomers in soil (Dasu and Lee, 2016). The biodegradation of toluene-2,4-di(8:2 fluorotleomer urethane) (FTU), containing an aromatic backbone, was investigated in a forest and an agrigultural soil. While hexamethylene-1,6-di(8:2 fluorotleomer urethane) (HMU), with an aliphatic backbone, was investigated only in forest soil. In agricultural soil little to no biodegradation of FTU occurred (94 ± 15 % recovery at day 180). A production of PFOA was observed. Nevertheless, the authors assume that the PFOA was produced from residual 8:2 FTOH in FTU (0.56 mol%). In the experiments with forest soil biotransformation of FTU and HMU occurred. The authors mentioned that this activity may be due to fungal enzyme activity which may be more effective in urethane bon cleavage. Nevertheless, this assumption was not further investigated. For FTU half-lives of 126 days (first-order model) and 148 days (bi-exponential model) were estimated. The degradation of HMU was more slowly resulting in estimated half-lives of 478 days (first-order model) and 667 days (bi-exponential model). At the end of the study (FTU: 117 days; HMU: 180 days) 73 % FTU and 76 % HMU still remained. The addition of toluene-2,4-dicarbamic acid diethyl ester (TDAEE) to the FTU microcosms at day 52, a structurally similar non-flourinated FTU analogous substance, enhanced the formation of terminal end products from 8:2 FTOH degradation. There was no clear evidence that TDAEE enhanced the cleavage of the urethane bond. Therefore, the authors appeared that TDAEE was only an additional carbon source. A second addition of TDAEE on day 74 appeared to retard subsequent degradation of FTU. The derogation of HMU was enhanced by re-aeration on day 106 indicating oxygen may have been limiting during some periods. Re-aeration of the FTU microcosm's occurred during TDAEE addition. Based on the enhancements in the FTU

microcosm 0.84 mol% PFOA, 0.11 mol% PFHpA, 0.07 mol% PFHxA and 0.11 mol% 8:2 FTOH were formed after 117 days. In the study with HMU 0.94 mol% PFOA, 0.14 mol% PFHpA, 0.06 mol% PFHxA, 0.88 mol% 7:2 sFTOH and 0.14 mol% 8:2 FTOH were observed at day 180. The authors estimated (KinGUI – Kinetic Graphic User Interface) final % PFOA yields from FTU and HMU are 1.5-1.9 % and 3-5.2 %, respectively. In the experiments with forest soil PFOA resulted from transformation of the 8:2 fluorotelomer urethane, since PFOA concentrations were well above what could result from residual 8:2 FTOH.

Conclusion: Based on the available data it can be expected that n:2 fluorotelomer urethane (monomers) will be degraded and transformed into C_x-PFCA (with x = n-2, n-1, n) in individual amounts greater than 0.1 % per year. For example, 6:2 fluorotelomer urethane (monomers) will be degraded to PFHxA.

Fluorotelomer ethoxylates (FTEO)

Biotransformation of fluorotelomer ethoxylates was reported by Frömel and Knepper (Frömel and Knepper, 2010). WWTP effluent was used under aerobic conditions. Zonyl FSH, a commercial mixture which contains fluorotelomer ethoxylates (8:2 FTOH residues = 0.29 %; 6:2 FTOH residues = 0.54 %) with perfluorinated chain lengths between four and twelve and a degree of ethoxylation between 0 and 18 was analysed. Fluorotelomer ethoxylates were rapidly degraded (half-life (primary degradation = 1 d). One significant metabolite was formed within the study duration of up to 48 days: Fluorotelomer ethoxylate carboxylate. The formation of 0.3 mol% PFOA and 2.5 mol% PFHxA was observed, but these PFCAs could have been formed from the FTOH-residuals. It can be assumed that studies with a longer time frame will result in higher PFCA concentrations.

Fluorotelomer sulfonate (FTS)

The aerobic biotransformation of 6:2 Fluorotelomer sulfonate (6:2 FTS) was investigated in closed bottles in diluted activated sludge from three WWTPs (Wang et al., 2011a). The biotransformation of 6:2 FTS was relatively slow, with 63.7 % still remained at day 90. The initial microbial aerobic desulfonation of 6:2 FTS may be the rate-limiting step. At day 90, 1.5 % PFPeA, 1.1 % PFHxA, 0.14 % PFBA and 0.12 % 5:3 acid were observed as stable transformation products. In addition, 2.6 % 5:2s FTOH and 0.8 % 5:2 ketone were detected. 6:2 FTOH and PFHpA were not observed during the 90-d incubation. The authors noted, that a substantial fraction of initially dosed 6:2 FTS (24 %) may be irreversibly bound to diluted activated sludge catalysed by microbial enzymes. 6:2 FTS primary biotransformation bypassed 6:2 FTOH to form 6:2 FTUCA directly, which was then degraded via pathways similar to 6:2 FTOH biotransformation.

Zhang et al investigated the biotransformation potential of 6:2 FTS in aerobic sediment and the biotransformation potential of 6:2 FTS and 6:2 FTOH in anaerobic sediment (Zhang et al., 2016b). In aerobic sediment 6:2 FTS was rapidly biotransformed with a half-life of less than five days. The rapid transformation of 6:2 FTS suggests that 6:2 FTA de-sulfonation occurred readily in aerobic sediment, possibly using monooxygenases to catalyse desulfonation. After 90 days 20 mol% PFHxA, 21 mol% PFPeA, 0.55 mol% PFHpA, and 16 mol% 5:3 acid were detected as stable transformation products. 6:2 FTOH was detected at low levels (< 2.5 mol%) over the study period, suggesting that 6:2 FTOH is an

initial transformation product of 6:2 FTS. After desulfonation, the biotransformation pathways of 6:2 FTS are the same as for 6:2 FTOH.

In the test with anaerobic sediment, no biotransformation of 6:2 FTS was observed over 100 days. In contrast, 6:2 FTOH was biotransformed to 60 mol% FTCA, 12 mol% 5:3 acid and 0.6 mol% PFHxA within 100 days in anaerobic sediment. These results confirm that the anaerobic experimental system was metabolically active and the molecular structure of 6:2 FTS hindered its biotransformation by microbes.

Conclusion: Based on the available data it can be expected that n:2 FTS will be degraded and transformed into C_x-PFCA (with x = n-2, n-1, n, n+1) in individual amounts greater than 0.1 % per year. For example, 6:2 FTS will be degraded to PFHxA.

Fluorotelomer thioether amido sulfonate (FTTAoS)

Harding-Marjanovic et al. investigated the aerobic biotransformation of Fluorotelomer thioether amido sulfonate (FTTAoS) in soil (Harding-Marjanovic et al., 2015). FTTAoS is a PFAS present in several widely used aqueous film-forming foam (AFFF) formulations. Beside 6:2 FTTAoS, which is the most abundant FTTAoS homologue, 4:2, 8:2, 10:2, 12:2, and 14:2 FTTAoS have also been detected in some AFFFs. In this study, the aerobic biotransformation of 4:2, 6:2, and 8:2 FTTAoS was investigated in soil slurries constructed with AFFF-impacted topsoil from a U.S. military base and enriched with an FTTAoS-containing AFFF formulation. The biotransformation of FTTAoS occurred in live microcosms over approximately 60 days and produced 4:2, 6:2, and 8:2 FTS, 6:2 FTUCA, 5:3 acid, PFBA, PFPeA, PFHxA, PFHpA and PFOA. An oxidative assay was used to indirectly quantify the total concentration of polyfluorinated compounds and check the mass balance. The assay produced near complete mass recovery of FTTAoS after biotransformation, with 10 % (mol/mol) of the amended FTTAoS accounted for in FTS, x:3 acid, and PFCA products (1.5 %). The transformation rates of identified products appear to be slow relative to FTTAoS, indicating that some intermediates may persist in the environment.

Yi et al. studied the biotransformation of 6:2 fluorotelomer thioether amido sulfonate (FTTAoS) under sulfate-reducing conditions (Yi et al., 2018). 6:2 FTTAoS is a component of several AFFF formulations. Pristine solids from the sediment of a creek and or AFFF-contaminated solids from a firefighting training area were used as microbial inocula. Approximately 75 % of FTTAoS had been transformed in in the pristine solid and AFFF-impacted solid microcosms after 270 days. Contrary to the study under aerobic conditions (Harding-Marjanovic et al., 2015), PFCAs and 6:2 FTS were not detected as transformation products under sulfate-reducing conditions within the test duration. In addition to the parent compound nine potential biotransformation products (e.g. 6:2 fluorotelomer thioether propionate) were observed. In addition, the authors used the TOP assay (total oxidisable precursor assay) for quantification of total PFASs. The complete PFAS mass balance (96 ± 8 % after 276 days) in the microcosms with pristine solids indicated that the remaining transformation products (other than 6:2 fluorotelomer thioether propionate) were converted into PFCAs (e.g. PFHxA) by the TOP assay. The mass balance in the AFFF-contaminated solid microcosm was incomplete (67 ± 6 % after 282 days) due to possible volatile transformation products or transformation products that were not converted into PFCAs by the TOP assay.

Conclusion: Based on the available data it can be expected that FTTAoS will be degraded and transformed into corresponding PFCAs.

Perfluoroalkyl phosphinic acids (PFPiAs)

In a review of Wang et al. available information on degradation of perfluoroalkyl phosphinic acids (PFPiAs) were collected and evaluated (Wang et al., 2016).

PFPiAs hydrolyse to yield perfluoralkyl phosphonic acids (PFPAs) and $C_nF_{2n+1}H$. $C_nF2_{n+1}H$ can be oxidized to form corresponding PFCAs (e.g. via reaction with OH radicals at high temperature or with alkaline conditions). Similary to PFCAs, PFPAs show high resistance to heat, oxidants, bases and aerobic biodegradation in surface water.

Formation of C6 and C8 PFPAs was also observed in rainbow trout after daily dietary exposure to C6/C6, C6/C8 and C8/C8 PFPiAs. A fast elimination from rat blood (half-lives: 1.8–9.3 days), lowrenal and fecal excretion (< 1 %) within 48 h after dosing, and lowbody storage (i.e. lowtomoderate liver-to-blood ratios) for C6–C12 PFPiAs were observed,which indicates that biotransformation likely occurred in rats, too. It is unknown if this biotransformation follows the same pathway as abiotic hydrolysis because $C_nF_{2n+1}H$ moieties were not measured. Furthmore, no degradation of C4/C4 PFPiA was observed in a 28-day OECD 301-F test on ready biodegradability. Thus, degradation of PFPiAs in a specific environment and biota, depends on actual conditions.

Conclusion: Based on the available data it can be expected that PFPiAs will be abiotic degraded and transformed into corresponding PFCAs.

Side-chain fluorinated polymers

The biodegradation potential of a fluoroacrylate polymer product was studied in four aerobic soils over two years (Russell et al., 2008). It was assessed whether the FTOH side chains covalently bonded to the polymer backbone may be transformed to PFCAs. The test substance itself was not directly measured. Instead, terminal transformation products like PFOA, PFNA, PFDA and perfluoroundecanoic acid (PFUnDA) were measured. The fluoroacrylate polymers contain the polymer itself and also residual raw materials and impurities ("residuals"). The fluoroacrylate monomer used for the polymer was prepared from 1 % 6:2 FTOH, 55 % 8:2 FTOH, 29 % 10:2 FTOH, 10 % 12:2 FTOH and 5 % 14:2 FTOH and larger. Major residuals present in the test substance were n:2 FTOH (n = 6, 8, 10), n:2 fluorotelomer acrylate monomer (n = 6, 8, 10), n:2 FTOH acetate (n = 6, 8, 10), n:2 fluorotelomer olefin (n = 8, 10). PFOA, PFNA, PFDA and PFUnDA were contained as impurities in the range of 2.3-9.9 ng/mg (0.004 – 0.02 µmol/kg).

Based on the rate of formation of PFOA in soil, estimated half-lives of the polymer ranged from 95 to > 2000 years (all soils combined 1160 years). The estimated half-lives of residuals were 12 to 43 days (all soils combined 27 days).

The maximum PFOA concentration ranged from 1.8 to 2.1 µmol PFOA/kg soil. The residual amount of PFOA in the test substance was 0.019 µmol PFOA/kg soil. Hence, PFOA is formed from degradation of residuals and possibly also from degradation of the side chains in the polymer. The maximum experimental PFOA concentrations are 24 – 28 % of the theoretical amount that could be derived from 100 % conversion of the residuals alone

(7.55 µmol PFOA/kg soil). If all 8:2 related analytes are summed 25 – 32 % of the theoretical amount of PFOA is formed from residuals.

Via an analogous degradation pathway to that for 8:2 FTOH, polymer side chains and residuals from FTOH with longer chains (e.g. 10:2 FTOH and 12:2 FTOH) are assumed to degrade to form PFCAs with longer chains. Similar to PFOA the concentrations of PFNA, PFDA and PFUnDA rise with time. The measurement of concentrations of higher PFCA-homologues (≥ C12-PFCA) was not included in this study. The maximum concentrations after 728 days ranged from 0.089 to 0.218 µmol PFNA/kg soil, 0.227 to 0.689 µmol PFDA/kg soil and 0.016 to 0.045 µmol PFUnDA/kg soil, respectively. Nevertheless, the amounts of longer chain FTOHs in the polymer were lower compared to 8:2 FTOH. Hence, lower concentrations of PFNA, PFDA and PFUnDA are not unexpected.

Detection of short-chain PFCAs like PFHxA was not in the scope of this study. Nevertheless, based on the observations for 8:2 FTOH and longer chain FTOHs an anlagous degradation pathway is also expected for 6:2 FTOH residuals and polymer side-chains. Even if the amount of 6:2 FTOH (25 ng/mg; 0.07 nmol/mg) in the polymer was lower compared to 8:2 FTOH (1200 ng/mg; 2.6 nmol/mg) and 10:2 FTOH (650 ng/mg; 1.2 nmol/mg).

The study from Russell et al. was commented by Renner (Renner, 2008). She noted that the bottles, which were used for the experiment, leaked and may have released degradation products. Furthermore, FTOHs that were added to sterile control bottles could not be recovered. Russell et al. justified this with irreversible binding to the soil. However, no evidence exists for this claim. Furthermore, the soil experiments did not maintain mass balance. It is stated that it is very difficult to determine the breakdown rate for the polymer because of the relatively large amount of the residuals. A degradability test with a polymer (also containing fluoroacrylate ester linkage) from another manufacture shows relatively rapid fluorochemical polymer breakdown (Renner, 2008). Therefore, the study from Russell et al. should not be given too much weight.

In a further study Russell et al. evaluated the formation of PFOA from the biodegradation of a fluorotelomer-based urethane polymer product in four aerobic soils (Russell et al., 2010). The fluorotelomer alcohol raw material in the polymer synthesis was composed of 34 % 6:2 FTOH, 31 % 8:2 FTOH, 18 % 10:2 FTOH, 9 % 12:2 FTOH and 8 % 14:2 FTOH and larger. The degradation of the polymer begins with the enzymatic cleavage of the fluorotelomer side-chain from the polymer backbone followed by the fractional conversion of fluorotelomer side-chains containing eight fluorinated carbons through a series of intermediates reactions forming PFOA. The maximum concentrations of PFOA (modelled; first-order reaction) formed after two years ranged between 0.5 and 1.3 µmol/kg soil (initial concentration of polymer = 77.6 µmol/kg soil; initial concentration of intermediates and PFOA = 0.032 µmol/kg soil. Including all data until day 728 in kinetic evaluation the calculated half-lives of the polymer ranged between 79 and 241 years (geomean = 132 years). Including all data until days 728 except one soil through day 273 in kinetic evaluation the estimated half-lives ranged from 28 to 241 years (geomean 102 years). In contrast to Russell et al. 2008 the PFOA formation from residuals was negligible in this study. Hence, the PFOA formation resulted from biodegradation of the fluorotelomer-based urethane polymer. PFNA, PFDA and PFUnDA were also formed during the experiment, but modelling of the polymer degradation only considered PFOA formation. Detection of short-chain PFCAs like PFHxA were not in the scope of this study.

Washington et al. also investigated the degradability of an acrylate-linked fluorotelomer polymer in soil (Washington et al., 2009). The tested acralyte-linked fluorotelomer polymer contained e.g. impurities and residuals of n:2 FTOH (n = 6, 8, 10, 12), n:2 fluorotelomeracrylate (n = 6, 8, 10), Cn-PFCAs (n= 6-12), etc. The polymer can be degraded in soil through attack on the carbon backbone and /or the ester linkage connecting the backbone to the fluoroalkyl side chains resulting in PFCAs via the intermediate FTOH. Estimated half-lifes of the tested coarse-grained polymers ranged from 870 to 1400 years. Modelling indicates much shorter half-lives (10-17 years) for more finely grained polymers assuming degradation is surface-mediated. The authors observed degradation of PFOA, PFHpA and PFHxA with an estimated half-life of 130 days, 37 days and 16 days, respectively. However, this result is contradictory to other studies which stated that PFCAs e.g. PFOA are not degradable in soil (Moody et al., 2003; OECD, 2006).

After extensive method development the authors investigated the degradation of two commercial acrylate-linked fluorotelomer-based polymers (containing ~ 50 % C8-fluorotelomer components, ~ 30 % C10-fluorotelomer components, ~10 % C12-fluorotelomer components and small amounts of larger fluorotelomer components) in four soils in a further study (Washington et al., 2015). The estimated half-lives ranged from 33 to 112 years. Compared with day 0, concentrations of C8-C14-PFCAs and FTOHs increased up to 12-fold and 28-fold until day 376. The authors estimated a half-life of 8:2 FTOH of ~ 1200 days. Due to discrepancy to literature values (half-lives < 28 days) a follow-up 8:2 FTOH degradation experiment was performed. After spiking microcosms with 8:2 FTOH a half-life of 210 days was estimated. Because the only design difference between the both experiments was the presence of the fluorotelomer-based polymer, the authors inferred the difference in half-lives to be due to presence of the fluorotelomer-based polymer. Furthermore, the authors performed a hydrolysis experiment with the fluorotelomer-based polymer. The results showed an increase of 8:2 FTOH in the pH 10 treatments, almost doubling over the 11-day experiment, while in the pH 3 treatments and dry controls the concentration remained constant. These results suggest that fluorotelomer-based polymer can undergo OH-mediated hydrolysis.

A further study on abiotic hydrolysis of a fluorotelomer-based polymer (containing ~ 50 % C8-fluorotelomer components, ~ 30 % C10-fluorotelomer components, ~10 % C12-fluorotelomer components and small amounts of larger fluorotelomer components) was investigated by Washington and Jenkins (Washington and Jenkins, 2015). The experiments were conducted at 25 °C and with eight pHs buffers over the range of 5-12. The concentrations of the hydrolysis products, 8:2 FTOH and 10:2 FTOH, were observed to increase until the end of the study (day 77) at each of the pH values. Compared to day 0, up to 34-fold concentration of 8:2 FTOH and 190-fold concentration of 10:2 FTOH were measured at day 77. In the range of pH 5 to 7 the rate of hydrolysis of the polymer is not a strong function of pH, whereas at higher pH, half-life decreased with increasing pH. For the fluorotelomer-based polymer hydrolytic half-life values of ~0.7 – 55 years based on 8:2 FTOH and 0.66 – 89 years based on 10:2 FTOH were estimated. Considering the large production volume of fluorotelomer-based polymers and the poor efficacy of conventional treatments for recovery PFCAs from waste streams, these results suggested that fluorotelomer-based polymers manufactured to date potentially could increase PFCAs fourfold to eightfold over current oceanic loads, largely depending on the integrity of disposal units to contain PFCAs upon hydrolytic generation from fluorotelomer-based polymers.

Rankin et al. investigated the biodegradability of a fluorotelomer-based acrylate polymer in soil-plant microcosm over 5.5 months in the absence /presence of wastewater treatment plant biosolid (Rankin et al., 2014). The biodegradation of the fluorotelomer-based acrylate polymer was observed via structural changes by direct analysis (matrix-assisted laser desorption/ionization (MALDI-TOF) time-of-flight mass spectrometry) and via determination of the degradation products by indirect analysis. A unique fluorotelomer-based acrylate polymer was synthesized by aqueous dispersion following two commercial patents. The polymer was determined to be solely a homopolymer of 8:2 fluorotelomer acrylate containing hydrogen and hexadecylthiol end groups and has primarily between two and 16 fluorotelomer appendages. The estimated half-lives ranged from eight to 111 years based on the 8:2 FTOH equivalent and summation of all intermediates and degradation products. Incubation of the fluorotelomer-based acrylate polymer results in the accumulation of PFHxA, PFHpA, and PFOA concurrently with the reduction of 8:2 FTCA and 8:2 FTUCA. PFOA was the dominant product, constituting 57, 70, and 80 % in all microcosm compartments in fluorotelomer-based acrylate polymer /soil, fluorotelomer-based acrylate polymer /plant, and fluorotelomer-based acrylate polymer /plant /biosolids, respectively.

Hydrolytic half-lives of 8:2 fluorotelomer acrylate polymer segments was estimated using SPARC software program (Rayne and Forest, 2010). The estimated half-lives were 170-270 years in marine systems (15 °C and pH 8.1) and < 1 year under landfill conditions (40-50 °C and pH 4-9). Under some saturated landfill conditions abiotic hydrolytic degradation of fluorotelomer acrylates could occur resulting in significant fluxes of FTOHs and their degradation products (e.g. PFCAs) into ground water and surface water.

Waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment was investigated in a comprehensive laboratory-scale by Taylor et al. (Taylor et al., 2014). The fluorotelomer composition of the polymer was not further described. Experiments were performed with a gas-phase residence time of two seconds at a mean gas temperature of 1000 °C. No detectable levels of PFOA were produced from the combustion of the fluorotelomer-based polymer composites. Hence, the authors concluded that waste incineration of these polymers is not expected to be a source of PFOA in the environment.

Conclusion: Based on the available data it can be expected that side-chain fluorinated polymers will be transformed via n:2 FTOH into corresponding PFCAs.

Other potential precursors

Other potential PFHxA precursors and UVCBs cannot in general be classified as classes of substances leading to release of PFHxA. However, substances containing $F(CF_2)_n(CH_2)_2$-groups will most probably result in release of n:2 FTOHs in the environment. Thus, using the weight of evidence approach they can be considered as a class of substances leading to release of PFHxA.

B.4.1.2.3 Prediction of biodegradation pathways of PFHxA-related substances

ECHA analysed potential PFCA-related substances (see chapters B.4.1.1.1 and B.4.1.1.2) with CATALOGIC to generate biotransformation pathways (European Chemicals Agency, 2018). Furthermore, ECHA compared in this project the degradability of the substances to investigate whether degradation mechanisms are independent from the chain length of the perfluorinated tail.

For the creation of degradation maps of potential PFCA-related substances CATALOGIC v.5.12.1 CATALOGIC 301C (v10.14) was used. Most of the substances were fully within the applicability domain or had only a small percentage of unknown fragments. Only for fluorotelomer iodide, incorrect fragments were identified, and the prediction may therefore not be reliable. Polyfluorinated silanes and perfluoroalkyl phosphinic acids were considered outside of the applicability domain after assessing the type of unknown fragments. The fluorotelomer citrate triester was above the molecular weight limit.

Predicted biodegradation of PFCA-related substances to corresponding PFCAs were in agreement with data from literature listed in chapters B.4.1.1.1 and B4.1.1.2 (exception fluorotelomer thioether amido sulfonate). All structures with n:2 elements (exception fluorotelomer thioether amido sulfonate) were predicted to be transformed via FTOH to PFCAs.

Furthermore, the length of the perfluorinated chain did not impact the biotransformation mechanism. The biodegradation pathways for the PFCA-related substances, which differ only in the chain length of the perfluorinated part, were similar.

In this project ECHA also screened potential precursor substances of PFHxA (European Chemicals Agency, 2018b). In a pre-processing step, all compounds with the substructure $CF_3(CF_2)_2$ were selected via the query tool in the QSAR Toolbox v4.1. Additionally, structures from a screening exercise (PFASs which are registered under REACH or being a constituent or impurity of a registered substance) were added to the list. Three profilers were created in QSAR Toolbox to identify the target structures within all transformation products (transformation via hydrolysis and biodegradation) of the pre-selected compounds. From 987 structures, 73 were identified as potential precursors for PFHxA (for more details see Appendix B.4.1).

B.4.1.2.4 Conclusion on degradation of PFHxA-related substances

In conclusion, all the presented PFHxA-related substances are degraded to PFHxA by abiotic and/or biotic processes in the environment. For those substances where no degradation studies are available it can be assumed that based on the chemical similarity (supported by modelling evidence) the substances will most probably be degraded in a similar way. Thus, based on the weight of evidence approach, PFHxA will most probably be released in the environment. Hence, these substances need to be considered as important sources of PFHxA in the environment.

B.4.2 Environmental distribution

B.4.2.1 Adsorption/desorption

For PFHxA no results from studies following one of the testguidelines commonly used under the REACH Regulation are known at the moment. Adsorption was tested in different laboratory or semi-natural set-ups.

Vierke (2014) investigated transit of PFHxA and other PFASs in a column (surface areas 1 m^2, length 1 m) under environmental conditions. The column was embedded in a natural slow sand filter basin and fed by the surrounding surface water. As it is supposed to represent river bank filtration water was saturated. The water, which was checked daily, was pumped through the sediment at a filter velocity of 1.1 m d^{-1}. The column was filled with coarse-grained medium sand, followed by 30 cm gravel. The sand had a content of 0.02 % nitrogen N, 0.07 % organic carbon OC, 0.3 % carbonate C and a C/N-ratio of 16.1. PFHxA and other PFASs were spiked as one initial pulse in the supernatant of the column. Concentration of PFHxA was determined in samples from the supernatant, but also in depths of 40 cm and 80 cm in the column over a period of two weeks. The pH value of the water samples ranged from 7.4 to 7.9. The test substances were mixed with a tracer (here 25 % sodium chloride (NaCl) solution) to quantify the sorption process for every analyte. The sorption R was calculated for every analyte with

$$R = t_{50(analyte)} / t_{50(tracer)},$$

with t_{50} (min) being the time at which half of the detected quantity of the tracer or analyte has passed the respective sampling point. The sediment-dissolved partition coefficient (Kd) takes sediment characteristics into account, acknowledging that partitioning in the sediment column is not expected to be at equilibrium. The Kd was calculated with equation

$$Kd = \frac{ne}{\rho B} \cdot (R-1),$$

where ρB (in g cm^{-3}) denotes the density of the sediment and ne the effective porosity (dimensionless), which was calculated as ratio of the linear flow velocity (va, in m d^{-1}) and the filter velocity (vf, in m d^{-1}). To describe the relation between partition coefficients and OC content of the sediment OC normalised partition coefficients (K_{OC}) were calculated.

The equation used for this purpose was

$$K_{OC} = Kd \cdot \frac{100}{f_{OC}},$$

with f_{OC} being the fraction of OC in the sediment. The distribution coefficient calculated for PFHxA based on the leaching was log K_d = -0.18/0.46 (in 40 cm / 80 cm) and log K_{OC} = 3.0/3.6 (in 40 cm/80 cm) for PFHxA. Furthermore, leaching of PFHxA through the column was faster than for long-chain PFCAs.

Gellrich et al. (Gellrich et al., 2012) also performed a column study. The columns were 60 cm long and 5 cm in diameter filled with loamy sand (LUFA standard soil no. 2.2; soil parameters: OC concentration 2.16 %, 13.9 %, particles < 0.02 mm, pH-value 5.4, cation

exchange capacity 10 meq/100g). No distribution coefficient was calculated. But the results confirm the results of Vierke et al. when comparing the breakthrough of PFHxA to long-chain PFCAs: Leaching of PFHxA was always faster compared to longer-chain PFCAs indicating less sorption. Furthermore, long-chain PFASs can displace shorter PFASs from their binding sites in the soil.

For PFHxA, Guelfo and Higgins evaluated for the adsorption/desorption coefficient an average value of log K_{OC} = 1.31 (Guelfo and Higgins, 2013). In this study the adsorption behaviour of various PFAAs in three different soils which were loamy sand (OC content 1.7 %, pH 6.1), loam (OC content 4.5 %, pH 7.8), sandy clay loam (OC content 0.8 %, pH 5.2) were investigated. All soils were dry sieved (2 mm) prior use.

This assessment is supported by the work of Sepulvado et al. (2011) , who investigated the fate of perfluorochemicals in soil. They investigated the presence of various PFASs in sewage sludge of several municipal sewage treatment plants together with occurrence of these PFASs in soils on which the sewage sludge was applied on for agricultural purposes over several years. The investigated soil types were silty clay loam (OC content 4.1 %), fine sand (OC content 1.1 %) and silt loam (OC content 4.7 %). Sepulvado et al. investigated in a first stage the presence of PFASs in the samples, followed by desorption experiments over 14 days to determine the time necessary for the soil-water mixtures to reach equilibrium. The resulting data enabled them to calculate the desorption-based K_{OC} values. The equation used was

$$K_{des} = \frac{Cs}{Cw} = \frac{m_s^0 - m_V - m_W}{m_W} \cdot \frac{V_W}{M_{soil}}$$

where C_S is the concentration of the analyte in the solid phase, C_W is the concentration of analyte in the aqueous phase, m_s^0 is the analyte in the solid phase before desorption, m_V is the mass of analyte lost to the desorption reactor vial, m_W is the mass of PFASs in the aqueous phase at equilibrium, V_W is the volume of the aqueous phase, and M_{soil} is the mass of soil in the reactor. Resulting K_{des} values were then relevant to organic carbon normalized to calculate K_{OC} by

$$K_{OC} = \frac{K_{des}}{f_{OC}}$$

For PFHxA they found the log K_{OC} in the range 1.63 – 2.35.

Zhang et al. (2013a) showed that PFHxA adsorbs to a lower amount to sewage sludge compared to longer-chain PFASs (average distribution coefficient Kd PFHxA 14.8, PFOA 32.4).

Research by Ahrens et al. (2010a) showed that the log K_{OC} of PFCAs increases with the length of the carbon chain (C_8-PFCA: log K_{OC} = 1.09, C_{11}-PFCA: log K_{OC} = 4.8). This assessment is supported by the work of Higgins and Luthy. They also determined an increasing adsorption/desorption coefficient from C_8-PFCA (log K_{OC} = 2.06) to C_{11}-PFCA (log K_{OC} = 3.3) (Higgins and Luthy, 2006). For a more detailed overview please see the read-across information in Appendix A.1 of this document.

Li et al (Li et al., 2011) investigated perfluorinated compounds in the Haihe River and Dagu Drainage Canal in Tianjin, China. They found that PFHxA has a partition coefficient log Kd (sediment and overlapping dissolved phase) in the range of log Kd = 1.4 – 3.1.

Campos Pereira et al. (2018) investigated the effect of cation composition and pH on the sorption of 14 PFASs to an organic soil horizon. For this study a mono layer soil sample with pH 4.8, containing 45 % C, 1.3 % N and 3.4 % ash content on a dry weight basis was used. The sample was sieved < 2mm prior to homogenization, and then stored at 5 °C in its field-moist state with 69 % water content until further use. The sorption was investigated regarding dependence from pH and added concentrations of aluminium (Al^{3+}), calcium (Ca^{2+}) and sodium (Na^{+}) ions. It was found that PFCAs adsorb less strongly than PFAS. For PFHxA the averaged adsorption coefficient was approx. log K_{OC} = 1.3 from all values for the different pH-values and cations added.

In summary the log K_{OC} values for PFHxA reported in the literature range from 1.3 to 3.6. Because no standardised test guideline was followed, the matrices used for measuring the adsorption behaviour differ between the cited studies. Depending on the used matrix there was a varying content of potential adsorption surfaces available to PFHxA because matrices such as sewage sludge and soil differ in compositon. They vary in parameters like water content, organic matter or ratio of clay minerals available. Therefore, it has to be kept in mind that adsorption does not only relate to the adsorption on organic matter, but also other binding mechanisms available need to be considered. This was shown by the study of Li et al. (2011).

The technical guidance documents of REACH define a range of log K_{OC} = 3.0 to 4.0 as threshold when a substance can be considered to have high potential for adsorption. In conclusion the available studies show that – compared to longer-chain PFCAs - PFHxA has a lower potential to be adsorbed on organic matter such as sewage sludge or on anorganic constituents that can be found in soil. This information indicates that PFHxA might be distributed more easily within and between the compartments of the environment compared to longer-chain PFCAs and therefore can be evaluated as mobile in the environment.

The environmental distribution of PFHxA especially with respect to a potential for long-range transport and for contamination of drinking water is further evaluated.

B.4.2.2 Volatilisation

Distribution processes are one of the reasons for removal of substances from a certain environmental compartment. Volatilisation describes the removal from the water phase to the overlaying air compartment and can therefore act as a source for emissions to the atmosphere. Depending on the substance properties and the resistance against direct and indirect degradation processes the atmospheric washout and (re-)volatilisation act as a motor for long range transport in air.

The Henry's Law constant describes the tendency of a substance to volatilise from water. It can be calculated by the following equation:

$HENRY = VP \cdot MOLW / SOL$[5]

Whereas HENRY is the substance specific Henry's Law constant, VP is its vapour pressure, MOLW is its molecular weight and SOL is its water solubility.

Using the information for physical chemical properties from section B.1.2 (estimated VP = 263.93 Pa; measured SOL = 15.7 g/L) the Henry's Law constant of PFHxA is 5.279 Pa · m³/mol.

For the structurally related substance PFOA the Henry's Law constant reads 0.183 Pa ·m³/mol when using the equation above together with MOLW = 414.07 g/mol, VP = 4.2 Pa and SOL = 9.5 g/L from the SVHC support document on PFOA (ECHA, 2013b).

Compared to this value the siloxanes octamethylcyclotetrasiloxane (D4, CAS-No. 556-67-2, EC-No. 208-136-7) and decamethylcyclopentasiloxane (D5, CAS-No. 541-02-6, EC-No. 208-764-9) show a dramatically higher tendency for volatilisation. Whereas the Henry's Law constant for D4 siloxanes was determined to be $1.21 \cdot 10^6$ Pa·m³/mol the value reads $3.34 \cdot 10^6$ Pa·m³/mol for D5 siloxane (UK HSE, 2015).

This is an indication that PFHxA has a low to moderate tendency to volatilize from water when compared to the threshold for volatile substances (HENRY > 250 Pa·m³/mol) from REACH Guidance R.16 (ECHA, 2016a). This shows that the aqueous environmental compartments are more relevant for PFHxA compared to the atmosphere. But it does not lead to the conclusion that volatilisation is unlikely.

As already indicated in the first paragraph of this section, (re-)volatilisation acts as a motor for long range transport. Because PFHxA has a photolytic degradation half-life of 20.57 days in the atmosphere the low to moderate volatility adds to the weight-of-evidence that PFHxA has the potential to undergo long-range transport via the atmosphere. Nevertheless, the majority of PFHxA will remain in the water phase. Long-range transport via this route therefore is also likely because the substance will not be subject to biotic or abiotic degradation processes (please see section B.4.1).

B.4.2.3 Distribution modelling

Distribution modelling covers several aspects of distribution of chemicals between different compartments. This covers both, natural and technical environments such as sewage treatment plants.

Waste water might be treated within an industrial on-site sewage treatment plant and/or municipal sewage treatment plant in the follow-up before it is released into the environment. It can be assumed that municipal sewage treatment plants contain various

[5] Equation R.16-4; REACH technical guidance document R.16: Environmental Exposure Assessment (ECHA, 2016a)

species of microorganisms that are normally not adapted to chemicals which are used within an industrial setting.

Different methods are available to evaluate the distribution of a substance within a municipal sewage treatment plant. This can be a simulation test in a laboratory with a downscaled sewage treatment plant but using mathematical models is more common. One of the models which is commonly used is the Simple Treat model (here Simple Treat v3.0 (debugged version), ©Dutch National Institute for Public Health and the Environment (RIVM), 1997). The model itself only provides values for the distribution and degradation of the substance in relation to the total amount contained in the influent waste water, it does not use influent concentrations nor provides concentrations in specific media like effluent water or sewage sludge.

A measured log K_{OC} = 3.0 (Vierke, 2014) was chosen for further distribution modelling as this value represents the upper range of the measured K_{OC} values and therefore shows adequate conservatism for rentention capacity in a sewage treatment plant. Using the physical-chemical properties water solubility and vapor pressure for PFHxA from section B.1.2 and the conclusion from section B.4.1 that PFHxA is "not readily biodegradable" the Simple Treat model provides the following distribution pattern:

Table 11: Modelling results for compartmental distribution pattern of PFHxA in municipal sewage treatment plants.

Summary of distribution pattern:	
Air	7.8 %
Water	80.9 %
Primary sludge	8.4 %
Surplus sludge	2.9 %
Degraded	0 %
Total	100 %

From this modelling results it becomes obvious that any PFHxA contained in the influent of municipal sewage treatment plants (or being a stable degradation product from the waste water treatment process) will be predominantly released to receiving waters. The sewage treatment plants acts as a point source for emissions to the aquatic environment. This is supported by data from environmental monitoring where PFHxA can be found in effluents of wastewater treatment plants (see section B.4.2.4.1 Occurrence of PFHxA in effluents from wastewater treatment plants and landfills and occurrence in receiving waters).

About eight percent might be emitted to air. Therefore, sewage treatment plants may act as a source for releases of PFHxA to air in case PFHxA contained in the influent of municipal

sewage treatment plants (or being a stable degradation product from the waste water treatment process). The emissions will be distributed in the environment leading to indirect exposure of soil and the aquatic compartments, even on a continental or global level (please see section on long range transport potential).

As evaluated in section "B.4.2.1 Adsorption/desorption" the substance shows a moderate tendency to adsorb to sewage sludge. The model predicts that about 11 percent of PFHxA in the influent will adsorb on sewage sludge. Just because application of sludge from municipal sewage treatment plants for agricultural purposes still is common practise in several European countries, PFHxA will be transferred to the terrestrial compartment. Sludge application therefore is one pathway for indirect exposure of soil and groundwater.

B.4.2.4 Measured levels in environmental compartments Field data

All monitoring studies summarized below and in Appendix B.4.2 have not only detected PFHxA but also its longer and shorter chained PFCA homologues as well as PFSAs and in some cases precursor compounds. A review on monitoring studies summarised that PFASs were ubiquitously found in the aqueous environment and that about 40 individual PFASs were detected (Ahrens, 2011).

B.4.2.4.1 Occurrence of PFHxA in effluents from wastewater treatment plants and landfills and occurrence in receiving waters

PFHxA is found by various studies in effluent and sludge of waste water treatment plants (WWTPs) and landfill leachates. Some of the studies (Ahrens et al., 2009b; Loi et al., 2013; Nguyen et al., 2019) also looked for pre-cursors in influent, effluent and sludge of WWTPs. Though PFHxA was not detectable in influent and effluent and sludge in the analysis of (Loi et al., 2013) diPAPs could be quantified. As there is no industrial source in this area (Hong Kong), this result shows that pre-cursor containing consumer products are a source for PFHxA. Likewise, the study by Nguyen detected higher concentrations of the precursor 6:2 FTS than PFHxA in two australien WWTPs. Only one study investigated influents over several years (Nguyen et al., 2019). Here daily influent samples were collected over one week at different seasons from 2014 to 2017. In this study for one of the two investigated WWTPs a significant positive trend for PFHxA was observed indicating a shift to short chained alternatives. Concentrations of PFHxA are lower in sludge than in effluent water. Concentrations of PFHxA in WWTP effluents range between < 0.25 to 57 ng/L with the hightest measuered value for WWTP at the River Elbe. Efluents were measured across Europe (e.g. Germany, Austria and Norway) aswell as in Nigeria, Australia and Hong Kong. Concentration found in sludge range between <0.0105 and 0.2458 ng/g d.w. Findings in landfill leachates are considerably higher ranging from < 0.37 ng/L to 4256 ng/L. All data compiled in Table 37 of Appendix B.4.2 are published in peer reviewed papers. The papers include a detailed description of the sample preparation, the analytical method used and analytical quality control and therefore are regarded as reliable. The table provides data from examples of currently available studies. In regard of its anticipated short history PFHxA has not been covered by monitoring studies as long as e.g. PFOA or PFOS.

B.4.2.4.2 Occurrence of PFHxA in surface water and oceans

PFHxA has been detected in several surface waters as well as oceans (see Table 38 in Appendix B.4.2). Concentrations in surface water is genenerally higher than in oceans. Nevertheless, the picture is relatively heterogeneous for surface water with concentrations from below the limit of quantification or detection up to 77 ng/L at different sites in the River Rhine and 3040 ng/L at different sites in the Moehne River and 1248 ng/lL in surface sample at different sites in the Ruhr area for instance (Skutlarek et al., 2006). This indicates a relatively high pollution with PFHxA. Concentration of PFHxA in Norwegian and Finnish rivers ranged between 0.1 – 7.97 ng/L ((Norwegian Institute for Water Research (NIVA), 2017c); unpublished data, available in database https://wwwp2.ymparisto.fi/scripts/kirjaudu.asp, 2018). In Guadalquivir and Ebro rivers (Spain) concentrations range between 9.6 – 31.4 ng/L. At the Ai River around a fluoropolymer plant within a 5 km radius of the plant in Osaka (Japan) 26.2 – 1130 ng/L PFHxA was measured. These results are comparable to the findings in the samples from the Ruhr area. Levels of PFOA decreased greatly, whereas those of PFHxA increased at the Ai river indicating a shift from longer chained PFASs to shorter chained PFASs. Samples were taken from 2003-2015 (Shiwaku et al., 2016). In comparison 40 river samples across the Hyogo prefecture, Japan showed concentrations from < 0.5 - 6.9 ng/L whereas in the same study 38 seawater samples across the Hyogo prefecture had concentrations ranging from 1.5 – 510 ng/L and therefore show higher concentrations (Takemine et al., 2014). Nevertheless, concentration in surface water is genenerally higher than in oceans.

Several samples taken during crusises into the Northern Atalantic, Canadian Arctic Ocean and Souther Atlantic Ocean show concentrations of PFHxA from < 0.0024 to 0.120 ng/L ((Benskin et al., 2012b); (Ahrens et al., 2010b); (Zhao et al., 2012)). Higher concentrations were found in the German Bighte near human activities with concentrations ranging between 0.47 – 9.56 ng/L (Ahrens et al., 2009a). Together with findings also in the deep sea at Cap de Creus Canyon (north-western Mediterranean Sea) in sedimentary particles with concentrations of 0.89 to 4.47 ng/g (depth of 300 m) and 4.57 to 10.66 ng/g (depth of 1000 m) these data show a wide spread occurrence of PFHxA even in areas where human activity is expected to be low.

B.4.2.4.3 Occurrence of PFHxA in drinking water resources and drinking water

Several studies report findings of PFHxA in groundwater and drinking water (please see Table 38 and Table 39 in Appendix B.4.2 with findings in surface and groundwater). All data compiled are published in peer reviewed papers. The papers include a detailed description of the sample preparation, the analytical method used and analytical quality control and therefore are regarded as reliable. Drinking water is mainly obtained from groundwater as well as from surface water.

The study of Gellrich et al. (2012) shows higher concentrations and frequency of detection (FOD) for PFOA in surface water than the short-chain PFASs such as PFHxA and Perfluorobutanoic acid (PFBA). In groundwater, however, this study did not detect PFOA unlike the short-chain PFASs indicating a higher mobility of the short-chain PFASs (Gellrich et al., 2012). However, as monitoring data not only reflect the intrinsic properties of a substance but depend on its tonnage, uses and emmissions the results are not always this clear.

Having in mind the specific properties of PFHxA it is assumed that the substance will be able to pass natural barriers in the environment and further distribute from surface water via bank filtration into sources of drinking water respectively from sewage sludge applied on agricultural soil into ground water used for drinking water purposes.

The sources of raw water used for drinking water production differ between the Member States of the EU. In average about 50 percent of the water for drinking water production is taken from groundwater, whereas the amount from surface water is about 36 percent (European Commission, 2016). Bank filtration is used to a varying degree in several Member States. According to the European Commission report from 2016 in Hungary about 40 percent of the raw water is obtained from bank filtration whereas in the majority of the Member States no use of bank filtration was reported.

In Germany about eight percent of the raw water is obtained by bank filtration. Additionally, 13 percent of the raw water is taken directly from surface waters like rivers or basins whereas about 60 percent is pumped ground water (Statistisches Bundesamt, 2015). The use of surface water as drinking water source may be in some regions also significantly higher. E.g., the City of Helsinki, Finland, acquires practically its complete drinking water from lake water[6].

PFHxA is also found in drinking water or tap water in the low ng/L range between 0.31 and 6.4 ng/L. The reported percentages of concentrations above the limit of detection or quantification range for instance between 6.3 % in Germany outside Ruhr area and in the Ruhr area to 66.6 % in samples from 26 waterworks along the Ruhr River (Skutlarek et al., 2006). The highest reported percentage was reported for tap water samples from six European Countries (Sweden, Italy, Belgium, Netherlands, Norway and Germany). PFHxA was found in concentrations between < 0.38 – 5.15 ng/L in 86 % of the samples (Ullah et al., 2011). Austria reported drinking water /ground water concentrations of PFHxA up to 4.7 ng/L with a detection rate of 32.4 % (n = 37, limit of detection = 1 ng/L, sampled in 2018)

[6] https://www.hsy.fi/en/residents/water/where-does-your-drinking-water-come-from/Pages/default.aspx (last access: 13.12.2019).

(personal communication). Concentrations of PFHxA in tap water range between 0.31 and 6.4 ng/L and are below the German guide value for drinking water (Trinkwasserleitwert) of 6 µg/L. However, in the light of the persistence of PFHxA and the difficulty to remove PFHxA from water, the concentration of PFHxA will increase if emissions to the environment – also from degradation of precursors – continue.

Concentrations in groundwater are below the limit of quantification up to 95 ng/L (von der Trenck et al., 2018). In observation wells downstream of potential PFAA sources in the Nethelands in a groundwater recharge area where sources are present (a former landfill, a military base and a small commercial /industrial area) concentrations ranged between 0.7 - 570 ng/L. In five pumping wells with a travel distance > 25 years approximately (based on hydrological modelling and tracers) concentrations ranged between 0.22 – 0.8 ng/L (Eschauzier et al., 2013). In comparison groundwater from an unlined firefighter training area at Ellsworth U.S. Air Force Base (AFFF used between 1970 and 1990) was especially highly contaminated with concentrations ranging between < 100 – 320 000 ng/L (Houtz et al., 2013). Well water of two wells near a fluoropolymer plant in Osaka, Japan had concentrations of PFHxA ranging between 64.3 - 220 and 110 – 970 ng/L (Shiwaku et al., 2016).

It has to be considered that not all of the groundwater dwells used for sampling in these studies are used for drinking water production. They might also be used for industrial or agricultural applications or even just for sampling (please see Appendix B 4.2. Table 39).

B.4.2.4.4 Occurrence in soil and sediment

In addition to the above given data on PFHxA in surface water, groundwater and drinking water, PFHxA is also found in soil and sediment. All data compiled are published in peer reviewed papers or reports. The papers include a detailed description of the sample preparation, the analytical method used and analytical quality control and therefore are regarded as reliable. Most reported findings of PFHxA in soil are from contaminated sites either former firefighter training area or accidential contamination. In soil (0.6 m below surface; n = 16) and aquifer solids (5 - 6 m below surface; n = 10) from an unlined firefighter training area at Ellsworth U.S. Air Force Base (AFFF used between 1970 and 1990) < 0.8 – 2 000 µg/kg and 16 – 210 µg/kg PFHxA were detected respectively (Houtz et al., 2013). Another study which investigated the same area reported a concentration range between < 0.05 – 2 761 µg/kg in soil and 0.445 – 297 µg/kg in aquifer solids (McGuire et al., 2014). With 0.18 – 18.5 µg/kg based on dryweight considerably lower concentrations were detected in soil from a fire fighting training ground at Flesland airport, Norway (Klima- og forurensningsdirektoratet (KLIF), 2010). In comparison for soil of five stations in Oslo, Norway 0.00043 µg/kg based on dryweight are reported.

PFHxA is more water soluble than other PFASs and thus less likely to bind to sediment (Higgins and Luthy, 2006) and might be present mostly in pore water, rather than bound to the particles of the sediment (Ahrens et al., 2009c; Zhao et al., 2012). Therefore, in their study, (Codling et al., 2018) did not exclude pore water. This approach reflects the conditions in the sediment water interphase and thus the compounds that benthic organisms will be exposed to and might enter the food chain after contamination. In this study in sediment from Lake Erie with layers in the core corresponding to 1959 to 2013, concentrations of both PFOS and

PFHxA increased from earlier to more recently deposited sediments. More details are given in Table 41 in Appendix B.4.2.

B.4.2.4.5 Case example for agricultural soil and drinking water contamination with PFHxA

There are several examples of environmental contamination from the intentional (e.g. use of fire fighthing foam) or unintentional (e.g. use of contaminated soil improver) release of per- and polyfluoroalkyl substances like PFOA and PFHxA from all over Europe and also worldwide. One of these examples is from Rastatt, Germany. Concentrations of PFHxA at this contaminated site range between 3.1 to 32.3 µg/kg soil. The situation and problems in Rastatt have been summarised by Brendel et al. (2018). PFHxA is one reperesentative of short-chain PFASs refered to in the following text quoted from Brendel et al. (2018):

"In the surroundings of Rastatt (Baden-Wuerttemberg, Germany), 480 hectares of former arable land are contaminated with short-chain PFAAs and precursors. The pollution was detected in 2013 and has probably been caused by the longstanding application of compost mixed with sludge from paper production, contaminated with various precursors. Over time, the precursors contained in the soil degraded to short-chain PFAAs and were enriched in plants. Local authorities derived thresholds for short-chain PFAAs in food (in the µg/kg range) [72], based on guidance values for drinking water [73]. Pre-harvest monitoring showed that the concentration of short-chain PFAAs in some crops exceeded these thresholds, preventing the use as food. Crops enriching high amounts of short-chain PFASs are recommended not to be cultivated for consumption on these contaminated fields (e.g.strawberries as well as asparagus and other vegetables). Despite the recommendations for cultivation, threshold values are in parts exceeded to date. This might be due to a strong influence of insufficiently predictable abiotic factors, such as organic carbon content, on the enrichment of short-chain PFASs in plants [74]. Over time, the very mobile short-chain PFASs and precursors in the soil also wash out into the groundwater. Irrigating crops with contaminated water are causing further emissions to soil and uptake into plants. Two groundwater wells for drinking water production had to be closed [72]. For several years, the dimension of the contamination and the problems arising with the contamination of short-chain PFASs has not been recognised. Estimations addressing all adverse environmental effects and socio-economic costs resulting from the contamination are not available, but according to information given by the water work solely the cost for water treatment with charcoal filters amounts to several million Euros. Until now, no practicable solution for removing the short-chain PFASs from the soil or groundwater has been found. Effective solutions, such as a removal and replacement of the top soil or "pump and treat" methods, would be far too expensive. Furthermore, there are still high concentrations of short-chain PFASs and unknown precursors contained in the soil and there is no applicable solution for stopping them from reaching the groundwater. Research to find an appropriate solution is ongoing. This Rastatt case clearly shows that once emitted to the environment, short-chain PFAAs cause irreversible contaminations, and thus causing high socio-economic costs and threats to man and environment." (Brendel et al., 2018)

Within this quote, cited references are:

72. Citizen information Rastatt. http://www.landkreis-rastatt.de/,Lde/PFC.html. Accessed 15 Jan 2018

73. German Environment Agency (2017) Fortschreibung der vorläufigen Bewertung von per-und polyfluorierten Chemikalien (PFC) im Trinkwasser (in German). Bundesgesundheitsblatt 60:350–352

74. Blaine AC, Rich CD, Sedlacko EM, Hyland KC, Stushnoff C, Dickenson ER, Higgins CP (2014) Perfluoroalkyl acid uptake in lettuce (Lactuca sativa) and strawberry (Fragaria ananassa) irrigated with reclaimed water. Envi-ron Sci Technol 48:14361–14368

B.4.2.4.6 Indirect exposure of humans via the environment and food

Sources of human exposure include food, drinking water, house dust, air and dermal contact to consumer articles. Apart from the exposure via the environment, also articles are a significant source of PFHxA for direct human exposure. Relevant articles such as furniture, textile and leather care articles or cosmetics are placed on the market and used in all EU Member States. A considerable share of articles containing PFHxA or related substances is imported from outside the EU.

Occurrence data were collected in the food surveillance programmes of Germany, in particular in the national monitoring and the federal control plan.

The national monitoring is a measurement programme in which foods from the German market are systematically examined for the presence of unwanted substances. It is performed jointly by the Federal Government and the Federal States. The national monitoring consists of pre-planned samples and thus aims on providing a realistic picture of the situation on the market.

The federal control plan is a risk-oriented monitoring programme. It consists of a yearly plan aiming at monitoring the compliance inter alia with food regulation. Therefore, it also consists of samples which were drawn based on some suspicion and may distort a realistic picture of the market situation. In the present evaluation these samples were not removed as they do not interfere with the aim of demonstrating the presence of PFHxA in food. The same is true for the very little number of risk-oriented samples that do not belong to one of the mentioned programmes.

The used data were collected between 2005 and 2018 and submitted by the Federal Office of Consumer Protection and Food Safety (BVL). In total, they consist of 3116 samples which were analysed for the presence of PFHxA. Of these, 3001 (96.3 %) were below the limit of quantification (LOQ) and 2933 (94.1 %) below the limit of detection (LOD). In the statistical analysis, these left-censored data were treated in the following way: Samples below the level of detection were replaced by zero. Samples below the level of quantification but above the level of detection were set to the level of detection. This approach is called the "modified lower bound" and gives the lowest possible value based on the available information. It was chosen here to only present non-zero values for samples where any amount of PFHxA was detected. The median LOD and LOQ for the samples is the same, being 1 µg/kg with an interquartile range of 0.5 µg/kg (LOD) and 1 µg/kg (LOQ).

Table 12: Overview of the PFHxA occurrence data from German food monitoring programmes.

Group	N total	N > LOD	N > LOQ	Mean [µg/kg]	P50 [µg/kg]	P95 [µg/kg]	Max. [µg/kg]
cereals	19	9	8	2.05	0	9.80	9.80
fish and seafood	1 180	107	71	0.17	0	1.25	15.00
fruits	173	4	3	0.03	0	0	1.80
meat and meat products	851	37	17	0.05	0	0	3.40
milk	70	1	1	0.006	0	0	0.006
mushrooms	78	3	0	< 0.01	0	0	0.12
potatoes and potato products	144	15	14	0.15	0	1.42	1.93
vegetables	601	7	1	0.02	0	0	3.10

Table 12 summarizes the monitoring data. Foods were grouped to general groups because of the low number of detects – for all groups except "fish and seafood" the number of detects is below 100, and below 20 for all other except "meat and meat products". Also, for some samples more detailed information to further specify the food category was not available.

Still, the groups consist mainly of foods that are regularly consumed by the German population (e.g. the vegetable group consists mainly of tomatoes, cabbages, carrots, salad, onions, etc.). The main exception is the "meat and meat products" group, which contains a large amount of liver and /or game samples and the "fruits" group of which about 100 samples are taken from strawberries.

In all food groups there is at least one value above the level of detection. The data from the German monitoring programme thus supports the presence of PFHxA in food. The percentage of detects is not very high, but it cannot be finally concluded whether this is due to the analytical limits or whether PFHxA is not that widely distributed up to now. Several detects are already from 2005 to 2010 and a time trend could not be derived by the underlying data.

Data from literature

A first search for the terms "PFHxA" or "Perfluorohexanoic" and "Food" or "Dietary Exposure" was performed on PubMed, Scopus, SciFinder, Web of Science and Science direct and yielded in total 89[7] sources. Each of the sources was further filtered using the following criteria:

1. Does the source contain occurrence data for PFHxA in food? (Exclude if no, 60 excluded)
2. Were the foods bought on markets inside the EU? (Exclude if no, 14 excluded)
3. Are any reported values above the LOD? (Exclude if no, 5 excluded)

The first filter excludes references which are not relevant for PFHxA or dietary exposure. The second filter was applied, as a REACH restriction is only concerned with the European situation. The last filter was necessary because a large fraction of values is below the level of detection. Still, many sources opted to report upper bounded values (i.e. non-detects were

[7] For two sources the full text could not be obtained in time.

set on the level of detection). This would compromise the aim of demonstrating the presence of PFHxA because most of the reported values would not be actual detects but reported upper bound concentrations. The five papers excluded due to criterion three might be interpreted as a further indication of low prevalence of PFHxA in food up to now. After applying these filters, ten sources remained and were further analysed. One additional source (Herzke et al., 2013b), was identified from the references of these screened sources and added to the analysis.

In a second search the first requirement was relaxed to the search term "perfluoroalkyl*" to also identify sources which did not list perfluorohexanoic acid explicitly but still measured it. From that second search, one additional source (Rivière et al., 2014) was classified as relevant. This source is referred to as (ANSES, 2011) because the latter document provides more detailed information on the results, which are from the Second French Total Diet Study (TDS).

The resulting references are summarized in Table 23 with the exception of (EFSA, 2012), which will be summarized separately. Only values above the level of detection were used in the summaries for the same reasons as explained above. Not all studies presented their results in the same way. Some reported single values for each food item, some only mean values. Some reported the values already aggregated to food groups, some provided detailed information of the specific food items. The latter ones were also aggregated to appropriate food groups for the sake of brevity. As it is the aim of this section to demonstrate the presence of PFHxA in food, this was not seen as an obstacle; however, the values cannot necessarily be compared from one study to another.

The heterogeneity of the studies also impedes the comparison with the results from the national monitoring. The literature generally reports lower values which is likely in large parts caused by lower detection limits (e.g. (Vestergren et al., 2012b) reports an MDL of 2.4 ng/kg and (Herzke et al., 2013b) a MQL between 2 and 50 ng/kg depending on type of PFAS).

One report, (EFSA, 2012), was excluded from the table because the data presented were collected from the national monitoring programmes of the member states of the European Union as well as from the PERFOOD project (Herzke et al., 2013a; Klenow et al., 2013; Vestergren et al., 2012a; Vestergren et al., 2012b). The former has overlap with the already presented data from the German monitoring program, the latter with some of the results presented in Table 23. In general, EFSA also reports large numbers of non-detects across all considered food groups. They also report lower and upper bound mean values. In comparison with Table 23 the reported lower bound values are lower and the upper bound values higher which is consistent with the different treatment of non-detects in the data analysis.

In general, also the data from the literature thus support the presence of PFHxA in food.

B.4.2.5 Summary and discussion of environmental distribution

PFHxA will not degrade under environmentally relevant conditions. The rate of degradation is unlikely to be measurable within the time frame of standard screening or simulation tests. Data from LC-PFCAs (longchain-perfluoroalkyl carboxylic acid/ perflouroalkyl carboxylate) indicate that the tendency for adsorption increases with the length of the fluorinated carbon chain. Studies on adsorption behaviour of PFHxA show log K_{OC} values in the range of log K_{OC} = 1.3 to 3.6.

The data on the adsorption behaviour indicates that PFHxA is a substance with moderate tendency to adsorb on organic matter and desorption is likely to occur. Compared to substances like D4/D5-siloxanes the volatility of PFHxA from water is about six orders of magnitude lower. Once emitted to water PFHxA will predominantly remain in the water phase. Because of its higher water solubility compared to PFOA and LC-PFCAs PFHxA can be distributed more easily within aqueous phases. In conclusion PFHxA is mobile in the aquatic environment and capable to reach remote aquatic areas or groundwater which was already proven by monitoring studies.

Monitoring data and physicochemical properties show that PFHxA will preferentially distribute in the aquatic environment (Ahrens and Bundschuh, 2014), including ground water. Due to the low adsorption coefficient, PFHxA cannot efficiently be removed in conventional water treatment plants, resulting in direct emissions in the aquatic environment (Zhang et al., 2013a). The environmental distribution of PFHxA illustrates a high potential to reach drinking water resources. This has been supported by several studies reporting findings of PFHxA in for example tap water. PFHxA has also been monitored in food (see Table 12).

B.4.3 Data indicating potential for long-range transport

The physical-chemical properties of PFHxA together with the data on persistency and the calculated atmospheric half life of 20.57 days indicate that the substance is capable to be transported to remote areas. To substantiate this assumption, the long-range transport potential was modelled using the OECD tool for estimation of the Long Range Transport Potential (LRTP-Tool; ©OECD, 2009) which is a spreadsheet formation containing multimedia fate models.

Using the adsorption coefficient log K_{OW} = 2.3 and the air water partition coefficient log K_{AW} = -2.66[8] as input parameters, the tool provides information for the characteristic travel distance (CTD, indicating the distance from a point source at which the chemical's

[8] calculated from HENRY constant (please see section B.4.2.2 Volatilisation), using equation R.16-5 from REACH Guidance R.16

concentration has dropped to 38 % of its initial concentration) and overall environmental persistence (P_{ov}) of PFHxA resulting in a CTD = 9598 km and a P_{ov} = 347 days.

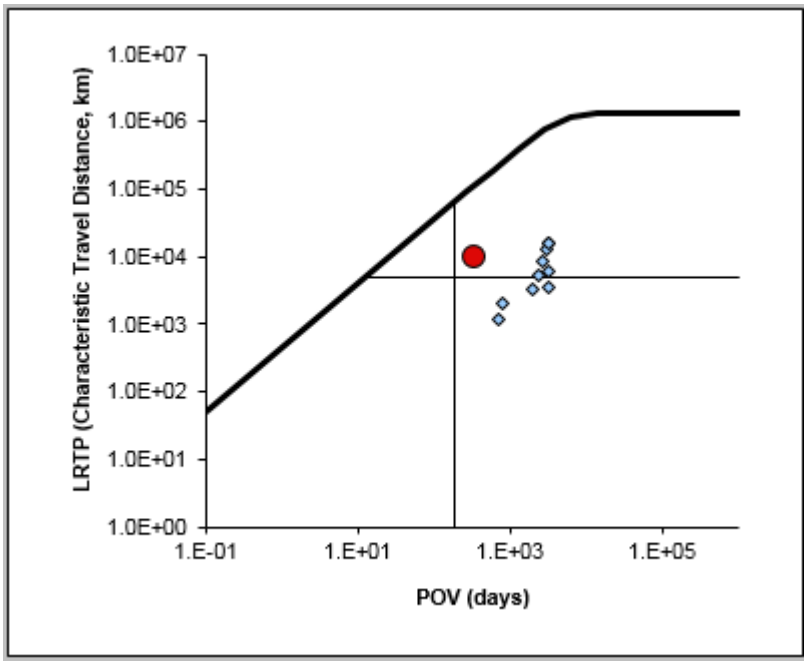


Figure 3: *Characteristic Travel Distance (CTD) and overall persistence (P_{ov}) of PFHxA and selected reference substances.*

Figure 3 shows the graphical output for the calculated CTD and P_{ov} for PFHxA (red dot) and seven chlorobenzenes which act as reference substances (blue squares). Substances with CTD and P_{ov} values of this magnitude are considered to show a high long-range transport potential.

Armitage et al. (Armitage et al., 2006) evaluated the oceanic long-range transport of perfluorooctanoate by using the GloboPOP model. The modelling provided a reasonable agreement to measured values in non-coastal areas where an impact from direct emissions can be assessed as negligible. This was especially true for areas in the north and the middle of the Atlantic Ocean, but also for regions in the northern polar zone. Armitage et al. concluded that long-range oceanic water transport is an important source for perfluorooctanoate that is found in the Arctic.

PFHxA has no known natural source. Nevertheless, different studies report findings of PFHxA also in remote regions which serve as evidence for long-range transport potential. Four examples are given in Table 42 in Appendix B.4.3. As shown in the literature (Kirchgeorg et al., 2013; Kirchgeorg et al., 2016), atmospheric decomposition is beside the transport via the water phase the major pathway of transport. Volatile precursors such as 6:2 fluorotelomer alcohol (6:2 FTOH) might contribute to a large amount to the long-range transport of PFHxA (Young and Mabury, 2010). PFHxA was also found in the air in remote regions such as the Norwegian Polar research station Zeppelin with a high detection frequency in 2013 but only detected in approximately 20 % of the samples in 2016 (Norwegian Institute for Air Research

(NILU), 2014; Norwegian Institute for Air Research (NILU), 2015; Norwegian Institute for Air Research (NILU), 2016; Norwegian Institute for Air Research (NILU), 2017b).

For comparison PFOA has been found in the Canadian Arctic in concentrations ranging from 0.0065 ng/L to 0.047 ng/L in the Canadian Arctic (Benskin et al., 2012b). In snow samples from the European Alps PFOA has been found in concentrations ranging from 0.2 - 0.6 ng/L (Kirchgeorg et al., 2013). Latest data from the Norwegian Zeppelin station ranged from 0.04 to 0.42 pg/m^3 (Norwegian Institute for Air Research (NILU), 2018a).

Even though the concentrations of PFHxA in remote areas are low they are a strong indicator for long range transport.

B.4.4 Bioaccumulation

In accordance with the numeric criterion as suggested in REACH Annex XIII (sections 1.3.2 and 3.2.2(a)) the potential for bioaccumulation is generally assessed by conducting a bioaccumulation test on fish. This approach, however, only addresses one compartment i.e. water and water breathing organisms i.e. fish. A comparative analysis of a homologues series of C7-C14 PFCAs and lipophilic organohalogens in an Arctic Marine Food Web by Kelly et al. (Kelly et al., 2009) shows an efficient respiratory elimination in water-respiring organisms due to high water throughput and high water solubility of PFCAs but very slow elimination and biomagnification in air-breathing animals of PFCAs. Acccordingly PFOA and PFHxS have been identified as PBT substances on the basis of their half-lives in humans (ECHA, 2013a; ECHA, 2017) and the C_9 and C_{10} PFCAs on the basis of biomagnification and trophic magnification in food webs including air-breathing homeotherms (ECHA, 2015b; ECHA, 2016b). Likewise, for PFHxA with its high water solubilty bioaccumulation in fish this may not be the most relevant endpoint to look at.

B.4.4.1 Bioaccumulation potential of PFHxA from laboratory and field studies

The biomagnification as well as the bioconcentration of short-chain PFAS in laboratory studies with fish is low. Martin et al. (Martin et al., 2003a; Martin et al., 2003b) conducted a bioconcentration and a biomagnification study with *Oncorhynchus mykiss*. Both studies investigated a homologous series of perfluoroalkyl carboxylates and sulfonates. Carboxylates and sulfonates with perfluoroalkyl chain lengths shorter than seven and six carbons, respectively, could not be detected in most tissues and were considered to have insignificant bioconcentration factors (BCFs). For detectable PFASs, carcass BCFs increased with increasing length of the perfluoroalkyl chain. Equivalenty the depuration rate constants in the dietary study decreased as the length of the fluorinated chain increased.

For the bioconcentration test juvenile rainbow trouts (*Oncorhynchus mykiss*) were exposed to a 1 000-fold dilution of the stock perfluorinated acids (PFAAs: C5 - C14) solution in a flow-through exposure design for 12 d, followed by 33 d of depuration in clean water. The water borne concentration in the bioconcentration study was 1.7 µg/L. Fish growth was monitored by weighing the total biomass. Three fish from the exposure tank and one from the control tank were sampled at each predetermined interval during the uptake phase of the experiment (4.5, 9, 18, 36, 72, 144, and 288 h). At 288 h, the remaining fish were transferred to new aquaria receiving clean water. During the depuration phase, three fish from the treatment

tank and one from the control tank were sampled at each time interval (4.5, 9, 18, 36, 72, 144, 288, 456, and 792 h). During the uptake phase, water samples were collected below the surface at 0.25, 4.5, 12, 18, 36, 72, 144, 197, 244, and 288 h. Water samples were also collected at 48 and 96 h of the depuration phase from both tanks to check for contamination. Sampled fish were anesthetized. The gut, consisting of esophagus, stomach, pyloric ceca, spleen, and intestines, was removed but not analyzed. The blood, liver, and carcass samples were analyzed separately for PFAAs at each sampling time to determine the kinetics of uptake and depuration. PFAAs were analysed by liquidchromatography–tandem mass spectrometry. PFAAs were not radioalabeled.

For the biomagnification study juvenile rainbow trouts (*Oncorhynchus mykiss*) for 34 days to PFCAs in the diet, followed by a 41 day depuration period were used. Though, the authors describe their results as bioaccumulation factor (BAF) the results of this study should rather be assigned as biomagnification factor (BMFs) as uptake only derived from the diet. During the uptake period, animals were daily fed with spiked food at a rate of 1.5 % food per body weight. Spiked food concentrations were 0.52 µg/g for PFHxA. Water samples collected before and after feeding revealed no traces of PFCAs in water. At six occasions during uptake period and during depuration period, fish were removed to determine the kinetics of uptake and depuration. The authors estimated the steady state to be reached after ten days. Carcass and liver concentrations were determined by using liquid chromatography-tandem mass spectrometry, and kinetic rates were calculated to determine bioaccumulation parameters. PFAAs were analysed by liquidchromatography–tandem mass spectrometry. PFAAs were not radioalabeled.

Both studies did not detect PFHxA in the investigated fish tissues and the biomagnification study concluded that the bioaccumulation potential of PFHxA was expected to be negligible, BAF < 0.1. The food borne concentration was 0.52 µg/g with uptake phases of twelve and 34 days respectively. No limits of detection in the studies are reported, otherwise the studies are regarded as reliable with a Klimisch code of 2.

Casal et al. (2017) reported bioaccumulation factors of 2.7 – 2.8 for oceanic plankton from the Indian Ocean for PFHxA. For comparison bioaccumulation factors ranged between 3.9 to 4.6 for PFOA and between 2.8 to 4.6 for PFOS. The BAF was determined from the concentration in plankton divided by the average seawater concentration.

B.4.4.2 PFHxA in biota and humans

Compared to some representatives of the long-chain PFAS there are very few monitoring data available for PFHxA in biota. All data compiled in Table 46 in Appendix B.4.5 are published in peer revieved papers. The papers include a detailed description of the sample preparation, the analytical method used and analytical quality control and therefore are regarded as reliable. Data in Table 46 in Appendix B.4.5 have either been published in peer reviewed papers or reports also containing of a detailed description of the sample preparation, the analytical method used and analytical quality control and therefore are regarded as reliable. The examined monitoring studies, with data from contaminated and uncontaminated sites, do not allow concluding on a possible bioconcentration or trophic magnification. In comparison with other long-chain PFASs such as PFOA, which is frequently found in biota and human serum, PFHxA concentrations in biota and human serum, urine and breast milk samples are more often reported below the limit of detection. In studies where PFHxA has been frequently

detected (> 50 %) in human serum the arithmetic mean of PFHxA is either 0.9 ng/mL using ND = LOD/2 or 1.4 ng/mL using ND = LOD (Frisbee et al., 2009). This study has been conducted in the framework of the C8 Health Project: a population study created to gather data that would allow class members to know their own PFOA levels and permit subsequent epidemiologic investigations. Serum samples were analyzed for ten PFASs. PFHxS, PFOA, PFOS and PFNA were detectable in almost all (> 97 %) samples. Li et al. (2017b) report a median concentration of 0.01 ng/mL PFHxA and a mean concentration of 0.07 ng/mL PFHxA in serum. In this study, eight perfluorinated alkyl substances and five thyroid hormones were determined in 202 human serum samples of the general population of Guangdong, Guangxi and Hainan provinces in southern China. PFHxA was found in all urine samples in Austrian adults aged 25-46 with a median creatinine adjusted concentration of 1.6 ng/L (Environment Agency Austria, unpublished data (publication in preparation)). PFHxA was also found in breast milk with a high frequency in South Korea with a median of 0.047µg/L (Kang et al., 2016).

It should be noted that there are obvious differences in the distribution patterns of PFCAs. For instance, the proportions of short-chain PFHxA shows large differences between serum (2 %) and the non-invasive samples (urine: 23 %; hair: 76 %) in a study conducted by Kim and co-Workers (Kim et al., 2019). Similar compositions of PFCAs and PFSAs were found in serum (PFCAs: 46 %; PFSAs: 54 %), while relatively higher proportions of PFCAs were observed in urine (97 %) and hair (71 %) in this study. In addition, the concentrations and frequency of detection (FOD) values of short-chain PFCAs were higher in urine and hair than in serum. PFHxA concentrations in human serum are often reported below the limit of detection however, in regard to the comparison of the results from blood, urine and hair samples, blood samples may not reflect well the exposure of humans to PFHxA.

PFHxA has been shown to accumulate in several human tissues (Perez et al., 2013). PFHxA was found in lung, brain, liver, kidney and bone. PFHxA represented the highest median PFAS-concentrations in brain and liver (brain: mean 180 ng/g and median 141 ng/g; liver: mean 115 ng/g and median 68.3 ng/g wet weight). The concentrations of 21 PFASs were analysed from 99 samples of autopsy tissues (brain, liver, lung, bone, and kidney) from 20 subjects which have been living in Catalonia, Spain. PFHxA showed the highest concentrations in the brain and liver. In brain, mean concentration of PFHxA was higher than all other PFAS and was detected in all the samples at concentrations ranging from 10.1 to 486 ng/g. In liver, PFHxA was detected in the samples at concentrations up to 353 ng/g. In general terms, the highest concentrations of PFASs were found in lung tissues (PFHxA mean: 50.1 ng/g and median 207 ng/g, ranging up to 559 ng/g). Mean concentrations of PFHxA in the bone and kidney were 36 and 6 ng/g. Results from this study support the conclusion that the substance is distributed to multiple organs and has a potential to accumulate in the human body.

19 PFASs were investigated in human milk collected in Stockholm (1972–2016) and Gothenburg (2007–2015), Sweden (Nyberg et al., 2018). A declining trend was observed for PFHxA.

Trend analysis of PFHxA in herring gull eggs from the North as well as the Baltic Sea show a negative trend from 1988 to 2017 (German Environmental Specimen Bank, unpublished data). However, there is a significant increasing trend for other short-chain PFAAs in the liver samples of cetacean species from 2002 to 2014 (Lam et al., 2016). For instance, the ratio of perfluorobutanesulfonic acid (PFBS) as an alternative to PFOS has significantly increased due

to restriction /voluntary withdrawal of the production and use of PFOS. The concentrations of PFHxA in biota may increase in future if PFHxA is used as an alternative for restricted PFAAs. Due to the extreme persistence of PFHxA, newly emitted PFHxA will add to what is already there, leading to a build up of the substance in the environment over time.

Findings of PFHxA in biota and human serum, urine and breastmilk are summarised in Table 47 to Table 51. In the examined studies PFHxA was detected in biota mainly in the low nanogram per gram range (< 0.04 - 2.22 ng/g ww). Solely, Llorca et al. (2012b) reported higher concentrations in fish and algae listed in the table in Tierra del Fuego. In this study the highest concentrations of PFHxA were monitored in penguin dung (17.3 - 237 ng/L) and guano (< LOQ - 2480 ng/L). PFHxA was also the predominant substance in algae and guano.

B.4.4.3 Half lives of PFHxA in humans and animals

Regarding the evaluation of the bioaccumulation potential, elimination half-lives have been proven to be of importance for long-chain PFASs. Elevated levels of PFOA in human blood and a half-life in humans of 2-4 years lead to the conclusion that PFOA is bioaccumulative (ECHA, 2013b).

In general, the reported half-lives for PFHxA in mammals are considerably lower when compared to PFOA. Half-lives of PFOA in mice, rats, pigs and monkeys are up to one order of magnitude higher compared to PFHxA, ranging from 0.08 days in female rat, 236 days in pig and several years in humans.

No threshold for elimination half-life could be derived by means of a benchmark evaluation based on empirical data with bioaccumulative reference substances. On basis of the considerably lower half-life reported for PFHxA of seven to 32 days in comparison to the half-lives of PFOA and PFHxS, it can be assumed that PFHxA may be less bioaccumulative due to a lower elimination half-life. However, the half-life in humans indicates that some accumulation in humans might take place as bioaccumulation is dependent on frequency of exposure and half-life. Thus, bioaccumulation potential in humans may not be directly deducible from toxicokinetic data on laboratory mammals.

For further details see chapter B.5.1 Toxicokinetics (absorption, metabolism, distribution and elimination) and Appendix B.5.1.

B.4.4.4 Protein binding of PFHxA

The affinity of PFAAs to proteins is chain-length dependent and increases up to a certain number of perflourinated carbons depending on the protein (Ng and Hungerbühler, 2014; Zhang et al., 2014; Zhang et al., 2013c). The relationship between structure (e.g. chain length) and affinity to proteins is complex and thus still a matter of research (Ng and Hungerbühler, 2014). Nevertheless, some toxicokinetic observations may be explained by certain protein bindings. The expression of organic anion transporters is gender as well as species specific. They function either as an aid for uptake or elimination and some are responsible for reabsorption from urine to blood. Binding to transporter proteins with a sex

and species dependent expression may explain observed significant differences in the half-lives between sexes and species. The activity of human reabsorption transporters activity was far more pronounced than for rats (Weaver et al., 2010; Yang et al., 2010) and may explain the significant differences in the half-lives of PFAAs in humans compared to laboratory rodents.

Bischel et al., 2011, investigated with equilibrium dialysis the binding of PFCAs to bovine serum albumin (BSA). More than 99 % of PFHxA bound to BSA and the protein water distribution coefficient log K_{PW} was 4.05 (Bischel et al., 2011). An increase in K_{PW} with increasing chain length was observed for PFCAs with four to six fluorinated carbons. For PFCAs with greater chain length than six fluorinated carbons, K_{PW} values generally decreased. The authors suggest that increased rigidity associated with long-chain PFCAs may contribute to the observed nonlinear relationship of K_{PW} with the fluorocarbon tail length. The comparison with PFOA shows that the fraction bound to BSA is is equally high with > 99 % and that the K_{PW} of PFHxA is higher than for PFOA.

In general, a high protein binding potential might lead to facilitated tissue distribution. This hypothesis is supported by the findings of Numata et al., 2014 who reported that PFHxA is effectively distributed to most organs in the body of pigs (see sectionB.4.4.3 Half lives of PFHxA in humans and animals). Nevertheless, the potential to bind to BSA may not fully explain the toxicokinetics. Transporter proteins as described above may also have an impact on toxicokinetics. Unlike the accumulation in adipose tissue, binding to proteins and accumulation in organs has a higher potential to cause adverse effects. Whereas the physiological role of adipose tissue is mainly energy storage, organs have specific functions. Accumulation of chemicals i.e. PFHxA may interfere with these functions. Apart from this, a study has shown that PFAAs binding to peroxisome proliferator-activated receptors. This plays a role in lipid metabolism, induces conformational changes of this receptor and may thus change the function of the protein (Zhang et al., 2014).

B.4.4.5 Summary and discussion of bioaccumulation

The biomagnification as well as the bioconcentration of short-chain PFAS in laboratory studies with fish is low. According to the BCF criteria outlined in REACH Annex XIII (sections 1.3.2 and 3.2.2(a)) the B criterion is not fulfilled. This approach, however, only addresses one compartment, i.e. water, and water breathing organisms, i.e. fish. Elimination half-lives have been proven to be of importance for long-chain PFASs such as PFOA. In general, the reported half-lives for PFHxA in mammals are considerably lower when compared to PFOA. Based on the considerably lower half-life reported for PFHxA in comparison to the half-lives of PFOA and PFHxS, it is concluded that PFHxA is less bioaccumulative. However, independent of the half-lives and regardless of the half-life in mammals the non-reversible environmental background concentrations lead to long-term continuous human exposure. Substances that have a low bioaccumulation potential could potentially reach similar levels in biota to substances that are known to bioaccumulate, provided that they are sufficiently persistent and mobile in the environment (Peter Fisk Associates Ltd, 2018). For example, calculations in the study show that a substance with a half-life of 365 days and a BCF of 800 L/kg may reach comparable concentrations in a system as a substance with a half-life of 60 days and a BCF of 5000 L/kg, if time allows for steady-state to be reached (Figure 3 in reference). Based on

their findings, the authors proposed screening criteria under the Stockholm Convention for substances that may be of concern in relation to their mobility.

PFHxA has a strong binding potential to proteins which may facilitate tissue distribution. Toxicokinetic studies show that PFHxA becomes well distributed within the organisms, mainly plasma, kidney and liver in rats and mice.

B.4.5 Enrichment in plants

As PFHxA has a good water solubility, high concentrations in the pore water are expected making it bioavailable for plants[9]. Several studies investigated the uptake of PFHxA and other PFASs from the surrounding environment into plants (see Table 13). These studies were conducted under strictly controlled laboratory conditions, under semi-natural conditions as well as under environmental conditions (field studies). Two studies of Felizeter ((Felizeter et al., 2012) and (Felizeter et al., 2014)) examined the uptake of PFAS by hydroponically grown lettuce, tomato, cabbage and zucchini plants. Especially in the edible parts and the roots the concentrations of PFHxA are considerably higher (ng/g) compared to the nutrient solution (ng/mL) with concentration factors between one and ten. Most of the PFHxA accumulates in leaves and fruits, which is attributed to the high water solubility and the resulting high potential for translocation. This is in line with (Krippner et al., 2014) reporting more than two times higher concentrations of PFHxA in maize shoots compared to maize roots. In another study with plants from biosolid-amended fields, PFHxA shows with a grass/soil accumulation factor of 3.8 the highest accumulation factor among all measured PFAS, indicating a high transfer potential from soil to grass (Yoo et al., 2011). Blaine et al. (2013) investigated the accumulation of PFHxA in lettuce and tomato grown on biosolid-amended soils and reported BAFs in lettuce up to 11.7 and in tomato up to 6.8. PFHxA does also accumulate in strawberry fruits (Blaine et al., 2014). A recent study by (Pi et al., 2017) reports uptake rates in submerged and free-floating aquatic macrophytes with whole-plant BCFs of 29.4 and 24.9 respectively.

Table 13: Uptake of PFHxA and other PFCAs in plants.

Method	**Plant**	**Regarded PFCAs**	**Results**	**Reference**
field study (biosolid amended soils)	wheat (*Triticum aestivum L.*) (roots, straws, husks, grains)	C4-12 PFCAs	root concentration factor (RCF) PFHxA = 3.28 $(ng/g_{root})/(ng/g_{soil})$ straw concentration factor (SCF) PFHxA = 1.24 $(ng/g_{straw})/(ng/g_{soil})$ transfer factor from roots to straws (TF_{r-s}) **PFHxA = 0.392 $(ng/g_{straw})/(ng/g_{root})$** grain concentration factor	(Wen et al., 2014)

[9] Please see REACH Guidance on Chemial Safety Assessment, Chapter R.7c: Endpoint Specific Guidance (2017)

Method	Plant	Regarded PFCAs	Results	Reference
			(GCF) PFHxA = 0.311 (ng/g_{grain})/(ng/g_{soil}) transfer factor from straws to grains (TF_{s-g}) **PFHxA = 0.253 (ng/g_{grain})/(ng/g_{straw})** all concentrations are measured and based on dry weight without normalisation for OC.	
climate chamber (100 µg/L of each individual PFCA per liter of nutrient solution at pH 5, pH 6 and pH 7) Analysis of plant material after 5 days of exposure.	maize (*Zea mays*)	C4-10 PFCAs	uptake rate by roots PFHxA = 0.35 µg/g root DW/d shoot:root ratios **PFHxA = 2.25** (transferred to shoot) all concentrations are measured and based on dry weight.	(Krippner et al., 2014)
pot experiment (soil was spiked with an aqueous solution of 0.25 mg individual PFCA/kg soil and 1.00 mg individual PFCA/kg soil). After 128 days straw and kernels were harvested.	maize (*Zea mays*)	C4-10 PFCAs	straw transfer factor (TF_{straw}): PFHxA = 3.19 (0.25 mg/kg treatment) and 2.82 (1.00 mg/kg treatment) kernel: Transfer factor ($TF_{kernels}$) **PFHxA = 0.123** (0.25 mg/kg treatment) **and 0.216** (1.00 mg/kg treatment) all concentrations are measured and based on dry weight.	(Krippner et al., 2015)
field study (biosolid amended fields)	grass (from biosolid-amended fields)	C6-14 PFCAs	grass /soil accumulation factors (GSAF): PFHxA (mean) = 3.8	(Yoo et al., 2011)
greenhouse – hydroponic system (PFCA-spiked nutrient solution with nominal concentration	lettuce (*Lactuca sativa*)	C4-14 PFCAs	root concentration factor (RCF): **PFHxA ≈ 1.2** (lowest RCF of all PFCAs) foliage to root concentration factor (FRCF): PFHxA ≈ 0.98	(Felizeter et al., 2012)

Method	Plant	Regarded PFCAs	Results	Reference
of 10 ng/L to 10 µg/L of each spiked PFCA)			transpiration stream concentration factor (TSCF): PFHxA ≈ 0.07	
greenhouse – hydroponic system (PFCA-spiked nutrient solution with nominal concentration of 10 ng/L to 10 µg/L of each spiked PFCA)	tomato (*Solanum lycopersicum* var. Moneymaker), cabbage (*Brassica oleracea* convar. *capitata var. alba*) and zucchini (*Cucurbita pepo* var. Black Beauty)	C4-14 PFCAs	root concentration factor (RCF): cabbage: PFHxA ≈ 15.8 zucchini: PFHxA ≈7.5 tomato*:* PFHxA ≈ 3.6 stem concentration factor (SCF): cabbage: PFHxA ≈ 2.4 zucchini: PFHxA ≈ 5.5 tomato: PFHxA ≈ 2.3 leaf concentration factor (LCF) cabbage: PFHxA ≈ 6.9 zucchini: PFHxA ≈ 10 tomato: PFHxA ≈ 19 => leaves show the highest concentration factors compared to other above-ground parts of the plants, the leaves also store the largest mass of all of the PFCAs twig concentration factor (TCF) cabbage: (no twig) zucchini: PFHxA ≈ 1.7 tomato: PFHxA ≈ 5.3 edible part concentration factor (ECF) (cabbage head and tomato and zucchini fruit) cabbage: PFHxA ≈ 3.6 zucchini: PFHxA ≈ 0.9 tomato: PFHxA ≈ 4.4	(Felizeter et al., 2014)

Method	Plant	Regarded PFCAs	Results	Reference
			transpiration stream concentration factor (TSCF) TSCF < 1 for all compounds in all plant species => transfer from the nutrient solution to the vegetative parts of the plants was inhibited cabbage: PFHxA ≈ 0.12 zucchini: PFHxA ≈ 0.06 tomato: PFHxA ≈ 0.12 edible part /leaf transfer factor: All factors were < 1, which indicates that leafy crops with open leaves (spinach or some lettuce) accumulate higher amounts in the edible part than fruit-bearing crops. Leafy crops pose a higher risk for human exposure	
semi-static mesocosm study. Uptake phase 15 days. Water concentration (nominal and measured): 20 µg/L	submerged and free-floating aquatic macrophytes: *Echinodorus horemanii* and *Eichhornia crassipes*		preferential translocation to leaf tissue: E. horemanii / E. crassipes: Leaf BCF_{ss}: 31.1 / 28.7 Root BCF_{ss}: 21.7 / 19.2 Whole-plant BCF_{ss}: 29.4 / 24.9	(Pi et al., 2017)
field and greenhouse study with biosolids-amended soil.	lettuce (*Lactuca sativa*) and tomato (*Lycopersicon lycopersicum*)		greenhouse, industrially impacted soil *L. sativa* / *L. lycopersicum* BCF: 11.7 / 2.9 Field trial *L. sativa* / *L. lycopersicum* BCF: < LOQ / 6.84	(Blaine et al., 2013)
greenhouse, water augmented with varying concentrations of PFAAs (nominal 0.2 - 40 µg/L).	lettuce (*Lactuca sativa*) and strawberry (*Fragaria ananassa*)		FCF (Fruit to soil concentration factor) for *F. ananassa* at 10 µg/L water concentration (0.4 % organic carbon content): 34.5 BAF for *L. sativa* at 10 µg/L water concentration (0.4 % organic carbon content): 415	(Blaine et al., 2014)

In conclusion PFHxA is taken up in plants, especially in leaves and fruits, often in the edible parts. This is of high concern, as the enrichment in plants might lead to an accumulation in other organisms. Plants, e.g. fruits and vegetables, are important nutritions for humans and are therefore a source for human exposure. Furthermore, agricultural land can be ruined when contaminated, as cultivated plants enrich PFHxA and can no longer be consumed (as it was the case in Rastatt Germany, see also (Brendel et al., 2018). PFHxA has been monitored in several food items in context of food monitoring programmes (see B.4.2.4.5).

B.4.6 Removal from the environment, decontamination and purification

Removal of PFHxA from different (environmental) media is important for example for lowering background concentrations in raw water used for the production of drinking water, for the purification of waste water and also for the remediation of contaminated sites.

In general removal could either happen by using special removal, remediation or purification techniques such as reverse osmosis /electrochemical oxidation or by natural physical /chemical /biological processes. For PFOA marine waters, especially the deep sea and sediments were found to be a sink in a study addressing the mass balance of PFOA in the Baltic Sea (Filipovic et al., 2013). It can be assumed that deep oceans might also function as a sink for PFHxA (Sanchez-Vidal et al., 2015). Sanchez-Vidal et al. analysed PFASs in particles sinking to the deep sea at 300 and 1000 m depth in the Cap de Creus Canyon, north-western Mediterranean Sea. The dominant PFASs was PFHxA with 60 % of the total PFASs. The transfer of particulate matter down to the deep is enhanced by storms and dense shelf water cascading. The authors estimated a total transport of 34.5 kg of PFHxA to the deep of 1000 m during the whole cascading period of 43 days (referring only to PFHxA sorbed to particles; dissolved phase not considered).

Due to the lower adsorption potential of PFHxA compared to PFOA, it is less likely that sediments act as a sink even though it is unclear what happens over long time windows, e.g. 50 to 100 years.

Data from wastewater treatment plants as well as from landfills as given in chapter B.4.2.4.1, already show that municipal wastewater treatment plants are only capable to remove PFHxA to some extent. They are emitting PFHxA via their effluents and sludge into the environment.

Several studies investigated the fate of PFASs including PFHxA in water treatment plants applying different treatment techniques:

Appleman et al. evaluated 15 full-scale treatment systems for the attenuation of PFASs in water treatment utilities through the U.S. using single or combined techniques for treatment of drinking water. The study demonstrated that full-scale conventional treatment processes in the U.S. which are also commonly used in the EU, such as coagulation followed by physical separation processes, and chemical oxidation, aeration and disinfection, and also anion exchange were unable to remove PFHxA in relevant quantities (Appleman et al., 2014). Granular activated carbon (GAC) filtration was able to remove 68 percent to 91 percent of PFHxA in the influent, but removal rate strongly depends on aging and reconditioning of the

GAC. Breakthrough times depend on various parameters such as presence of dissolved organic matter in either the groundwater or surface water but also occurrence of longer chain PFASs because of the competitive effects with the sorbing species. It is expected by Appleman et al. that longer chain PFAS and dissolved organic matter lead to desorption and release of already adsorbed short-chain PFASs over time. Reverse osmosis is shown to be the most effective treatment technique. It was able to remove more than 97 percent of PFHxA in the water. Despite its effectiveness, reverse osmosis is the most costly method for removal. Also disposal of the remaining concentrate, which will contain the rejected PFASs, adds to the cost of operation of these systems.

The work of Appleman et al. was taken up by Dickenson and Higgins, who investigated the local treatment and mitigation measures to remove PFHxA from water for about 20 sites. The averaged removal rates were only provided as broad ranges (less than ten percent, ten to 90 percent, above 90 percent) as this depends on the local situation, such as whether or not there is a cascade of treatment steps. For the different processes the observed remediation rates were (Dickenson and Higgins, 2016):

- Less then 10 % for aeration,
- less than 10 % for combination of coagulation /dissolved air floatation,
- less than 10 % for specific individual combinations of coagulation /flocculation /sedimentation /granular filtration /microfiltration,
- less than 10 % for anion exchange,
- less than 10 % for oxidation by chemical processes or UV photolysis with or without advanced oxidation (hydrogen peroxide),
- 10 to 90 % for granular activated carbon,
- above 90 % for nanofiltration (bench scale),
- above 90 % for reverse osmosis (bench scale).

Rahman et al. summarised several studies in a review on the fate and behaviour of PFASs in drinking water treatment (Rahman et al., 2014):

- Granulated activated carbon (GAC) failed to remove PFHxA (Eschauzier et al., 2012),
- powdered activated carbon at practical dosages would not achieve significant removal of PFHxA (Dudley, 2012),
- ion exchange in a full-scale drinking water treatment plant did not remove PFHxA (Dickenson et al., 2012),
- in full scale drinking water treatment plants removal of PFHxA ranged from 0 to 100 % ((Quinones and Snyder, 2009), ((Thompson et al., 2011)).

Thompson et al. (2011) investigated the removal of PFHxA in two Australian drinking water treatment plants. They sampled one plant twice (plant A), the other three times on different days respectively (plant B). For plant B the author themselves state that assessment of removal with the data is difficult, because grab sampling was performed and hydraulic

retention times were not taken into account. Reversed osmosis is in this plant, the treatment step responsible for removing PFHxA from the water (enriching it in the reversed osmosis concentrate) (Thompson et al., 2011), leading to 100 % removal (Rahman et al., 2014). In treatment plant B removal ranged from +20 to -48 % (Rahman et al., 2014) making it hard to conclude.

Quinones and Snyder took influent and effluent samples from seven drinking water treatment plants in the US. The only removal observed in their study was in a plant with reversed osmosis (Quinones and Snyder, 2009).

The removal of PFASs (PFBA, PFOA, PFBS, PFOS from contaminated drinking water in batch and continuous pilot plants was investigated by (Zaggia et al., 2016) using strong anion exchange resins. The following dependency was shown:

1. The higher the hydrophobicity of the functional group of the resin the higher is the sorption capacity for PFASs;

2. the shorter the fluorinated chain the lower the sorption capacity;

3. the sorption capacity for carboxylic group is reduced to the stronger sulphonic group (Zaggia et al., 2016).

Boiteux et al. (2017) investigated the ability of three drinking water plants to remove per- and polyfluoroalkyl substances (PFASs incl. PFHxA) from the raw water. Different techniques in those plants like sand filtration, coagulation followed by sedimentation, chlorination and activated carbon filter, did not significantly remove perfluorinated carboxylic acids from the water.

In addition to those studies investing removal efficiency in full-scale treatment plant, several investigations were also performed on a laboratory scale. As it is difficult to state how such approaches would perform under real world conditions, only some of these studies are summarized in the following:

Lundgren (2014) investigated the removal efficiency of PFASs using four different treatment techniques. Removal of PFHxA from different types of water were (Lundgren, 2014):

- less than 20 % for anion exchange using MIEX® resins,
- less than 5 % for coagulation with iron (III) chloride ($FeCl_3$),
- less than 10 % for adsorption using powdered activated carbon (PAC) and
- less than 30 % for nanofiltration (NF) membrane.

Soriano et al. (2017) investigated in laboratory scale experiments how PFHxA can be treated efficiently by nanofiltration followed by electrochemical degradation of the nanofiltrate concentrate. They found that the specific membrane used for this experiment was capable to reach 96.6 - 99.4 % rejection of PFHxA. The achieved rate for electrochemical degradation was up to 98 %.

Also Steinle-Darling and Reihnhard (Steinle-Darling and Reinhard, 2008)) investigated the rejection of PFHxA and other PFASs by four nanofiltration membranes. Rejection of PFHxA and other ionic PFASs in deionized water was greater than 95 %.

Karnwadee (2015) investigated the adsorption of PFHxA from synthetic and industrial wastewater onto GAC, non-ion exchange polymers and anion exchange polymers. The study reports adsorption kinetics and isotherms. The results show that adsorption rates and capacities of PFHxA in synthetic wastewater were higher than those in industrial wastewater onto all adsorbents and that ionic strength and dissolved organic carbon (DOC) are the most relevant parameter influencing adsorption (increasing ionic strength and DOC lead to decreasing adsorption of PFHxA) (Karnwadee, 2015). Lindegren (2015) found close to 100 % PFHxA removal by nanofiltration in a pilot plant (using ground water which contained PFHxA). Furthermore, she tested the removal efficiency of PFHxA on GAC (47 ± 28 %) and anion exchange (21 ± 38 %) in a column study (by using spiked drinking water) (Lindegren, 2015).

(Bruton and Sedlak, 2017) investigated heat-activated persulfate chemicals oxidation in batch experiments. This technique was supposed to be applied *in-situ* in cases of contaminated groundwater due to exposure with PFASs-containing fire fighting foams. Therefore, the batches contained two different foams in a water-sediment mixture. Results show the conversion of PFCA-precursors to PFCAs and further degradation of PFCAs. Nevertheless, in the end some short-chain PFCAs were still present. Also the production of potentially hazardous concentrations of HF could not have been excluded (Bruton and Sedlak, 2017).

Electrochemical mineralization was shown by Niu et al. in a laboratory scale with only PFHxA and four other PFCAs in aqueous solution using "Ce-doped modified porous nanocrystalline PbO_2 film anode" (Niu et al., 2012). Also Zhou et al showed degradation of PFHxA on a boron doped diamond (BDD) anode in a laboratory experiment (Zhuo et al., 2012). (Gomez-Ruiz et al., 2017) also used a BDD anode for the electrochemical treatment of eight PFASs (e.g. PFHxA, 6:2 fluorotelomer sulfonic acid). The authors investigated degradation of PFASs at environmentally relevant conditions in the effluent from a PFASs contaminated industrial WWTP at laboratory scale. 99.7 % PFASs removal was observed after ten hours and a current density of 50 mA/cm². At lower current densities initial degradation of 6:2 fluorotelomers into PFHxA were observed. For large scale implementation the high energy consumption is a challenge (Gomez-Ruiz et al., 2017).

Murray et al. (2019) investigated the removal of PFASs in a bench-scale system using super-fine powder activated carbon (SPAC, particle diameter < 1 µm) coupled with ceramic membrane filtration (CMF). AFFF-contaminated groundwater and diluted firefighting contaminated tank water were used in the study. No 10 % breakthrough (defined as 10 % of the influent concentration of individual PFAA present in the CMF permeate or column effluent) was observed for PFHxA after 77 hours of filtration in the experiment with the groundwater. Based on total PFAA mass loading, the authors compared the results with results from a GAC pilot-scale system - SPAC/CMF is at least 1.5 times more effective than GAC. In the experiments with the highly contaminated tank water 10 % breakthrough was observed for the short-chain PFAAs (e.g. PFHxA) after 42-196 hours (Murray et al., 2019).

Zhang et al. summarised in a review nanotechnologies applied in remediation of water contaminated by PFASs (Zhang et al., 2019). Deng et al. stated that adsorption of PFASs on carbon nanotubes was lower than on other conventional sorbents (e.g. activated carbon, resins) and that adsorption of PFASs on carbon nanotubes decreased with decreasing chain

length (Deng et al., 2012). Unfortunately, most of the current research cited in the review focused on PFOA. (Zhang et al., 2019) concluded that most of the current studies were conducted in deionized water containing much higher PFASs concentrations than real contaminated water. Hence, performance of the applied nanotechnologies might be overestimated.

Ateia et al. reviewed removal techniques from water for short-chain PFASs (Ateia et al., 2019):

- lower removal efficiencies for short-chain PFASs compared to long-chain PFASs for adsorption on different carbonaceous material were confirmed (e.g. GAC, activated carbon filters, and carbon nanotubes) (Deng et al., 2012; Kothawala et al., 2017),
- > 80 % removal of short-chain PFASs by ion exchange resins; but desorption at lower PFASs concentrations (McCleaf et al., 2017; Zaggia et al., 2016),
- only very little data are available for removal of short-chain PFASs by membranes (e.g. reverse osmosis and nanofiltration) and advanced oxidation processes (studies are already mentioned/discussed above).

For these results from laboratory scale experiments it is not clear whether these results can also be achieved under real conditions where the water to be treated usually consists of a wide variety of constituents. At least the above summarized studies investigating full-scale water treatment plants indicate, that the situation is complex and PFHxA cannot be removed efficiently in all plants. Ross et al. investigated the potential of water treatment techniques to remove long-chain / short-chain PFCAs, but provided no quantitative removal efficiencies for PFHxA (Ross et al., 2018). By assessing a large number of available literature, they found that GAC is less effective for short-chain PFCAs and PFCA-precursors compared to long-chain PFCAs. The same general conclusion was drawn for injectable particulate carbon where proprietary products containing activated carbon are used for *in-situ* treatment of groundwater by injection of the product in the aquifer where it acts as a trap for the perfluorinated substances. The authors also mentioned that many ion-exchange resins on the market are more effective for long-chain PFAS than for the short-chain ones like PFHxA, but novel resins might have higher sorption capacities for both long-chain and some short-chain PFASs compared with GAC. Ion-exchange resins are an established technology for many common contaminants in both the municipal and groundwater treatment. It has to be kept in mind that co-contaminants such as chromates, chlorides or nitrates are within the waste water stream or (naturally) within aquifers. Normally these are present at concentrations orders of magnitude greater than PFASs, resulting in significant competition with PFAS for adsorption sites. For ozofractionation (e.g. via Ozofractionative Catalysed Reagent Addition – OCRA), effective removal of total PFASs was observed in full-scale. Nevertheless, this process represents only a part of a treatment train, and further technology to destroy the concentrated PFASs in the aqueous phase is necessary. Further effective removing processes for PFASs regardless chain length (including many types of precursors) are reverse osmosis and nanofiltration. In the context of groundwater treatment, it is important to assess the suspended solids and water geochemistry to prevent fouling or deterioration of the membranes.
The authors of the article mentioned that currently no treatment technologies for water and soil are available that can both remove and destroy PFASs (especially short-chain PFASs and precursors) simultaneously.

Full scale remediation installations are specifically adapted to local conditions and are facing several challenges and are shown by the following study: Bruton and Sedlak investigated the potential use of aqueous film forming foams (AFFF) for *in-situ* chemical oxidation. But this technique also requires the use of heat activated persulfates ($S_2O_8^{2-}$) and low pH-values (pH ≤ 3). It was observed that the organic solvents in the AFFF and also aquifer sediments decrease the efficiency of the remedial process. The process is also challenged by the creation of acidic conditions in the subsurface, the potential for generation of undesirable transformation products and the release to toxic metals (Bruton and Sedlak, 2017).

The behaviour of PFHxA in treatment plants is triggered by its low adsorption potential (see chapter B.4.2.1) and the persistence (see chapter B.4.1.1). When looking on results from studies on a laboratory scale there seems to be some promising approaches which are able to remove PFHxA at least to some extent. But the investigation under real world conditions show that the situation is more complex. None of the investigated plants is capable to fully remove PFHxA. More effort would be needed, first in terms of research and second for applying such newly developed techniques on a broad scale, for being able to fully remove PFHxA from different environmental media. But for the current state of technology it can be concluded that it is very difficult to remove PFHxA from (waste) water or from the environment.

B.5 Human health hazard assessment

B.5.1 Toxicokinetics (absorption, metabolism, distribution and elimination)

The free undecafluorohexanoic acid (PFHxA) is in equilibrium with undecafluorohexanoate (PFHx), the conjugate base; however, due to its low pK_a (< 1), PFHxA primarily exists in the environment as an anion. However, some laboratories report results for the acidic form of PFHxA and the standards used by some laboratories to perform toxicity testing include various PFHxA salts, such as ammonium perfluorohexanoate (CAS-No 21615-47-4) and sodium perfluorohexanoate (CAS-No 2923-26-4). This is important, as the acid has been shown to be more irritating than associated salts. However, regardless of the administered compound, once absorbed into the bloodstream, the PFHx-anion will form. Additionally, when the salt or acid exists in liquids, it will dissociate and the salt or acid will break off, resulting in the anion (Luz et al., 2019).

In general, the main elimination pathway for PFHxA in mammals seems to be excretion via the urine (Chengelis et al., 2009a; Gannon et al., 2011a; Numata et al., 2014). Essentially 100 % of the dose was eliminated in urine in rats and mice (Gannon et al., 2011a). PFHxA was mainly found in plasma, kidney and liver in rats and mice with higher concentrations in male rats and female mice in kidney than in the liver but with a higher concentration in the liver in male mice (Gannon et al., 2016). Numata and coworkers report that accumulation in fattening pigs mainly occurs in plasma, fat and muscle tissue (i.e. meat), liver and kidney. The average elimination half life for PFHxA in fattening pigs calculated by Numata et al. (2014) is 4.1 days. Chengelis et al. (Chengelis et al., 2009a) examined elimination half-lives of PFHxA in monkeys (intravenous administration) and rats (oral and intravenous administration) in the range of several hours (two to five hours) based on serum concentrations. The authors reported a gender specific difference in PFHxA serum clearance in rats, as female rats eliminated PFHxA about two to three times faster (0.42 h compared to 1.0 h). This would be in line with Gannon et al. (2011a) observing also serum elimination half lives of PFHxA in rats

and mice in the range of hours, with two- to three-fold faster elimination half-lives in female rats compared to male rats. However, there was no appreciable gender-specific difference in the extent or rate of urinary elimination and based on the short elimination time of PFHxA and the limited number of animals used. The gender difference in Sprague-Dawley rats remains to be established, especially in view of the conclusions drawn by Russell et al. (2013) who stated that "the half-lives of PFHxA in mice, rats, monkeys and humans were proportional to body weight with no differences observed between genders, indicating similar volumes of distribution and similar elimination mechanisms among mammalian species."

In general, the reported half-lives for PFHxA in mammals are considerably lower when compared to PFOA. For PFOA, half-lives of PFOA in mice, rat, pig and monkey are up to one order of magnitude higher compared to PFHxA, ranging from 0.08 days in female rat, 236 days in pig and several years in humans.

The shorter half-life of PFHxA in mammals is due to the rapid excretion via the urine (Chengelis et al., 2009a; Gannon et al., 2011a; Numata et al., 2014). Chengelis et al. (2009a) reported that after intravenous dosing of PFHxA approximately 80 % of the administered dose was recovered in the urine during 24 h post-dose. Following repeated oral dosing of PFHxA, approximately 90 % of the administered daily dose was recovered in the urine 24 h post dose in male rats, whereas in female animals, urinary elimination varied between 70 and 100 % of the administered dose during 24 h post-dosing.

For further details see Appendix B.0.

B.5.2 Repeated dose toxicity

One oral **subacute toxicity study**, two oral subchronic toxicity studies and one oral chronic toxicity study of PFHxA in rats are available. All studies show treatment-related effects. The subacute study showed an influence of PFHxA on clinical chemistry such as altered liver enzyme levels of AST, ASAT and ALP in both sexes. Additionally, altered organ weights were observed in males and females. The relative liver and kidney weights were increased in both sexes. Furthermore, PFHxA had an effect on haematological parameters: haematocrit, reduced levels of red blood cells and haemoglobin exceeded the 10 % level at doses of at 250 mg/kg bw/d. Degeneration and hyperplasia of the olfactory epithelium was observed in both sexes in dose-dependent manner, relevant increases in incidences were noted at 250 mg/kg bw/d and above. The most sensitive effect was a significant reduction of total T3, total T4 and free T4 at all dose groups of males justifying a LOAEL of 62.6 mg/kg bw/d (NTP, 2018).

The first **subchronic study** with PFHxA showed significantly lower mean body weights of males at 50 and 200 mg/kg bw/d group and similar (but not significant) trends in female rats at 50 and 200 mg/kg bw/d. Slight effects (< 10 % ranges) on haematological parameters were seen in 200 mg/kg bw/d-rats of both sexes. Furthermore, the liver enzymes ALT, AST and ALP were increased in 200 mg/kg bw/d in male rats. This was accompanied by minimal centrilobular hepatocellular hypertrophy in seven of ten animals. Kidney effects such as increased relative kidney weight at 50 mg/kg bw/d were not accompanied by other histopathological findings. Based on this subchronic study a LOAEL of 50 mg/kg bw/d could be derived based on lower body weight throughout the dosing peroid in male rats (NOAEL 10 mg/kg bw/d) (Chengelis et al., 2009c).

The second **subchronic study** was performed with sodium PFHxA and showed lower body weights in high-dose males in comparison to control values. Furthermore, liver weights (without any other abnormality) were increased in male rats at 100 and 500 mg/kg bw/d. The relevant adverse effect is the mild to minimal degeneration/atrophy of the olfactory epithelium in male and female rats at 100 and 500 mg/kg bw/d. The NOAEL was derived with 20 mg/kg bw/d (Loveless et al., 2009b).

After **chronic** gavage administration of PFHxA to Sprague Dawley rats a dose-dependent decrease in survival rate was observed in female animals only. In histopathological investigations the kidney and liver of female rats of the 200 mg/kg bw/d group showed tubular degenerative/papillary necrotic lesions. Thus, kidneys and livers represented the main targets for non neoplastic effects after chronic administration of PFHxA. Up to oral doses of 100 (males) and 200 (females) mg/kg bw/d over 104 weeks, no carcinogenic effects were observed. Thyroid hormone levels, shown to be sensitive effects in subacute studies, were not investigated in this chronic study. Histological examination of the thyroid was not performed. According to the protocol cited by the authors (Fiette and Slaoui, 2011) the thyroid gland with the parathyroids should have been weighed, but the results were not given in the publication (Klaunig et al., 2015b).

For further details please see Appendix B.0.

B.5.3 Mutagenicity

The dossier submitter concludes on PFHxA that the studies presented give no evidence for mutagenic properties of PFHxA.

For further details please see Appendix B.0.

B.5.4 Carcinogenicity

Based on the information available there is no indication for carcinogenic properties of PFHxA. However, this conclusion is based on the publication of study results available in public literature. The original study report was not available for evaluation.

For further details please see Appendix B.0.

B.5.5 Toxicity for reproduction

In an one generation reproductive toxicity study with sodium perfluorohexanoate (NaPFHxA) in rats no substance-related effects were observed on mating, fertility, gestation length, number of implantation sites, estrous cyclicity, sperm parameters, litter size, sex ratio, pup clinical observations, pup survival, or F1 adult developmental landmarks at any dose tested. Substance-related effects were observed during lactation at 500 mg/kg bw/d on mean pup weights (17-18 % decrease compared to controls) (Chengelis et al., 2009c).

In a study on prenatal developmental toxicity of NaPFHxA in rats, there were no substance-related deaths or gross post-mortem findings in dams at any dose. Maternal and developmental toxicity occurred at 500 mg/kg bw/d and consisted of reductions in bodyweight (Loveless et al., 2009b).

In a study on prenatal developmental toxicity of ammonium perfluorohexanoate in mice adverse effects on offspring occurred at 175 mg/kg bw/d and higher whereas no maternal toxicity was observed up to 500 mg/kg bw/d. The number of stillborn pups and pups dying on day 0 and from day 1-4 postpartum were significantly increased on day 0 postpartum at 500 mg/kg bw/d. The significant increase of stillborn pups furthermore indicated an effect from exposure of the fetuses during maternal treatment due to placental transfer of the compound. Additionally, the pup weight was reduced dose-dependently from 1.6 g to 1.4 g; the first effect was noted at 175 mg/kg bw/d.

A developmental NOAEL of 100 mg/kg bw/d was derived for lower absolute fetal body weights.

In comparison to the developmental LOAEL of PFHxA of 175 mg/kg bw/d, the restriction dossier of PFOA reported LOAEL values of 1.0 (maternal) and 3.0 (foetal) mg/kg bw/d (ECHA, 2015a) for developmental toxicity. In conclusion, there are indications that PFHxA has a considerably lower potency when compared to PFOA under the experimental conditions of the tests conducted so and thus presumably a lower potential to affect fertility and development.

For further details please see Appendix B.0.

B.5.6 Derivation of DNEL(s)/DMEL(s)

Table 14: Summary of animal studies and the estimated LOAEL and/or NOAEL for PFHxA.

Species and dose	**NOAEL mg/kg bw/d**	**LOAEL mg/kg bw/d**	**Effect at LOAEL/ NOAEL**	**Reference**
subacute studies				
Harlan Sprague-Dawley Rats 10 animals/ sex /dose were dosed via gavage with 0/ 62.6/125/250/500/1 000 mg/kg bw/d for 28 d	-	62.6	decreased level of free and total T4 and total T3	(NTP, 2018)
subchronic studies				
Crl:CD(SD) rats 10 animals/sex/dose were dosed via gavage with 0/10/50/200 mg/kg bw/d for 90 d	10	50	lower body weight*(11 % at 50 mg/kg bw/d and 8 % at 200 mg/kg bw/d)	(Chengelis et al., 2009a)
Crl:CD(SD) rats 10 animals/sex/dose were dosed via gavage with 0/20/100/500 mg/kg bw/d for 90 d	20	100	nasal lesions (degeneration/ atrophy of the olfactory epithelium)	(Loveless et al., 2009a)
chronic studies				

Crl:CD(SD) Rats 10 animals/sex/dose were dosed via gavage with 0/2.5/15/100 mg/kg bw/d (males) and 0/5/30/200 mg/kg bw/d (females) for 104 weeks	30 (females)	200 (females)	Kidney necrosis	(Klaunig et al., 2015a)
developmental and reproductive studies				
Crl:CD(SD) rats 10 animals/sex/dose were dosed via gavage with 0/20/100/500 mg/kg bw/d for 90 d	100 (maternal) 100 (fetal)	500 (maternal) 500 (fetal)	lower body weight gain* lower fetal body weight gain*	(Loveless et al., 2009a)
Crl: CD I (ICR) 20 females/dose were dosed via gavage with 0/100/350/500 mg/kg bw/d of APFHx from GD 6-18	- 100 (fetal)	500 (maternal) 175 (fetal)	no effects lower absolute body weight*	Hoberman (2011a) (Hoberman, 2011b)

*in comparison to the control group.

Table 15: Overview of DNEL-derivations for general population, long-term, systemic effects, all routes.

Effect at NOAEL/ LOAEL	**NOAEL mg/kg bw/d**	**LOAEL mg/kg bw/d**	**$DNEL_{oral}$ mg/kg bw/d (AF)**	**$DNEL_{inhalation}$ mg/m³ (AF)**	**$DNEL_{dermal}$ mg/kg bw/d (AF)**	**Reference of NOAEL and/ or LOAEL**
decreased level of free and total T4 and total T3	-	62.6	0.03 (1 800)	0.11 (450)	0.031 (1 800)	(NTP, 2018)
lower body weight*	10	50	0.03 (300)	0.1 (75)	0.03 (300)	(Chengelis et al., 2009a)
nasal lesions	20	100	0.067 (300)	0.21 (75)	0.06 (300)	(Loveless et al., 2009a)
Kidney (papillary) necrosis	30	200	0.3 (100)	0.94 (25)	0.27 (100)	(Klaunig et al., 2015a)
lower fetal body weight gain*	100	500	1 (100)	3.13 (25)	0.9 (100)	(Loveless et al., 2009a)
lower absolute fetal body weight*	100	-	0.57 (175)	4.80 (25)	0.51 (175)	Hoberman (2011a) (Hoberman, 2011b)

*in comparison to the control group

For further details please see Appendix B.5.6.

B.6 Human health hazard assessment of physicochemical properties

Not relevant.

B.7 Environmental hazard assessment

B.7.1 Aquatic compartment (including sediments)

B.7.1.1 Short-term toxicity to fish

Table 16: Summary of short-term effects on fish.

Substance	Method/Organism	Results	Reference
PFHxA	fish acute toxicity test (OECD 203) *Oncorhynchus mykiss*	LC50 (96h) > 99.2 mg/L	(Hoke et al., 2012)

(Hoke et al., 2012) are describing the study as follows: "The test was conducted in accordance with the OECD 203[10] guideline. Acute 96-h static testing with the rainbow trout, O. mykiss, was conducted in 26-L stainless steel tanks containing 15 L of test solution. A well water control and nominal test substance concentrations of 0.1, 1, 10 and 100 mg/L were tested using one replicate tank per concentration or well water control. Seven fish that were 28-68 d post-hatch were used per replicate tank. Testing was conducted in a waterbath maintained at 12 ± 1 °C with a photoperiod of 16 h cool white fluorescent light (approximately 250–500 lx) and 8 h darkness Measurements of pH, DOC and temperature were made at test start, at total mortality in a test concentration, and at test end. Observations of mortality and sublethal effects were made every 24 h until test end." (Hoke et al., 2012). The study is conducted in accordance with the OECD guidline and a detailed report is available. Hence the study is reliable without restriction.

B.7.1.2 Long-term toxicity to fish

Table 17: Summary of long-term effects on fish.

Substance	Method/Organism	Results	Reference
PFHxA	Fish early life-stage toxicity test (OPPTS Biological Effect Test Guideline No. 850.1400 *Oncorhynchus mykiss*	LOEC: hatching success, survival, length and weight > 9.96 mg/L	(Burke, 2008)

[10] OECD Guideline for testing of Chemicals – fish, acute toxicity test; method 203; guideline adopted 1992

The study investigated the effect of the ammonium salt of PFHxA on growth and development of embryos and larvae of the freshwater fish species *Oncorhynchus mykiss* (rainbow trout) in a Fish Early-Life Stage (FELS) Toxicity Test. The study was performed in accordance with the OPPTS Biological Effect Test Guideline No. 850.1400, Fish Early-Life Stage Toxicity Test (1996). The test was conducted at nominal concentrations of 0.095, 0.304, 0.972, 3.110 and 9.960 mg/L active moiety, equivalent to 0.2, 0.641, 2.05, 6.56 and 21.0 mg/L in terms of PFHxA ammonium salt with a purity of 50 % and a conversion factor of 1 054. These concentrations were based on the results of an acute toxicity test. Both solvent and dilution water controls were included in the test design, with duplicate test vessels at all exposure concentrations including the controls. The test was conducted with a flow through test design. Concentrated stock solutions and test media were analysed during the test. Measured concentrations of PFHxA active moiety in the concentrated stock solutions ranged between 98 and 100 % of the nominal concentrations, test media concentrations ranged between 94 and 108 % of nominal concentrations corresponding to geometric mean measured concentrations of 0.103, 0.310, 0.916, 3.14 and 10.1 mg/L. Hatching success in the control group was 74 %, satisfying the validation criterion for hatching success (> 66 %). The NOEC and LOEC for hatching success were determined as 9.96 and > 9.96 mg/L, respectively. Larval survival until day 28 post-hatch in the control group was 93 % thereby exceeding and satisfying the validity criteria for post-hatch survival (70 %). Posthatch survival across all remaining treatments ranged between 96 and 100 %. In terms of nominal concentrations, the NOEC and LOEC for post-hatch larval survival until day 28 were both considered to be equal to or greater than 9.96 mg/L. For fish total lengths, the NOEC and LOEC determined on day 28 post-hatch were 9.96 and > 9.96 mg/L PFHxA active moiety, respectively. For fish dry weights, the NOEC and LOEC determined on day 28 post-hatch were 9.96 and > 9.96 mg/L PFHxA active moiety, respectively. The study is described likewise in the publication. The study is conducted in accordance with the OECD guidline and a detailed report is available. Hence the study is reliable without restriction.

B.7.1.3 Short-term toxicity to aquatic invertebrates

Table 18: Summary of effects on aquatic invertebrates.

Substance	Method/Organism	Results	Reference
PFHxA	OECD Guideline 202 (Daphnia sp. Acute Immobilisation Test) *Daphnia magna*	LC_{50} (48 h) > 96.5 mg/L	(Hoke et al., 2012)
PFHxA	OECD Guideline 202 (Daphnia sp. Acute Immobilisation Test) *Daphnia magna*	EC_{50} (48 h) = 1 048 mg/L based on: mobility	(Barmentlo et al., 2015)

(Hoke et al., 2012) are describing the study as follows:"The test was conducted following the OECD test guidelines 202 with minor deviations, e.g., 10 daphnids were used in a single

beaker per treatment instead of four beakers each with five daphnids per treatment,The D. magna 48-h static exposures were conducted using 200 mL of test solution in 250 mL beakers. A well water control and nominal test substance concentrations of 0.1, 1, 10 and 100 mg L^{-1} were used for testing with one beaker per concentration or well water control. Each beaker contained 10 neonate daphnids that were <24-h old at test start. Daphnids were not fed during the test. A recirculating water bath was used to maintain mean temperature in the test chambers during the 48-h test at approximately 20.0 °C. A photoperiod of 16 h of cool-white fluorescent light (approximately 600–900 lx) and 8 h darkness was employed. Measurements of pH, DO, and temperature were made at study start and end. Immobility and behavioral observations were made daily. The statistical calculation of the EC50 was based on immobility at 48 h". (Hoke et al., 2012)

(Barmentlo et al., 2015) tested acute immobility after 48 h of exposure also according to OECD guideline 202[11]. Daphnid neonates were exposed to the four compounds at five to eight concentrations (including control) in ISO medium. Four to six replicates per concentration were tested, each replicate consisting of a 50 mL polypropylene Greiner tube with the appropriate amount of the stock solution dissolved in 20 mL of ISO medium, containing five daphnid neonates (younger than 24 h). The uncovered vessels were randomly distributed in a climate controlled fume hood (20 ± 1 °C) with a 16:8 h light:dark photoperiod. The daphnids were randomly distributed over the test vessels and not fed during the experiments. After 24 and 48 h of incubation, the daphnids were checked for immobilisation. Daphnids were considered immobile when they were not able to swim after 15 s of gentle stirring, according to the guideline.

The studies are conducted in accordance with the OECD guidline and a detailed report is available. Hence the studies are reliable without restriction.

B.7.1.4 Long-term toxicity to aquatic invertebrates

Table 19: Summary of long-term effects on aquatic invertebrates.

Substance	Method /Organism	Results	Reference
PFHxA	OECD Guideline 211 (Daphnia magna Reproduction test) *Daphnia magna*	EC_{50} (21 d) = 776 mg/L based on: reproduction EC_5 (21 d) = 724 mg/L based on: reproduction EC_{50} (21 d) = 853 mg/L based on: population growth rate EC_5 (21 d) = 779 mg/L	(Barmentlo et al., 2015)

[11] OECD Test No. 202: Daphnia sp. Acute Immobilisation Test; guideline adopted in 2004

		based on: population growth rate	

The chronic toxicity of PFHxA was determined in a 21 d daphnid reproduction test, following OECD guideline 211[12] (2008). Per test concentration 15 replicates were prepared, each consisting of one daphnid kept in 40 mL PFHxA containing Elendt M4 medium in a 50 mL Greiner tube. The tubes were randomly distributed in a climate controlled fume hood (20 ± 1 °C), with a light:dark regime of 16:8 h. The experiment was started by introducing one neonate (younger than 24 h) into each tube using a disposable transfer pipette. Each day the number of animals not responding to gentle stimulation by tapping on the tube was scored. Juveniles and ephippia (winter eggs) were also counted and removed daily. The daphnids were fed daily with a suspension of the algae *Scenedesmus subspicatus*. The daphnids were transferred to new exposure tubes containing renewed test concentrations three times a week. The study is conducted in accordance with the OECD guidline and a detailed report is available. Hence the study is reliable without restriction.

B.7.1.5 Algae and aquatic plants

Table 20: Summary of effects on algae and aquatic plants.

Method/Organism	**Results**	**Reference**
OECD guideline 201 Freshwater Alga and Cyanobacteria, Growth Inhibition Test *Pseudokirchnerella subcapitata*	EC_{50} (72 h) > 100 mg/L based on: biomass EC_{50} (72 h) > 100 mg/L based on: growth rate	(Hoke et al., 2012)
Geitlerinema amphibium	IC_{50} (72 h) = 998.7 mg/L based on: optical densitiy	(Latala et al., 2009)
Chlorella vulgaris	IC_{50} (72 h) = 4032 mg/L based on: optical densitiy	(Latala et al., 2009)
OECD guideline 201 Freshwater Alga and Cyanobacteria, Growth Inhibition Test *Scenedesmus subspicatus*	EC_{50} (72 h) = 86 mg/L based on: growth rate NOEC (72 h) = 50 mg/L based on: growth rate	(ENVIRON, 2014)

[12] OECD Test No. 211: Daphnia magna Reproduction Test, guideline adopted in 2008

The test by (Hoke et al., 2012) was conducted following the OECD test guideline 201 with minor deviations. Two instead of three replicates were used per treatment in the algae studies. Testing with *P. subcapitata* used an AAP control and nominal test substance concentrations of 0.1, 1, 10 and 100 mg/L prepared in AAP medium. The AAP medium was pH adjusted to approximately 7.5 and the medium was filter-sterilised. 50 mL of each test or control solution was placed in each of two replicate 250 mL Erlenmeyer flasks with foam stoppers for gas exchange. An appropriate aliquot of algal inoculum from a logarithmically growing stock culture was aseptically transferred to each replicate test flask to achieve the desired nominal concentration of 10000 cells/mL at test initiation. The test flasks were placed on a shaker table in an environmental chamber at 24 ± 2 °C using 24 h cool-white fluorescent illumination at 6000–10000 lx. The test solutions were not renewed and pH measurements were made of all test solutions at test start and end. *P. subcapitata* growth was determined by taking from a 0.2 mL sample from each flask approximately 72 h from study initiation. The statistical calculation of the ErC_{50} (growth rate) or EbC_{50} (biomass) was based on mean healthy cell counts.

The toxicity test on *Scenedesmus subspicatus* was conducted in accordance with OECD test guidelines 201 (ENVIRON, 2014).

The acute toxicity of PFHxA on Baltic microalgae was investigated by (Latala et al., 2009). The test algae were batch-cultured in f/2 medium prepared in distilled water. Salinity was similar to that in the southern Baltic Sea. All experimental parameters (pH, salinity and light intensity) were maintained unchanged throughout the study. The tests were carried out on the algae using modified versions of the methods recommended in the European Committee for Standardisation's guidelines (EN ISO, 1995; EN, 1993). The main modifications involved the use of an f/2 medium, selected test strains and a 16:8 photoperiod. The final batch cultures used in the experiments were obtained by mixing a known number of cells in the log growth phase with sterile medium. The initial cellnumber was constant and was measured as the optical density. 9.5 cm^3 aliquots of algal suspension were transferred to 25 cm^3 glass conical flasks, to each of which, in turn, 0.5 cm^3 of different concentrations of aq. PFCA or distilledwater (control) was added. All the toxicity tests involved three replicates per treatment plus controls. After 72 h incubation in culture chambers, the number of cells was determined by measuring optical density spectrophotometrically (Latala et al., 2009).

The studies are conducted in accordance with the OECD guideline and a detailed reports are available. Hence the studies are reliable without restriction.

B.7.1.6 Other effects

B.7.1.6.1 (Sub)lethal effects

A study (Blanc et al., 2017) compared the gene expression induced by 3,3',4,4',5-pentachlorobiphenyl (PCB126) with mixtures of PCB126 + PFHxA, PCB126 + PFOS and PCB126 + PFOS + PFHxA in *Danio rerio* embryos. The results showed that PFHxA could enforce PCB126 toxicity in a mixture. A significant induction of *gpx1a* (involved in oxidative stress) for example only took place in a mixture of PCB126 + PFHxA and a mixture of PCB126 + PFOS + PFHxA. This means that PFHxA could be involved in a synergistic effect with PCB126 during the upregulation of *gpx1a*. A role in increasing cell membrane permeability induced by

PFHxA and PFOS is dicussed by the authors as a probable cause for the synergistic effect. A recently published paper has studied the amphilic properties of PFASs and their potential to accumulate in phospholipid bilayers (Nouhi et al., 2018). Longer chain PFASs showed higher tendency to penetrate into the bilayer compared to the short-chain compounds. Nevertheless the authors state that in dependence of the concentration PFHxA can also disturb the bilayer. This would support the assumption made by (Blanc et al., 2017).

B.7.1.7 Summary and discussion of the environmental hazard assessment

Standard tests on ecotoxicity are available for algae, daphnia and fish covering acute as well as chronic toxicity. In the study of (Hoke et al., 2012) no effects on fish and daphnia in the acute toxicity tests were observable up to > 99.2 mg/L and > 96.5 mg/L respectively. Also no effects were observable for algae up to 100 mg/L.

Barmentlo and coworkers (2015) report an EC_{50}-value of 1 048 mg/L for acute toxicity on daphnia. The acute toxicity of PFHxA on Baltic microalgae investigated by (Latala et al., 2009) is 998.7 mg/L for *Geitlerinema amphibium* and 4 032 mg/L for *Chlorella vulgaris. Scenedesmus subspicatus* seems to to considerably more sensitive as an EC_{50}-value of 86 mg/L and a NOEC of 50 mg/L is reported (ENVIRON, 2014). Long term effects on hatching success, survival, length and weight of *Oncorhynchus mykiss* were not observable up to > 9.96 mg/L (Burke, 2008). The reported EC_{50} (21 d) value based on reproduction of daphnia is 776 mg/L. The EC_5 (21 d) value is not considerably lower (724 mg/L) (Barmentlo et al., 2015).

Likewise, there is no considerable difference between EC_{50} (21 d) and EC_5 (21 d) based on population growth rate (853 mg/L and 779 mg/L).

The studies described above all address the toxicity of PFHxA as a single substance. As Ahrens and coworkers (Ahrens and Bundschuh, 2014) concluded in their review on various monitoring studies of the aquatic environment, PFASs are continuously introduced into aquatic ecosystems and are ubiquitously present in complex mixtures. There is sufficient scientific evidence and a recently published paper has pointed out that neglect of mixture effects can cause chemical risks to be underestimated (Kortenkamp and Faust, 2018). In a multicomponent mixture of xenoestrogens experiment where each chemical was present at levels well below its NOEC and EC_{10} produced significant effects in a YES assay (Silva et al., 2002). Mixture toxicity are ecotoxicollogically relevant as for instance has been shown by (Junghans et al., 2006). 25 pesticides, which reflected a realistic exposure scenario in field run-off water, showed mixture effects on the reproduction of the freshwater alga *Scenedesmus vacuolatus.* Chronic ecotoxicological tests do not take into account any cross generational effects as anticipated for PFASs. The exposure is continuous and even if releases would be regulated now, the mass already present in the environment will still cause exposure over a very long time period, even much longer than other substances being "very persistent" according to Annex XIII to REACH. The possible risk of extremely persistent organic fluorochemicals for humans and the environment has also been emphasised by leading scientists (Blum et al., 2015a; Scheringer et al., 2014).

B.8 PBT and vPvB assessment

B.8.1 Assessment of PBT/vPvB Properties – Comparison with the Criteria of Annex XIII

See section 1.3.7 assessment of PBT properties.

B.8.2 Emission Characterisation

Due to the considerable economic importance of PFCAs these synthetic compounds are ubiquitously present in the environment.

PFHxA and its salts are non-degradable as well in waste water treatment plants (WWTP) as in the natural environment. However, many precursors like 6:2 FT(M)A or 6:2 diPAP may degrade fairly quickly to 6:2 FTOH, with a half-life of about 1.3 days (Liu et al., 2010b). PFHxA again is formed by degradation of 6:2 FTOH. The majority of 6:2 FTOH precursors and the degradation routs are unknown. For degradation of the sum of the unkown precursors, the formation ratio of 1 t 6:2 FTOH forms 39 kg PFHxA is used as a surrogate for further calculations (calculated based on data from Liu et al. 2010). These substances unrelieved getting to surface water and into the sewage sludge (Günther et al., 2009). A further source of water and soil contamination with PFHxA is landfilling. In her PhD-thesis (Vierke, 2014) investigated samples from WWTP as to the distribution of PFASs in the environment. Air-water concentration ratios were higher for short chain PFCAs compared to long chain PFCAs. But an enrichment of PFHxA and its related substances in water is likely, too.

The mobility of a substance in the environment depends on its occurrence in mobile environmental compartments, e.g. air and water and the mobility of these compartments (Ballschmiter, 1992). Diffusive and non-diffusive transport mechanisms are relevant for distribution of substances. Non-diffusive transport takes place as advection, e.g. in water or air currents and in rain or snowfall. Diffusive transport is the dispersion of a substance between different environmental media, e.g. from soil or water to air and from water to sediment (Mackay, 2001); (Schwarzenbach et al., 2003). For partitioning behaviour of substances the chemicals' properties, like vapour pressure or solubility, as well as the characteristics of the environmental media, e.g. sediment properties are decisive (Ballschmiter, 1992).

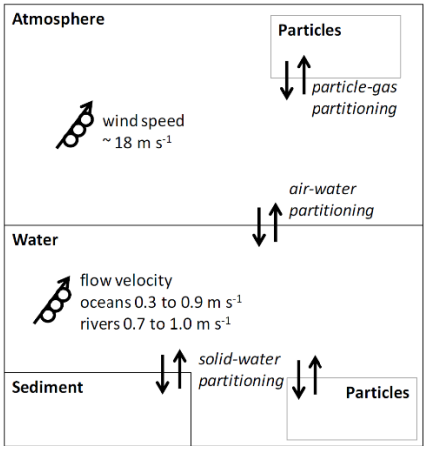


Figure 4: *Distribution of substances (equilibrium arrows) to mobile environmental media (circled arrows) (based on (Ballschmiter, 1992) and multimedia models ((Mackay, 2001); (Scheringer, 2002)).*

Concluding, PFHxA, its salts and related substances could be found as well in water and air as in sediments. Water and air are highly mobile compartments. Hence, a long-range transport of these PFCAs is likely. On the other hand, soil and sediments serve as depot for the persistent PFCAs.

Numerous direct and indirect sources of PFHxA, its salts and related substances contribute to the overall environmental emission of these substances. As described in chapter E.2, PFHxA, its salts and related substances are used in many applications and were detected in various consumer products such as textiles, carpets, upholstery, paper, leather, toner, cleaning agents and carpet care solutions, sealants, floor waxes, paints and impregnating agents. The substances are released into the environment during different life cycle steps via various emission pathways.

Direct sources include emissions from the manufacture and use of PFHxA or its salts and during the life-cycle of products that contain these substances as a constituent, impurity or residue. For example, fluoroelastomer-based products contain the ammonium salt of PFHxA as residue when the substance has been used as processing aid.

Indirect sources refer to the formation of PFHxA and its salts from their related substances (categorisation comparable to that of (Wang et al., 2014)).

Certain PFHxA-related substances, such as 6:2 FTOH, are volatile substances. They are released into air and waste water during manufacture of the substances themselves, from side-chain fluorinated polymers and during use and disposal of consumer articles treated with PFHxA-related substances. When emitted to the atmosphere, they can be degraded to PFHxA, too. As well the related substances as PFHxA are deposited on soil or surface waters. They are also washed out from the atmosphere via precipitation.

Although due to the large number of uses it is not possible to elaborate on every single one, information on emissions of the selected sources is generally applicable to other uses as well.

Data on emissions are available on a top-down approach. However, large data gaps exist on the downstream user level. PFHxA and related substances are used in various applications which are wide dispersive.

Therefore, if a quantitative approach is not applicable, a qualitative approach has been chosen for the description of emissions and mainly worst case estimates of environmental emissions are given based on environmental release categories according to ECHA Guidance R.16 (European Chemicals Agency, 2016a).

B.9 Exposure assessment

B.9.1 General Discussion on releases and exposure

Not assessed.

B.9.1.1 Summary of the existing legal requirements

Not assessed.

B.9.1.2 Summary of the effectiveness of the implemented operational conditions and risk management measures

Not assessed.

B.9.2 General Assumptions made for environmental exposure estimations

To the Dossier Submitter's knowledge, PFHxA itself is not used in products and articles. Therefore, PFHxA is the main degradation product from many (unknown) precursors. There are indications, that the degradation of the precursors occurs fairly rapid via forming 6:2 FTOH (see chapter B.4.1). 6:2 FTOH itself degrades to PFHxA. Therefore, the degradation of 6:2 FTOH to PFHxA is used as surrogate for the degradation of all non proteinbound precursors to PFHxA. Based on data from Liu et al. 2010, it was calculated that about 39 kg PFHxA is emitted by 1 tonne 6:2 FTOH.

Above that, from the extremely large amount of undetected unknown precursor compounds only a fractional part could be detected directely. By oxidising the conglomeration of substances to be investigated with OH-radicals, an increase of possible precursors of more than 50 % in minimum could be expected. If the PFHxA precursors are linked to proteins, assumingly only 1 – 5 % of the possible precursors are being detected without oxidation (e.g. Larsson et al. 2018, Dauchy et al. 2017). For exposure estimation the measured concentrations of none oxidised precursors and /or PFHxA is doubled. If a linkage to proteins is likely, the measured concentrations of none oxidised precursors is considered as 5 % from total amount of precursors.

If there is no or insufficient information regarding the environmental exposure available, default parameters for environmental release rates according to the Guidance on information requirements and Chemical Safety Assessment, Chapter R.16 were used. The environmental

release category (ERC) describes the broad conditions of use from the environmental perspective.

From the articels and products in use a global deposit of about 60 % in landfills is assumed (Geyer et al., 2017). Subsequentely, thogether with the articles and products the containing PFHxA, its salts and related substances are also deposited in the same share.

Based on data from Lang et al. 2016, the average annual release of PFHxA from degradation of perfluorinated C6 side chain polymers was assumed with 425 mg PFHxA/ ($t_{polymer}$/a).

For further rough estimations environmental concentration at European level the following modified standard values from the Guidance on information requirements and Chemical Safety Assessment, Chapter R.16 and values used in EUSES were considered.
Definition of default European area:
- Area of Europe: 4 476 000 km²,
- area fraction water: 10 % (scenario north – values representing Scandinavian countries),
- area fraction water: 1 % (scenario south – values representing countries like Spain),
- average water depth: 4 m.

That results in a fresh water body of 1 790 km³ (scenario north) and 179 km³ (scenario south).

Definition of default European marine surface water (coastal territorial waters):
- EU coastline: 68 000 km,
- width: 22.22 km (12 sm),
- average water depth: 10 m,

The regarded water body has a size of 15 110 km³.

- Area of North Atlantic (including the North Sea): 41 490 000 km², average depth 3 300 m,
- area of Mediterranian Sea 2 596 000 km², average depth 1 430 m,
- area of the Baltic Sea 413 000 km², average depth 52 m.

From manufacturing, formulating, using by several users and finally depositing the substances, the whole lifecycle of PFHxA, its salts and related substances (including its precursors and polymers) occurs widely distributed over the EU. According to the Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.16, in that case a fraction of 10 % of the whole used tonnage at EU level is attributed to the region by default while most of it (90 % by default) is attributed to the continental scale. Therefore, releases at continental scale will contribute as a background to the regional concentration. For further calculations it is assumed that about 80 % of precursors are found in water.

B.9.3 Manufacturing and uses at industrial sites

B.9.3.1 Environmental release

Due to their unique properties, perfluorinated substances are used for manufacturing of articles and products in large quantities in the EU. In general, two main methods are used for

manufacturing perfluorinated substances: direct fluorination (electrochemical fluorination, ECF) and telomerising (Prevedouros et al. 2006). The perfluorinated substances produced may then react further, manufacturing different derivatives and polymers (Kissa 2001).

By passing an electrical current through a solution of dissolved or dispersed organic compounds and a liquid hydrogen fluoride, the organic compounds become fluorinated. This reaction is extremely vigorous and mixtures of perfluorinated substances are produced. The compounds in the mixture are varying in the lengths of carbon chains. Branched chains may also occur. Telomerising is a process in which a perfluorinated molecule reacts with an unsaturated molecule. The compound formed through this reaction is called telomere. Fluorinated telomers are characterised by the molecule containing a perfluorinated carbon chain bonded to a short carbon chain, usually two carbon atoms with hydrogen atoms. Telomers are produced and used commercially as mixtures. Because of the restriction of C8 to C14 perfluorinated substances, manufacturers shifted in using perfluorinated short chain substances (C6 and lower) and perfluorinated ethers, in addition to the existing uses. Chains shorter than eight carbon atoms represent approximately two percent by weight in the telomere mixture. Therefore, further processing and cleaning steps are necessary to concentrate the desired C6 telomere molecules. Large quantities of the perfluorinated C6 side chained substances are further used for polymer manufacturing.

A survey among manufactures carried out to collect data on tonnages and uses of perfluorinated substances. Mainly, the given tonnages were average values between 2016 and 2018. The substances, which may degrade to PFHxA were grouped into major classes of chemicals in use. The maximum given amounts for a substance / class of chemicals stated by manufacturers were summarised, respectively. Using these summarised tonnages, a tonnage band for manufacturing [t/a] in the EU was derived for each substance class. Additionally, these data were compared with the public available data from ECHA[13]. The registered annual tonnages of PFHxA, its salts and related substances are summarised in Table 21.

Several single substances, like some esters with C6 perfluorinated (side-)chains are manufactured in tonnages far below 10 t/a. The bulk amount of single perfluorinated substances (87 %) are precursors for manufacturing of polymers. Thereof, 36 % are monomers used for polymerisation.

From the single substances recorded in these data, 7 % are used as surfactant in firefighting products (without dynax). Only a very small amount of these fluorinated single substances directly is used as surfactants in surface coatings and lacquers (< 0.5 %).

[13] https://echa.europa.eu/de/search-for-chemicals (last access: 13.12.2019).

Table 21: Used tonnages (= manufacturing + import – export) of substances with C6 perfluorinated (side-)chains in the EU.

	tonnage band [t/a] derived from max. tonnages manufactured in the EU	
	min	max
non polymeric Substances		
PFHxA and its salts	10	100
perfluorohexanesulfonic acids	100	1 000
aliphatics with C6-perfluorinated (side-)chain	100	1 000
6:2 fluorotelomer iodides	1 000	10 000
6:2 FT-alcohols	1 000	10 000
esters with C6-perfluorinated (side-) chain	10	100
6:2 fluorotelomer sulfonamides	100	1 000
6:2 fluorotelomer phosphates	1	10
acrylates with C6-perfluorinated (side-) chain	1 000	10 000
6:2 fluorotelomer substances (not further described)	10	100
further substances made with PF-C6	100	1 000
Polymers		
acrylate polymers with C6 fluorinated side chains	1 000	10 000
further polymers made with PF-C6	10	100

For estimation of environmental releases of PFHxA, its salts and related substances at manufacture (ERC 1) the standard estimation according to REACH guideline Annex R.16 was used. In this standard scenario a release of the substance of interest to air of 5 %, to water (before sewage treatment plant) of 6 % and to soil of 0.01 % of the annual tonnage manufactured is assumed.

Currently, no registrations are available for PFHxA itself. Therefore, direct releases of PFHxA into the environment by manufacture in the EU could not be assumed.

Ammonium perfluorohexanoate, the ammonium salt of PFHxA (APFHx) is imported as watery solution into to the EU. Therefore, no data for manufacturing are available. APFHx is used at industrial sites as processing aid to manufacture polymers, leading to inclusion into articles.

As well as 6:2 fluorotelomer iodides as 6:2 fluorotelomer-alcohols are intermediates to produce 6:2 acrylates (like 6:2 FTA as of 6:2 FTMA). These 6:2 acrylates are monomers for manufacturing of acrylate polymers with C6 fluorinated side chains. Applying the REACH guideline standard worst-case scenario, the annual emission of 6:2 acrylates to air may range between 50 – 500 tonnes, to water between 60 – 600 tonnes and to soil between 0.1 and 1 tonnes. However, the production of these monomers occurs under strictly controlled and enclosed conditions and mitigation measures are applied. The majority of substances is regained and recycled at the production process. Residues in wastewater and air are captured e.g. with activated carbon or absorber resins. Finally, the release of C6 fluorochemicals via WWTP and into the air is considered less than 10 t/a. For exposure estimations the release of C6 fluorochemicals at manufacture in the range of 1 – 10 t/a is assumed. As well the absorber materials, the sludge from the WWTS, as the air from the processes are exhausted and incinerated.

Concluding, the release of PFHxA, its salts and related substances seems to be very low during manufacturing process of these substances.

The main purpose processing perfluorinated substances is the manufacture of homo- and copolymers with C6 fluorinated side chains. Acrylate polymers with C6 fluorinated side chains are produced in the EU in a range between 1 000 and 10 000 tonnes per annum. The majority of these polymers serve as repellent and finishing agent in textile and paper industries. 57 % of the manufactured polymers with C6 fluorinated side chains are used in textile treatment, and 18 % in paper treatment. For additives in surface treatment baths and in-home fabrics about 5 % are used. In fire fighting products, as additive in lacquers and in not further specified products below 1 % of these polymers are applied, respectively.

The release of PFHxA, its salts and related substances into the environment from polymers is discussed in the following chapters (polymers and plastic materials, textiles, paper).

B.9.4 Polymers and plastic material

B.9.4.1 General information

Polymers are an extremely large family of very different materials with different characteristics, properties and uses. These materials offer specialized solutions to a wide range of requirements in numerous products, applications and sectors. Among the polymers fluoropolymes are high-performance materials.

The overall trend in global manufacturing and consumption of fluorotelomer and fluorotelomer-based polymers is a shift from ≥ C8 to C6 fluorotelomer chemicals (FluoroCouncil 2012 cited in Lassen et al. (2013)). Since the use of long-chain PFASs such as PFOA and its related substances has been restricted, manufactures shifted the production to short-chain fluorinated homologues (Luz et al., 2019). For fluorotelomer based products, this meant a shift to products that contained a six-carbon perfluoroalkyl moiety like 6:2 FTOH. In

a recent survey (Ökopol, 2018), Europe-based manufacturers, formulators, article assemblers, and associations provided information on the establishment of the C6 fluorotelomer technology.

A large group of fluoropolymers are polyacrylates with C6 perfluorinated side chains. Acrylates can be formulated as thermoplastic or thermosetting resins, or as water emulsion latexes. The use of C6 perfluorinated polyacrylates makes other materials water, oil and dirt repellent. Hence these polymers are used wide dispersively as textile and paper coatings and in surface coatings, lacquers and polishes, these acrylate polymers are also used as additives to give dyes more brightness and stability against UV radiation. They serve as wetting agents in waxes and polishes, as antifoaming compounds and as antisticking substances in cosmetics, too (BUND, 2015). Therefore, polyacrylates with C6 perfluorinated side chains are manufactured up to 10 000 t/a in Europe. Impurities in the polymers and the partial degradation of the polymers may lead to an emission of PFHxA, its salts and related substances into the environment. Emissions occur during service life and at the lifes end (deposition in landfills) of articles treated with or containing acrylates with C6 perfluorinated side chains.

APFHx is used at industrial sites as processing aid to manufacture fluoroelastomers. The annual consumption of APFHx in the EU amounts from 10 to 100 t/a. The ammonium salt may occur as impurity in these fluoroelastomers.

B.9.4.2 Exposure estimation

B.9.4.2.1 Environmental exposure

The annual tonnage of fluoropolymers sold on the EU market results in the European manufacturing plus the import, minus the export from the EU. According to (Amec Foster Wheeler Environment & Infrastructure UK Limited, 2017), 51 000 t of fluoropolymers were manufactured in the EU and 21 500 t were imported in 2015. Reducing this amount by 20 500 t fluoropolymers exported from the EU, finally 52 000 t fluoropolymers were sold on the EU market in 2015. This is about 20 % of the global annual demand on fluoropolymers. However, North America and the Asia Pacific region are major consumers of fluoropolymers with a market share together of about 60 %. Several sources from industries report a market growing on this sector with a rate between five and eight percent. (Personal information from industries, (Amec Foster Wheeler Environment & Infrastructure UK Limited, 2017; European Chemicals Agency, 2015a).

C6 side chain acrylates
Based on data evaluated from 2016 to 2018, in the EU 1 000 to 10 000 t C6 side chain acrylates were manufactured annually. Assuming for the C6 side chain acrylates the same shares between manufacturing, import and export as for fluoropolymers in general, the amount of import and export is roughly in balance. However, there has been a geographical shift of manufacturing and industrial uses of perfluorinated substances from North America, Europe and Japan to emerging Asian economies. China has become one of the largest manufacturer and user of such substances (Liu et al., 2015b; Meng et al., 2017; Wang et al., 2014). Many articles made or treated with perfluorinated substances are imported into the EU in large quantities from the Asia Pacific region. Therefore, the import of articles containing C6 side chain acrylates is much higher than the manufacture of such articles in Europe. As a consequence, a higher release of C6 side chain acrylates than the release calculated using

the above stated tonnage range is expected. The consequences of this gap are discussed in chapter B.9.4 for the textile sector exemplarily.

As well the C6 side chain acrylate polymers as their monomers may be released into the environment as well by manufacturing products and articles as using these treated articles and products at all life cycle stages. By degradation, the polymers and their monomers are a source for PFHxA release into the environment. For the use of monomers in polymerisation processes at industrial site (inclusion or not into/onto article) the default release factors according to ERC 6c can be applied for environmental release estimitation. So, manufacturing 1 000 to 10 000 t/a of C6 related polymers, 5 to 50 t/a of PFHxA precursors are released into air and water respectively at a service life of 10 years. Concluding, **10 to 100 t/a of PFHxA precursors** are released into the environment via C6 side chain (co-) polymers.

However, depending on the setcor of use, the amounts released are very variable. But, for the life span of the polymer containing article an assumption using default worst-case release factors for the respective environmental release cathegory is possible. About 75 % (treatment of textiles and paper) of the C6 side chain acrylate polymers are used wide dispersively for indoor products with low releases. Thus, a use of 750 – 7 500 t/a of these polymers could be assumed in this sector. Applying the default release factors, for an average service live of 5 years for these articles, 0.15 to 1.5 t/a of the fluoropolymers are released to water and air, respectively (ERC 11a). At anerobic conditions these polymers partially may degrade to PFHxA. Assuming the remaining 25 % of the manufactured polymers are used wide dispersively for outdoor products with low releases, the release factors for ERC 10a have to be applied. Following, annually 3.23 to 32.25 t/a polymers are released to water and soil respectively during an articles servicelife. At its end-of-life every article becomes waste. Waste management includes sewage treatment systems, landfills, incineration and recycling. About 60 % of articles are deposited in landfills globally (Geyer et al., 2017). Applying this amount to articles containing or treated with C6 side chain acrylate polymers, together with the respective articles 600 to 6 000 t/a of these polymers are deposited in landfills.

According to several authors, the half-life of a C6 side chain acrylate polymer ranges from 870 to 1700 years. Later works indicates a half-life of the fluorotelomer based acrylate polymers between 20 and 60 years. Modelling experiments from (Washington et al., 2009) demonstrated that more finely grained polymers in soils might have half-lives of about 10-17 years. Aditionally, the perfluorinated side chains may be dissociated from the backboon polymer partially. It is highly likely, that the formed fluorotelomer acrylate is subject to degradation to form n:2 FTOH, and further via a series of oxidation transitory intermediates to form n:2 fluorotelomer carboxylic acids (Russell et al., 2008). According to Washington et al. 2015, shorter perfluorinated side chains undergo a more rapid substitution in soil (see Chapter B.4.1). So, surface soils and landfills constitute a major global reservoir for PFAS (Washington et al., 2019). Consequently, these authors measured concentrations up to 4.26 µg PFHxA in leakage of landfills. For exposure estimations it is important to relate these results to the amount of source where the measured concentrations of PFHxA come from. Lang et al. 2016 composted carpet and clothing refuses treated with fluorinated acrylate polymers in bioreactors. For exposure estimations the Dossier Submitter normalised these results to the average content of fluorinated polymers in textiles. In average, per tonne acrylate polymers containing C6 side chains, up to 425 mg PFHxA are released mainly to water per year. Using this value for calculations, the annual release of PFHxA into the environment during service life of these polymers (about 10 years) is in the lower milligramme

range. However, from landfills an emission of PFHxA up to 2.55 kg/a could be expected from the 10 000 t of C6 side chain acrylate polymer used in the EU. Looking at these results, it is important to bear in mind that the estimated number of unreported releases could be much higher due to import of articles containing these polymers.

Conclusion: The partial degradation of C6 side chains from the acrylic polymers could be a source for release of PFHxA into the environment that should not be underestimated especially if large timeframes are investigated.

Fluoroelastomers containing APFHx
A large sector of use of the fluoroelastomers containing APFHx as impurity is used as seals and tubes in automotive and aviation. So, a wide dispersive outdoor use of these articles with a low release of APFHx could be assumed. Applying the default release factors for this release category (ERC 10a) and a service lifetime of 10 years, up to 0.65 t/a of the ammonium salt from the 10 to 100 t APFHx used in the EU are released to water and soil, respectively. Assuming, a low release of APFHx by leachate from landfills (60 % of articles are deposited in landfills) up to 387 kg may be released into water annually. Concluding, **0.1 to 1.0 t/a APFHx** could be released into the environment by the use of APFHx in fluoroelastomers. However, the estimated number of unreported releases could be much higher. The amount of articles imported into the EU containing fluoroelastomers or other products with APFHx as impurity is unkown.

B.9.5 Textiles

B.9.5.1 General Information

One of the largest sectors using perfluorinated substances is the textile manufacturing sector. In the European Economic Area (EEA) more than 61 000 installations that may use or emit PFAS working in this sector (Goldenman, 2019). The most important uses in the textile sector are uses for household textiles (e.g. furniture, carpets, curtains, awnings), for occupational, for outdoor wear and for clothing.
In the EU 380 000 t of carpets and other textile floor coverings were used in 2018. 247 000 t (65 %) are manufactured in the EU (calculated based on data from United Nations Commodity Trade Statistics Database, 2019). In 2015 6.4 million tonnes of clothing were used in the EU. That contains a share of 95 000 t of occupational wear (Rijkswaterstaat, 2017). 1.6 million t were manufactured in the EU and 4.8 million t were imported into the EU.
For treating textiles made in the EU up to 10 000 t/a of perfluorinated compounds are used. About 5 700 t/a thereof are polyacrylates with C6 perfluorinated side-chains. 4 300 t are substances that fairly easy degrade to PFHxA, like 6:2 FTOH or polyfluoroalkyl phosphate esters.
In industrial finishing processes, the side-chain fluorinated polymers (SFPs) are applied as a thin film on the fabric surface by a so-called pad-dry-cure process (Gremmel et al., 2016). In this process, the untreated fabric is passed through an application bath containing the SFPs and is then squeezed between two rollers to remove excess liquid, followed by drying and curing in an oven at temperatures up to 180 °C. The curing promotes the cross-linking of the polymer to the fabric. Typically, 0.2 – 0.5 % (w/w) of polymer is applied to the fabric, resulting in a fluorine content of 0.04 – 0.25 % (w/w) (BfR, 2012).

B.9.5.2 Exposure estimation

B.9.5.2.1 Environmental exposure

European textile treatment – generic overview
About 5 700 t/a of polyacrylates with C6 perfluorinated side-chains and 4 300 t of substances that fairly easy degrade to PFHxA (like 6:2 FTOH or polyfluoroalkyl phosphate esters) are used for textile treatment in the EU (derived from stakeholder consultations). Due to the large amount of industrial sites for textile treatment in Europe, the release of PFHxA, its salts and related substances by manufacturing of fabrics, garment and textiles is wide dispersively.
The release of PFHxA from the side chain fluoropolymers is considered very low during the textiles service life of about five years (median from different sector of uses). However, the used 6:2 FTOH or polyfluoroalkyl phosphate esters may be released into air and water during articles service life. According Liu et al. 2010, 6:2 FTOH biodegradation in mixed bacterial culture was rapid with an estimated half-life of 1.3 d. The sum of the stable products at steady state in soil was significantly less in the flow-through system (23 %) than in the enclosed closed system (56 %) (occurrence of PFHxA in the flow-through system: 4.5 mol%; occurrence of PFHxA in the flow-through system: 8.1 mol%). Due to the volatile losses, more than the half of the initially used substances that fairly easy degrade to PFHxA may be lost to air and water during service life. Polyfluoroalkyl phosphate esters also may degrade to or via 6:2 FTOH. 6:2 FTOH itself is semi volatile. From textile articles manufactured in the EU, about 430 t/a 6:2 FTOH are released into air and water during the service life, taking the above mentioned results from (Liu et al., 2010b).
Based on data from (Liu et al., 2010b) and assuming a PFHxA precursor degradation following the first order kinetics, one tonne of the easily degradable substances may emit 39 kg PFHxA kg/a. Hence, by easy to PFHxA degradable textile treatment substances, 17 t PFHxA may be released to the European environment annually. Due to its high water solubility the majority of this amount is getting into water, finally. From deposition of these textiles about 10 t PFHxA per year are released from indirect sources.

Clothing in general
Clothing are finished with durable water and dirt repellents (DWR), like polymers with perfluorinated side-chains or polyfluoroalkyl phosphate esters and n:2 fluorotelomer alcohols. Before the restriction of C8 perfluorinated substances was introduced, finishing agents with C8 side chain polymers were used. Exemplarily, Figure 5 summarises the possible mechanisms for diffuse emissions of DWR-related substances during the garment's use-phase. This includes the wash-out of water-soluble residuals such as PFOA, the evaporation of volatile residuals such as 8:2 FTOH and the potential degradation of the polymer by UV-light, abrasion, and washing. C6 perfluorinated substances act in the same way.

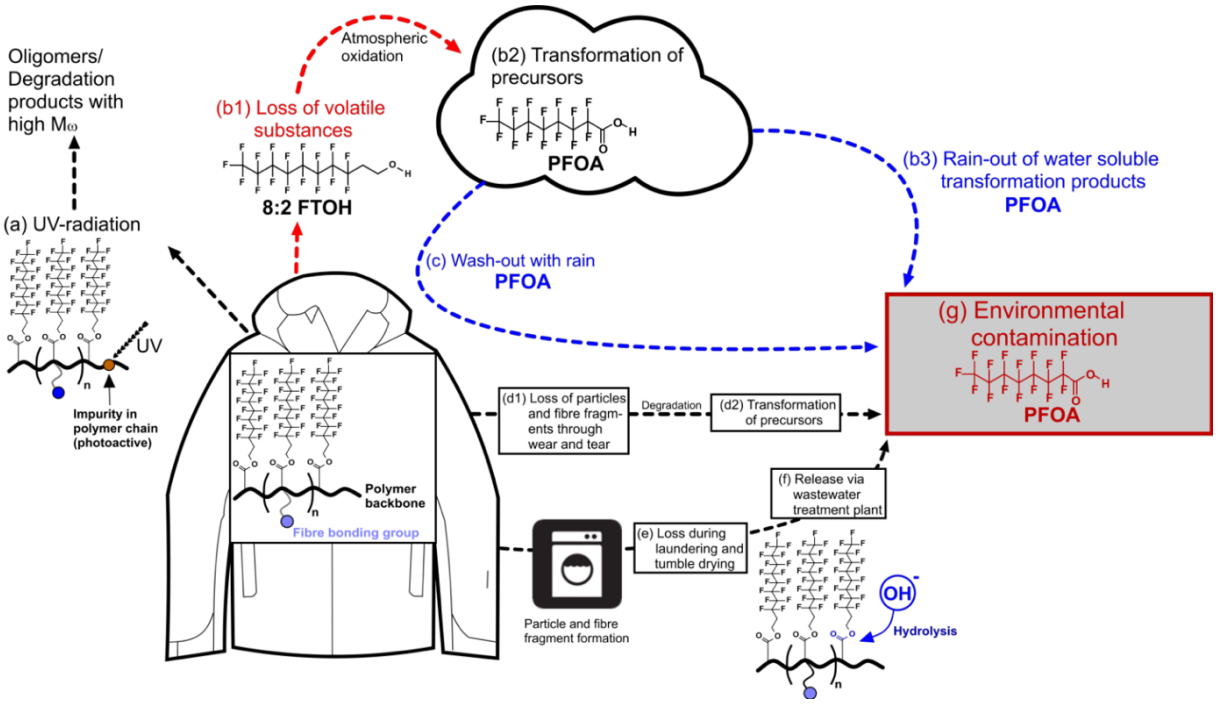


Figure 5: *Possible mechanisms for the diffuse emissions of DWR-related substances during the garment's use-phase. Reprinted from Environment International 94, H. Holmquist,S. Schellenberger,I. van der Veen,G.M. Peters,P.E.G. Leonards,I.T. Cousins, Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing, 251-264., Copyright (2016), with permission from Elsevier.*

In 2015 1.6 million tonnes of clothing were manufactured in the EU. However, 6.4 million tonnes of clothing were used in the EU. That implies, 4.8 million tonnes were imported into the EU (Rijkswaterstaat, 2017), mainly from the Asia-Pacific Region (China, Vietnam, Indonesia). From the total 6.4 million tonnes of clothing a share of about 95 000 t of occupational wear and about 150 000 t of outdoor clothing are assumed.

Fabrics as well as the garments are frequently treated with perfluorinated substances to provide water and dirt repellency. Which finishing agents are being applied depends on the intended use and the design of the garment. Occupational wear and outdoor clothing are treated more intensely and preferably with perfluorinated side chain polymers than everyday clothes. For 95 % of the on the European market available textiles production steps are outsourced abroad partially or even entirely. So, emissions of PFHxA, its salts and related substances via manufacture of textile fibers and fabrics are considered as very low in Europe. Otherwise, the abroad use and finally the content of the perfluorinated substances is difficult to predict (Greenpeace, 2012).

For textile treatment both, substances that fairly easily could be removed from the fabric such as n:2 FTOHs or n:2 FTMA and on the other hand substances that are firmly connected to the fibers like polymers are in use. Several authors investigated the extractable content of perfluorinated substances in fabrics (see chapter E.2.11). The range of measurements goes from below the detection limits up to 8 500 µg 6:2 FTOH /kg garment and up to 546 µg PFHxA /kg garment. These values are strongly interlinked with the easily removable substances because, as mentioned above, curing with the polymers promotes the cross-linking to the fabric. Therefore, these substances are not as easy extractable. Typically, 0.2 – 0.5 % (w/w) of fluoropolymers are applied to the fabric (BfR, 2012).

Volatile substances like n:2 FTOHs are released into air and water entirely at the clothing's service life by washing and wearing the garments (Tissier et al., 2001). However, not all precursors are volatile at all. Therefore, based on the investigations from Liu et al. 2010, the loss during the service life is considered with 50 %.
For the further worst case estimations the median value of the reported minimum and maximum concentration are used.
During the two years service life of clothing manufactured in the EU, between 26 and 64 t/a C6 related polymers, 43 to 924 t/a precursors and 0.3 to 59 t/a PFHxA may be released into the environment by direct emission. The release of PFHxA from polymerdegradation is assumed with < 2 kg at service life and from landfills.
In contrast to that, making the same assumptions, from imported textiles 5 to 12 t/a polymers, between 116 and 2 466 t/a precursors and about 1 to 158 t/a PFHxA may be released into the European environment. Due to a short service life of clothing the majority of the environmental releases results from deposit of the textiles.

The release of PFHxA from polymer degradation is assumed with < 6 kg at service life and from landfills. The emitted amount of PFHxA and of the precursors by imported garments is about three times higher than the release by garments manufactured in the EU. The following discussed releases of C6 polymers, of precursors and of PFHxA itself from outdoor clothing and from occupational wear represent only a part from the total amount of clothes used in the EU. The release e.g. from daily wear, socks and hosieries or from sports wear are not discussed.

Outdoor clothing
For release estimation the measured concentrations mentioned above are used. Non polymeric substances for garment treatment are also bound to the fibers. However, volatile substances like n:2 FTOHs are released into air and water entirely at the clothing's service life by washing and wearing the garments (Tissier et al., 2001). Therefore, standard release factors according ERC 11a are used, too. For outdoor clothes a service life up to five years is considered (Tissier et al., 2001). Using these data related to the annual use of 150 000 t of outdoorclothes, an annual release of 4 - 86 t/a 6:2 FTOH could be assumed. This indirectly results in an environmental release of PFHxA. Finally, the summary of direct and indirect emissions of PFHxA from outdoor clothes during the service life and from landfills is 0.03 to 6 t/a.
Calculating with data from Lang et al. 2016, the annual release of PFHxA from outdoorclothes by polymer degradation in landfills is negligible (below 200 g/a).

Occupational wear
There are no special investigations of occupational wear textiles regarding the content of PFHxA, its salts and related substances known. However, it could be assumed that more polymers than easy extractable substances are used for oil repellent clothes. However, the quality of clothes wearing in the medical sector are comparable to outdoor clothes. Therefore the measured concentrations of the compounds in outdoor clothes are used for environmental release estimation by occupational wear.
The typically to fabric applied polymer concentration 0.2 – 0.5 % (w/w) (BfR, 2012) was used. For occupational wear a service life of two years is considered (Tissier et al., 2001). These data are related to the annual use of 95 000 t of outdoor clothes in Europe. So, 3 -55 t/a 6:2 FTOH are released into the environment. In summary, 0.2 to 3.5 t/a of PFHxA are released into the environment during the service life of occupational wear by direct and indirect emission.

Carpets and other textile floor coverings
In 2018, about 380 000 tonnes of carpets were imported and about 180 000 t were exported.[14] So, about 200 000 t of textile floor coverings were used in Europe. The total demand on carpets in Europe shares into 55 % for residential buildings, 39 % for non residential buildings and 6 % for other sectors like shipbuilding, automotive, trains, and aviation. Annually 1.6 million tonnes of carpets are becoming waste. Thereof 60 % are deposited in landfills, 37 % are incinerated and only 3 % of the textile floor coverings are recycled (European Public Health Alliance, 2016).

The concentration of 6:2 FTOH in carpets and other textile floor coverings reported by different authors (see chapter E.2.11). The measured precursor content is between 170 and 2 200 µg/kg and PFHxA was measured in concentrations between 0 and 11 µg/kg. The compounds are released from carpets during its service life by degassing, by cleaning and by development of house dust. For textile floor coverings a service life up to 15 years is considered. Calculating the release of 6:2 FTOH and PFHxA as described for occupational wear accordingly, during service life of carpets 2 -30 t/a of 6:2 FTOH are released, resulting in an indirect release of up to 1.2 t PFHxA, annually. In total about 2 t PFHxA per year are released via direct and indirect emissions. The share resulting from degradation of polymers is again negligible (a few gramm per year).

Industrial textile fabrics:
An important sector of use for PFHxA, its salts and related substances are textiles for industrial uses. European producers are world leaders in markets for technical/industrial textiles and non-wovens (industrial filters, hygiene products, products for the automotive and medical sectors, etc.), as well as for high-quality garments with a high design content. The tonnage used in Europe gained by backcalculation using data for industrial textile fabrics for 2018 from UN comtrade database and the average prime costs for truck tarpaulin fabrics. So, the use of about 100 000 t/a could be assumed in Europe.

On behalf of the German Environment Agency various industrial fabrics (28 samples in total) were investigated for per- and polyfluoroalkyl substances like PFHxA, 6:2 FTOH and 6:2 FTS (Janousek et al., 2019; Knepper and Janousek, 2019). The samples included seat covers (furniture upholstering, bus /train seat upholstering, car seat upholstering; n = 11), covers for truck trailers (n = 3), covers for maritime applications (e.g. boat cover, seat cover, bimini tops; n = 5), awnings and tarpaulins (e.g. marquee awning, party tent; n = 9). All samples were collected between October 2016 and August 2017 and analyzed as soon as possible. The following limits of quantifications were determined: for 6:2 FTOH 40 µg/kg, for PFHxA and 6:2 FTS 2 µg/kg. PFHxA was found in one seat cover, two maritime covers and five marquee awnings. Concentrations of PFHxA ranged from 2.4 – 18 µg/kg (average 7.7 µg/kg) in aqueous extracts and 2.6 – 18 µg/kg (average 9.9 µg/kg). 6:2 FTOH was found in one seat cover, one tarpaulin for truck trailers, two maritime covers and three marquee awnings with concentrations ranging from 40 to 790 µg/kg (average 350 µg/kg). 6:2 FTS was not detected above the LOQ in any of the samples.
Using the minimum and maximum values, from the study above and applying the default release factors for a wide dispersive use of outdoor products with low releases (ERC 10a) over

[14] Comtrade, U. N. (2018). UN Comtrade database. *UN Comtrade Online*.

a service life of ten years, 2.8 to 7 t/a C6 related polymers, up to 0.2 t/a precursors and up to 0.03 t/a PFHxA are released from industrial fabrics into water and soil.

B.9.6 Paper

B.9.6.1 General information

Side-chain fluorinated polymers are used in the surface treatment of paper and packaging to impart grease, oil and water resistant properties, especially for food contact materials (plates, food containers, bags and wraps) but also for non-food applications (folding cartons, containers, glossy papers, carbonless forms and masking papers) (Federal Office for the Environment, 2009).
The most important application field is the production of paper and board for the packaging and preparation of food. The PFHxA related substances are used in the paper pulp as well as for surface refining. They are applied to create water- and grease /oil-repellent paper products, which can be used at higher temperatures without burning and adherence to food or other materials. Typical articles are baking paper, packaging of pet food, packing of take away food, table cloths, microwave popcorn bags, cupcake forms and sandwich papers (Blom and Hanssen, 2015; Borg and Ivarsson, 2017; Jensen et al., 2008; UBA, 2018).
Evaluating Data from UN comtrade database about 47 000 t of grease proof paper were used in Europe in 2018. According to industries, the content of side-chain fluorinated polymers is about 0.3 – 1.5 %, depending on the specific purpose of the treated material (stakeholder consultation).

B.9.6.2 Environmental exposure

The release of PFHxA and its precursors as well as perfluorinated side chain polymers at manufacturing of grease proof papers is considered as low, due to closed loop of materials and the recycling of treatment emulsions. According to industries, the content of C6 side-chain fluorinated polymers in paper is about 0.3 – 1.5 % (141 -705 t/a), depending on the specific purpose of the treated material (stakeholder consultation). PFHxA and 6:2 FTOH are only found in few samples of grease proof papers (in about 70 %). The median values from the literature described concentrations, are 5 000 µg/kg C6 precursors and 7 µg/kg PFHxA (summarising data from (Bokkers et al., 2019). The measured concentrations base on non-oxidative sample preparation.

In general, the service life of grease proof paper materials is very short – from days to a couple of weeks. Therefore, a share of 10 % is assumed for the release of easily extractable substances per year. From grease proof papers **0.235 to 0.470 t/a PFHxA** are released from direct and indirect sources during its life cycle in Europe. Via landfills about 2.5 t PFHxA per year are released into the environment. The share resulting from degradation of polymers is negligible (a few grammes per year).

B.9.7 Firefighting Foams

B.9.7.1 General Information

PFAS containing firefighting foams are usually used to extinguish liquid fires (class B), such as large storage tank fires and aviation accidents. For firefighting foams in general fluorosurfactants like PFHxA and 6:2 FTOH or perfluorinated sulfonic acids are in use. Only in a few cases polymeric substances may be added to the foam concentrate. In newer foams poly- and perfluorinated fluorotelomere surfactants and polyfluorinated alkyl betaines (PFAB) and other proteins are used (see Annex E.2.3.2 Use and functions). Additionally, several glycol ethers, probably with poly- and perfluorinated side chains, are added to concentrate. Between 1 500 – 3 000 t/a of fluorosurfactants are placed on the market in Europe within foam concentrates.

B.9.7.2 Environmental exposure

The formulation of fire-fighting concentrates at industrial sites occurs under strictly controlled conditions. Therefore, the release of PFHxA and its related substances is assumed to be below 100 -250 kg/a during formulation.

In 2014, the Swedish Chemicals Agency investigated several fire fighting foam concentrates from various manufacturers. Samples were taken from open containers from users as well as from distributors or intact containers and were diluted in water and methanol. The investigated samples had a broad concentration variety from 76 to 14 217 µg PFHxA / kg concentrate. The presence of PFHxA was associated with remaining residues from the manufacturing process or due to storage degradation of the precursors.

The concentrates are diluted with water for ready to use foams with the final concentration of 1 or 3 % of the concentrate. A synthetic foam concentrate intended for dilution at 3 % into water contains PFCAs and / or their related substances from 0.9 – 1.5 % (mean 1.2 %) of the total weight (Pabon and Corpart, 2002). So, the ready to use foam includes usually up to 0.45 % fluorosurfactants (Sontake and Wagh, 2014). The share of PFHxA from total fluorosurfactant content varies between 0.9 to 61 % (median 17 %). For further estimations the median value of 1 328 µg / kg is used.

For professional firefighting an annual use of fluoro-surfactant containing firefighting foam concentrate of about 12 500 t was estimated in Europe (personal communication Blunk, University of Cologne 2017). Taking the median concentration of PFHxA in foam concentrates from the KEMI-study, 16.6 kg PFHxA are released into the European environment annually by professional firefighting operations. In Germany about 2 000 t/a of foam concentrate is demanded for professional firefighting. That results to an estimated annual release of 2.7 kg PFHxA (calculating with the values from the KEMI study).

In a survey German local volunteer fire brigades were asked for their use habits of firefighting foams in field operations (Keutel and Koch, 2016). Because only seven fire brigades answered the questions, the results can give only an indication for the local use of fire firefighting foams. However, personal communications with several volunteer firefighters support the data presented. The use of perfluorinated substances in the AFFF foams by volunteer fire brigades already has been reduced within in the last years from 3 or 1 % to 0.1 % foam solutions. At their operations fluorinated foams mainly were used as surface-active agent in a

concentration of 0.1 %. At each operation in average about 1 150 kg ready to use foam was used. Calculating with the median concentration of 1 328 µg PFHxA/kg concentrate from the KEMI-study, 1.5 g PFHxA are released into the local environment at each fire fighting operation. Foams with perflourinated substances are deployed at about 20 operations per year by a volunteer fire brigade. In Germany exist about 24.000 volunteer fire brigades. This results in a direct wide dispersive release of about 0.73 t PFHxA by the volunteer fire brigades in Germany per year. Assuming roughly the same ratio between professional and volunteer fire operations in Europe as in Germany, about 4.6 t/a PFHxA are released into the environment at fire operation by volunteer brigades. Different from professional firefighting, often it is not possible to collect and to recycle the extinguishing water.

However, PFHxA in fire-fighting foams is assumed to be a residue and occuring from PFHxA precursors and other PFCAs which are intentionally added as fluorosurfactants. Therefore, releases of PFHxA are presumably higher due to usage of fire-fighting foams as such precursors are assumed to degrade to PFCAs as PFHxA. Studies by Dauchy et al. (2017) and Larsson et al. (2018) used oxidation to transform PFCA-related substances into the end-stage products in samples of fire-fighting foams. Thus it is possible to estimate the overall contribution of PFHxA and its precursors in AFFF to exposure in the environment. The average PFHxA concentration of three oxidized foams was 314 880 µg /L (Dauchy et al., 2017; Larsson, 2018). Looking at the percentage of measured PFHxA concentrations, it appears that in protein free firefighting foams about 50 % of PFHxA precursors are not detetectable without the oxidation step. Investigating protein containing foams even 99 - 95 % of the precursors are not covered without oxidation. Amending the by KEMI measured PFHxA concentrations with the data from Dauchy et al. (2017) and Larsson et al. (2018), 520 kg PFHxA (chemically bound in several precursors) are released into the environment by professional uses in Europe, annually. However, the bulk of 143.8 t/a is released wide dispersively by volunteer fire brigades in Europe (Dauchy et al., 2017; Larsson, 2018).

Concluding, **4.6 to 144.4 t/a PFHxA** (chemically bound in precursors) are released with extinguishing agents by professional and skilled workers into the European environment.

Fire-fighting foams will not be incinerated during an event of fire. As a worst case estimate, 100 % of the remaining AFFF will be emitted into the environment. In average 48 g PFHxA may be released to local environment at each fire fighting operation. Therefore, large concentrations of the surfactants were found locally after fire-fighting operations, mainly in water. (Hähnle and Arenholz, 2011) studied per- and polyfluorinated surfactants in different water samples after cases of fire. The primary polyfluorinated substance used as fluorsurfactant and known as potential precursor for PFHxA were measured with concentrations of up to 6 900 µg/L in the extinguishing water. PFHxA was detected after the cases of fire in the discharge into the sewage treatment plant, in water bodies, in extinguishing water and in the treated effluent of a sewage treatment plant. After one case of fire PFHxA concentration was 3.3 µg/L in an effluent into water bodies.

A quantification of samples downstream of sites where AFFF were used showed the important impact of local sources. Dauchy et al. 2017 measured PFHxA concentrations in water samples from groundwater and surface water close to an oil storage depot, an international civilian airport, a military airport and a training center for firefighters. In samples of all sites, PFHxA could be detected, within surface water close to the training centre for fire fighters and downstream of the discharge pipe showing the highest concentration (up to 178 ng/L).

However, large amounts of AFFF are stored in stock and will only be used in exceptional cases. No information is available on these amounts of AFFF in stock and the actual fraction thereof used. It is not always clear, whether concentrations of PFHxA and PFHxA-related substances originate from the use of old generation AFFF or new generation AFFF. Due to the long keepability of the concentrates, the stocks often still contain PFOA and related substances. However, some manufacturers formulated their foams already with PFHxA and related substances in the past. Therefore, even if it originates from old generation AFFF, it can be assumed that emission from new generation AFFF will exceed released concentration of PFHxA and PFHxA-related substances due to structural shift of fluorsurfactants based to C6 chemistry.

B.9.8 Building materials (incl. laqueurs)

B.9.8.1 General Information

Fluorinated substances are aplicated in laqueurs, coatings and paints to a large amount of very different building materials to improve flow, wetting, and levelling. It is primarily in water-based paints where these properties are required and PFASs can be present at concentrations of about 0.05 percent (European Chemicals Agency, 2018a).

B.9.8.2 Environmental exposure

There are currently no sufficient data available on tonnages used in those applications and for the release of perfluorinated substances from building and construction. In a stakeholder consultation the use of fluorosurfactants in coatings that are used in building material treatment were mentioned without further details and tonnages. Once, the use of 100 - 1 000 t/a in "manufacture of plastics products for including compounding and conversion in inks and films, for manufacture of furniture, for building and construction work, for manufacture of firefighting foams and paper finishing" was stated. But the shares of the different sectors of use are unknown. Therefore, a quantitative exposure assessment is not feasible. Coatings with fluorosurfactants especially are used outdoors. So, a direct release of perfluorinated surfactants from the sector building and construction into the environment is considered as very likely in significant amounts.

B.9.9 Cosmetic products

B.9.9.1 General Information

CosIng is the European Commission database for information on cosmetic substances and ingredients. A search using the database did not identify PFHxA as an intentionally added ingredient of cosmetic products. Instead, the search identified more than 70 perfluorinated substances e.g. polyfluoroalkyl phosphonic acids (PAPs) which according to CosIng, serve as emulsifiers and surfactants. Other PFAS (e.g. perfluorinated polymers, ethers and esters) are added to cosmetic products for binding, bulking and skin/hair conditioning purposes. According to a recent study by the Danish Environmental Protection Agency, 0.7 % (78 out

of 11 108) cosmetic products contained fluoroalkyl substances or other fluorinated compounds (Brinch et al., 2018).

A literature search identified only a few studies which analysed the PFHxA content of cosmetic products, whereas no studies report on FTOH 6:2 concentrations. It is to note that product selection in all three studies focused on cosmetic products with declared PFAS content. A recent study by the Danish EPA found PFHxA in 15 of 18 products, whereas a study conducted in Sweden detected PFHxA in 10 of 31 products (Brinch et al., 2018; Schultes et al., 2018). An older study from Japan sampled cosmetic products in 2009 and 2011 (Fujii et al., 2013). In this study also sunscreens were analyzed and 18 of 23 products contained detectable levels of PFHxA. The studies had in common that high levels (> 1mg/kg) of PFHxA were measured in foundation make-up, which are leave-on cosmetic products with direct and prolonged skin contact. As it is very likely that PFHxA is dermally absorbed it has to be considered that cosmetic products may pose an additional relevant source for human exposure. Since PFHxA is not an ingredient of cosmetics, it is probably an impurity in and /or a degradation product of intentionally added PFAS. This assumption is in line with finding of the Swedish study in which a high PFHxA level in foundation make-up seems to be correlated with a high concentration of PAP (more than 100-fold higher). In addition, there is no data on the stability of PFAS such as PAP during dermal application under real-life conditions involving solar UV light radiation, skin bacterial metabolism, and skin metabolism (see Table 43 in Appendix B.4.4).

B.9.10 Chrome plating

B.9.10.1 General Information

For chrome plating 6:2 FTS is used as a surfactant mainly as a mist suppressing agent. Emissions of 6:2 FTS during plating processes originate e.g. from the rinsing steps between the electrolytes and from replacement of used solutions (Blepp, et al., 2017). In Germany about 150 t/a of fluorosurfactants are used as well for decorative as for hard chrome plating. Based on Germanys share of the European GDP, for the EU a use of about 800 t/a was derived (tonnage band 100 – 1000 t/a).

B.9.10.2 Environmental exposure

Chromate solution containing the mist suppressing agent has a limited usage lifetime and has to be changed regularly. The used solution is treated as chemical waste, where chromium is isolated. The wastewater is treated in WWTPs. Release of 6:2 FTS from chrome plating process into the environment is possible via industrial waste water and air. 6:2 FTS has a low adsorption potential and is difficult to remove during water treatment processes and will be released in receiving waters. Furthermore, the substance will be degraded to PFHxA (see chapter B.4.1.2). Exposure to the environment is also possible via waste from the chrome plating processes (e.g. chromium hydroxide sludge), which may contain 6:2 FTS. Another, in the literature so far barely mentioned, emission source of 6:2 FTS could be the process of dechroming. 6:2 FTS was detected in demetallisation agent and degreasing agent (Willand et al., 2019). As these agents as well as the rinsing waters from these processes are mostly not treated PFAS-specific, 6:2 FTS will be released to waste water.

According to the German national metal plating association (ZVO), in Germany about 200 companies are working in the sector of hard chrome plating, about 400 in the sector of decorative chrome plating and about 30 in the sector of plastic products chrome plating. Due to the use of stronger acids for hard chrome plating the concentration of 6:2 FTS is about 2.5 times higher concentrated than for decorative chrome plating. For plastic products chrome plating two separated plating steps are necessary. For one step the low concentration of surfactants as for decorative plating is used. For the second step a similar high concentration is necessary as for hard chrome plating. The ZVO states that in the case of Germany only 20 % of the applied surfactant is lost (Brunn Poulsen et al., 2011). Applying these share of 20 % 6:2 FTS is lost to the in the EU used amount of the surfactant, about 160 t/a **(min 20, max 1 000 t/a)** are released by chrome plating into water. Calculating with the assumed surrogate for the annual degradation of precursors to PFHxA, it is assumed that about 6 t/a of PFHxA **(min 1 t/a, max 8 t/a)** are released into water. The releases of surfactants into air by spraying are unknown. However, it is highly likely that the major part of the surfactants is released via waste water. A subsequent service life is not relevant.

B.9.11 Inks and photographic uses

B.9.11.1 General Information

C6-based fluorinated surfactants are used in small tonnages in photographic equipment or in coatings when manufacturing conventional photographic films (Stakeholder Consultation, 2018).

Perfluorinated substances are added to printing inks for hydrophobisation of surfaces, for example of textiles, paper, and glass, building materials or adsorbents. In addition, it is possible for them to be used as interface promoter or emulsifier or viscosity reducer in paints, coatings or adhesives. (UNEP, 2012b). During stakeholder consultation it was confirmed that C6 based short-chain fluorinated surfactants are used in some water based inkjet inks and latex inks. Only these fluorinated surfactants provided the required performance of the inks. The use of about 15 t/a of these substances in Europe is assumed as worst case estimation.

B.9.11.2 Environmental exposure

The exact amount of the in photographic equipment used surfactants and the release rates at manufacturing and throughout the life cycle are unknown. However, due to small used tonnage in this sector the release of PFHxA and its related substances is considered as very low.

Many PFHxA precursors show certain volatility. Therefore, for estimation of PFHxA release from printing inks, the CPA SpERCs for volatiles are used. According to SpERC CPE4 (formulation of water borne coatings and inks in large scale), 330 kg/a PFHxA precursors (0.022 % of the used tonnage) are released to air during formulation. With the consumer applications (according CEPE 20) about 150 kg/a of the precursor are released into the air. When a loss of about 50 % of the surfactants during the life cycle of the imprinted papers is assumed, about 7.4 t/a of the precursors are released into air and from air into water in a further step. Considering a deposit of 60 % of the imprinted papers to landfills and a total release of the perfluorinated surfactants, an annual release of 4.5 t of the C6 based short-

chain fluorinated surfactants (= 174 kg/a PFHxA) could be assumed. Considering a tonnage band from 10 to 100 t/a of C6 precursors used in printing inks an environmental release between **8 and 80 t/a** could be assumed.

B.9.12 Semiconductors

B.9.12.1 General Information

Short-chain PFASs are used as chemical processing agents in microchip production. Semiconductor manufacturing is performed in a cleanroom. However, they are possibly emitted from the process. Furthermore, short-chain PFAS materials are presumed to be contained in some fluoropolymers and fluoroelastomers which might become part of semiconductor manufacturing equipment and fabrication plant-related infrastructure (Stakeholder Consultation, 2018). Short-chain PFASs are included in anti-reflective coatings (ARC) and photoresist formulations.

B.9.12.2 Environmental exposure

The overall amount of PFASs used in semi conductor industry is assumed to be < 10 t per year (Stakeholder Consultation, 2018). Short-chain PFASs possibly may be emitted from the process of microchip manufacture. The, into the environment released amount of PFHxA, its salts and related substances is unknown. However, the release is considered as very low. Most ARCs are solvent based and drained in a solvent collection system, which stream is treated off site via distillation to reclaim solvent constituents while the residue is incinerated. It cannot be excluded that fractions of PFASs are carried over into further steps along the subsequent (development, cleaning) processes and enter wastewater stream. Moreover, as some ARCs are water based formulations, they are drained into waste water (Stakeholder Consultation, 2018). (Lin et al., 2010) studied effluents from a semiconductor plant in Taiwan and measured a concentration of 71.5 ± 16.5 ng/L PFHxA with concentrations of other PFASs being considerable higher (e.g. PFOS: 5663.3 ± 427.4 ng/L). Indicating a complete switch to short-chain PFASs not being implemented at that time (World Semiconductor Council (WSC), 2019). In a more recent study analyzing PFAAs concentrations in effluents, influents and sludge from industrial waste water treatment plants in Korea effluents of a semiconductor plant contained a sum of 65.9 ng/L PFAAs (eleven PFAAs measured including PFHxA) including 17.7 ng/L PFOA and 22.6 ng/L PFOS (Kim et al., 2016).

Worst case assumptions regarding concentration levels of perfluorinated substances in ARCs are 0.1 % wt/wt. The release of PFHxA, its salts and related substances from semiconductors during the service life is considered as very low.

B.9.13 Mixtures for consumer uses

Due to their advantageous characteristics, perfluorinated substances have been produced and used since the 1950s. PFCAs are not only used for industrial uses. These substances are used in various mixtures intended for end-use by consumers. Such consumer mixtures are, for example, (water)proofing agents, ski or floor waxes, car care and polishes and cleaning

products ((Jensen et al., 2008); (Swedish Chemicals Agency, 2006); (Swedish Chemicals Agency, 2015b); (Knepper et al., 2014); (Posner et al., 2013)). The substances most commonly used in products are fluorotelomers as stated during stakeholder consultations. They are used either as independent active ingredients or as a component in more complex matrices (like in waterproofing agents).

Perfluorinated substances are used in low concentrations in cleaning agents such as floor polish, waxes, window cleaning agents, and car care products. In such products 6:2 FTOH up to 26 mg/kg and up to 1.5 mg/kg PFHxA were detected. Ski waxes that are used to improve slide properties of the skis on snow also containing PFCAs. In ski waxes up to 1.7 mg/kg PFHxA were reported. Further mixtures used by consumers are impregnating sprays to regain or to keep the water-, oil- and dirt repellency of shoes and textiles. In these sprays 6:2 FTOH was measured in concentrations up to 1 800 mg/kg (see also Table 30 "Reported concentrations of PFHxA and 6:2 FTOH in consumer mixtures" in section E.2.9.2). Typical concentrations in articles (e.g. impregnated textiles, treated skis) are below one percent. Polish agents contain fluorinated chemicals primarily to give them good flow properties. Surface improvement agents like spray polish are used after polish has been applied to improve the polish film. Products that maintain hard wax surfaces and also have a cleaning effect, may contain fluorinated compounds, too.

There is only limited information available about used tonnages of the mixtures and of the perfluorinated substances. However, the potential release of PFCAs from consumer mixtures should not be underestimated.

B.9.13.1 Environmental exposure

The manner of application of the several consumer mixtures leads to a direct release of the containing perfluorinated substances into air, water and soil.

For example, cleaning products and polishes are used wide dispersively and are directly released into wastewater and into WWTPs. In the WWTPs the perfluorinated C6 side chained substances are degraded fairly quickly. However, by degradation of these substances persistent PFHxA is formed. Due to the high water solubility of PFHxA and the difficulties in removing it from water, PFHxA is released into surface water. The applied polish remains on flooring materials for three to four years. Polish layers may be rapidly worn and new polish layers are applied over this time. None volatile shares of the containing C6 PFCAs are released into soil by abrasion. Some perfluorinated C6 side chained substances show a certain volatility and may be released into air at application and during the service life of the polish layers.

Emissions to the environment by consumer mixtures can be significant due to the assumed large quantities and qualities of several consumer mixtures used in the EU.

B.9.14 House dust

Abrasion of fibres from carpets and furniture is a relevant source for the generation of house dust. In consequence, PFHxA is emitted to house dust from textiles and other consumer products.

A first search regarding the PFHxA content in house dust was performed in February of 2019 with the terms "PFHxA" OR "Perfluorohexanoic" AND "dust" in Pubmed, Scopus, SciFinder, Web of Science and Science Direct. In order to find articles that might report on PFHxA without mentioning it in their title, keywords or abstract, a broader search was performed with the keywords "Perfluoroalkyl*" AND "dust" in Pubmed, Scopus, Web of Science and Science Direct. 80 relevant articles were identified. As a counter check, the references in the review by Anderson et al. (2019) were evaluated. A further study known by experts from the BfR was added. All articles were further filtered by the following criteria:

1) Does the source contain occurrence data for PFHxA in house dust?
2) Were the house dust samples taken from European Countries?
3) Were the dust samples taken from private households?

The first filter excludes references that were not relevant for PFHxA or house dust, the second was applied because the restriction dossier refers to the European situation, and the third excludes offices and other working environments which may have different sources of exposure.

All in all, ten studies with measured data on PFHxA in dust from European households were found The median PFHxA contents range between 0.3 ng/g and 28 ng/g and the maximum contents between 2.9 ng/g and 96 ng/g. ((Huber et al., 2011), (D'Hollander et al., 2010), (Haug et al., 2011), (Ericson Jogsten et al., 2012), (Eriksson and Karrman, 2015), (Lankova et al., 2015), (Karaskova et al., 2016), (Winkens et al., 2018), (Bohlin-Nizzetto et al., 2015), (Padilla-Sánchez and Haug, 2016)) More information on these data can be found in Table 44 of Appendix B.4.4.

The house dust samples were taken between 2008 and 2015 and may still reflect PFHxA contaminations from C8-chemistry, as driving products for the contamination of house dust like carpets or decoration textiles have a long service life. However, in newer studies, there are indications for C6-chemistry, too. Due to the ongoing changes in PFAS uses, it is not possible to deduce future concentrations of PFHxA in house dust from these data.

The overall number of analyzed samples is small compared to the number of room types in the different regions of the EU. Also, the studies are limited to a few countries and far away from representativeness for the European situation. It should be noted that if the number of analyses for a certain product type is low, the observed maximum value may still underestimate the concentration in a realistic worst case.

Also, the reported studies differ in their sampling strategies. For example, higher surfaces may be cleaned less often than floors, and dust on these surfaces may absorb contaminants for a longer time. There is no harmonized method for the detection of PFAS in house dust, neither for sampling nor for analysis. The analytic procedures for detection of PFHxA are complex and they differ in the reported studies. This makes it difficult to compare the results, with reported medians ranging over two orders of magnitude.

Taken together the differences within the samples, the low number of samples with comparable conditions and methods, and the lack of data for many countries, the database gives indications on some orders of magnitude rather than the present distributions of PFHxA concentrations in European house dust.

B.9.15 Indirect exposure of humans via the environment

Sources of human exposure include food, drinking water, house dust, air and dermal contact to consumer articles. Apart from the exposure via the environment, also articles are a significant source of PFHxA for direct human exposure. Relevant articles such as furniture, textile and leather care articles or cosmetics are placed on the market and used in all EU Member States. A considerable share of articles containing PFHxA or related substances is imported from outside the EU.

B 9.15.1 Food

Occurrence data were collected in the food surveillance programmes of Germany, in particular in the national monitoring and the federal control plan.

The national monitoring is a measurement programme in which foods from the German market are systematically examined for the presence of unwanted substances. It is performed jointly by the Federal Government and the Federal States. The national monitoring consists of pre-planned samples and thus aims on providing a realistic picture of the situation on the market.

The federal control plan is a risk-oriented monitoring programme. It consists of a yearly plan aiming at monitoring the compliance inter alia with food regulation. Therefore, it also consists of samples which were drawn based on some suspicion and may distort a realistic picture of the market situation. Additionally, there are some indications that the data obtained from the monitoring programme might originate from places with elevated concentrations of PFHxA. These are mainly samples collected in the vicinity of Rastatt, where increased concentrations have been caused by contaminated sludge being used as fertilizer. In the present evaluation these samples were not removed as they do not interfere with the aim of demonstrating the presence of PFHxA in food. The same is true for the very little number of risk-oriented samples that do not belong to one of the mentioned programmes.

The used data were collected between 2005 and 2018 and submitted by the Federal Office of Consumer Protection and Food Safety (BVL). In total, they consist of 3116 samples which were analysed for the presence of PFHxA. Of these, 3001 (96.3 %) were below the limit of quantification (LOQ) and 2933 (94.1 %) below the limit of detection (LOD). In the statistical analysis, these left-censored data were treated in the following way: Samples below the level of detection were replaced by zero. Samples below the level of quantification but above the level of detection were set to the level of detection. This approach is called the "modified lower bound" and gives the lowest possible value based on the available information. It was chosen here to only present non-zero values for samples where any amount of PFHxA was detected. The median LOD and LOQ for the samples is the same, being 1 µg/kg with an interquartile range of 0.5 µg/kg (LOD) and 1 µg/kg (LOQ).

Table 22: Overview of the PFHxA occurrence data from German food monitoring programmes.

Group	N total	N >LOD	N > LOQ	Mean [µg/kg]	P50 [µg/kg]	P95 [µg/kg]	Max. [µg/kg]
cereals	19	9	8	2.05	0	9.80	9.80
fish and seafood	1 180	107	71	0.17	0	1.25	15.00
fruits	173	4	3	0.03	0	0	1.80
meat and meat products	851	37	17	0.05	0	0	3.40
milk	70	1	1	0.006	0	0	0.006
mushrooms	78	3	0	<0.01	0	0	0.12
potatoes and potato products	144	15	14	0.15	0	1.42	1.93
vegetables	601	7	1	0.02	0	0	3.10

Table 22 summarizes the monitoring data. Foods were grouped to general groups because of the low number of detects – for all groups except "fish and seafood" the number of detects is below 100, and below 20 for all other except "meat and meat products". Also, for some samples more detailed information to further specify the food category was not available.

Still, the groups consist mainly of foods that are regularly consumed by the German population (e.g. the vegetable group consists mainly of tomatoes, cabbages, carrots, salad, onions, etc.). The main exception is the "meat and meat products" group, which contains a large amount of liver and /or game samples and the "fruits" group of which about 100 samples are taken from strawberries.

In all food groups there is at least one value above the level of detection. The data from the German monitoring programme thus supports the presence of PFHxA in food. The percentage of detects is not very high, but it cannot be finally concluded whether this is due to the analytical limits or whether PFHxA is not that widely distributed up to now. Several detects are already from 2005 to 2010 and a time trend could not be derived by the underlying data.

Data from literature

A first search for the terms "PFHxA" or "Perfluorohexanoic" and "Food" or "Dietary Exposure" was performed on PubMed, Scopus, SciFinder, Web of Science and Science direct and yielded in total 89[15] sources. Each of the sources was further filtered using the following criteria:

4. Does the source contain occurrence data for PFHxA in food? (Exclude if no, 60 excluded)
5. Were the foods bought on markets inside the EU? (Exclude if no, 14 excluded)
6. Are any reported values above the LOD? (Exclude if no, 5 excluded)

The first filter excludes references which are not relevant for PFHxA or dietary exposure. The second filter was applied, as a REACH restriction is only concerned with the European situation. The last filter was necessary because a large fraction of values is below the level of detection. Still, many sources opted to report upper bounded values (i.e. non-detects were

[15] For two sources the full text could not be obtained in time.

set on the level of detection). This would compromise the aim of demonstrating the presence of PFHxA because most of the reported values would not be actual detects but reported upper bound concentrations. The five papers excluded due to criterion three might be interpreted as a further indication of low prevalence of PFHxA in food up to now. After applying these filters, ten sources remained and were further analysed. One additional source (Herzke et al., 2013b), was identified from the references of these screened sources and added to the analysis.

In a second search the first requirement was relaxed to the search term "perfluoroalkyl*" to also identify sources which did not list perfluorohexanoic acid explicitly but still measured it. From that second search, one additional source (Rivière et al., 2014) was classified as relevant. This source is referred to as (ANSES, 2011) because the latter document provides more detailed information on the results, which are from the Second French Total Diet Study (TDS).

The resulting references are summarized in Table 23 with the exception of (EFSA, 2012), which will be summarized separately. Only values above the level of detection were used in the summaries for the same reasons as explained above. Not all studies presented their results in the same way. Some reported single values for each food item, some only mean values. Some reported the values already aggregated to food groups, some provided detailed information of the specific food items. The latter ones were also aggregated to appropriate food groups for the sake of brevity. As it is the aim of this section to demonstrate the presence of PFHxA in food, this was not seen as an obstacle; however, the values cannot necessarily be compared from one study to another.

The heterogeneity of the studies also impedes the comparison with the results from the national monitoring. The literature generally reports lower values which is likely in large parts caused by lower detection limits (e.g. (Vestergren et al., 2012b) reports an MDL of 2.4 ng/kg and (Herzke et al., 2013b) a MQL between 2 and 50 ng/kg depending on type of PFAS).

One report, (EFSA, 2012), was excluded from the table because the data presented were collected from the national monitoring programmes of the member states of the European Union as well as from the PERFOOD project (Herzke et al., 2013a; Klenow et al., 2013; Vestergren et al., 2012a; Vestergren et al., 2012b). The former has overlap with the already presented data from the German monitoring program, the latter with some of the results presented in Table 23. In general, EFSA also reports large numbers of non-detects across all considered food groups. They also report lower and upper bound mean values. In comparison with Table 23 the reported lower bound values are lower and the upper bound values higher which is consistent with the different treatment of non-detects in the data analysis.

In general, also the data from the literature thus support the presence of PFHxA in food.

Table 23: Ocurrence of PFHxA in food.

Data Source	Countries	Foods with detects	Range of reported Detects [µg/kg]	N (no bracket: Samples, []: Groups)	N > LOD	LOD [µg/kg]	Remarks
Fromme et al. (2007)	Germany	whole diet	0.1 - 3.18	214	19	0.2	
Ericson Jogsten et al. (2009)	Spain	meat, vegetables	0.012 - 0.118	40	5	0.001	
Clarke et al. (2010)	UK	fish	2 - 7	252	3	1	
Haug et al. (2010)	Norway	vegetables, potato, dairy products, cereals, egg, fish	0.00098 - 0.014	16	7	0.0001-0.66	
ANSES (2011)	France	fish	0.002	591 [25]	1	0.0029-0.194	1 out of 25 groups had > 1 detect
Domingo et al. (2012)	Spain	fish and seafood, dairy products	0.031 - 0.007	40 [12]	2		2 out of 12 groups had > 1 detect
Vestergren et al. (2012a)	Sweden	oils, cereals, egg, vegetables, fruit, potatoes, sugar and sweets, softdrinks	0.0014 - 0.011	36	22	-	
Vestergren et al. (2012b)	Sweden	whole diet, vegetables, meat	0.0099 - 0.131	[5]	3	0.0024	3 out of 5 groups had > 1 detect
Gebbink et al. (2015)	Sweden	sugar and sweets	0.0156 - 0.107	14 / 22*	6	-	*14 Samples, of which 8 were measured unprepared and prepared
Herzke et al. (2013b)	Belgium, Czech Republic, Italy, Norway	vegetables	0.00289 - 0.099	62	19	0.002-0.05	
Yamada et al. (2014)	France	fish	0.03 - 4.01	481 [46]	36	0.007-0.95	36 out of 46 groups (all fish) had > 1 detect

B.9.15.2 Consumer exposure

To gain information on exposure levels of consumers to 6:2 FTOH and PFHxA, the scientific literature has been screened using search engines such as Scopus, PubMed and Web of Science. Key words used in the literature query included 6:2 FTOH, PFHxA, per- and polyfluoroalkyl substances, textiles, garments, waterproofing, surface treatment and consumer products. This approach identified several publications covering a broad spectrum of consumer product types ranging from outdoor textiles to swimming costumes. Additionally, data on the occurrence of PFHxA in clothing textiles sampled from the German market in 2010 – 2014 were included in the assessment as well. These data were obtained within the framework of the national monitoring program and were submitted by the German Federal Office of Consumer Protection and Food Safety (BVL).

The studies referred to below looked for the presence of residual non-polymeric PFASs (of different chain lengths) such as FTOHs, PFCAs, fluorotelomer acrylates, PFSAs and precursors. The spectrum of the detected and quantified substances in a given textile fabric provides a fingerprint that hints towards the underlying technology. For example, several products from more recent sampling campaigns contained 6:2 FTOH as the dominant residue, with PFHxA as degradation product sometimes being the second-dominant residue. This fingerprint indicates the use of state-of-the-art C6 fluorotelomer technology. There are, however, other examples showing, e.g., a distribution of 6:2 to 10:2 FTOHs with 8:2 FTOHs forming the peak of the distribution. It should be noted that products with such a fingerprint will no longer be on the European market because of the restriction of long-chain PFASs. These examples show that the concentrations of 6:2 FTOH and PFHxA reported below cannot be used as an indication that a C6 fluorotelomer technology was used, since alternative technologies can give rise to the occurrence of these compounds as by-product. Insofar, the data cannot be regarded as being representative for the C6 fluorotelomer technology unless confirmed by fingerprint.

Santen and Kallee (2012) analysed outdoor textiles purchased in 2012 for their PFASs content. Six and eight of twelve jackets were tested positive for 6:2 FTOH and PFHxA, respectively, with maximal concentrations of 3520 and 32 µg/kg of fabric.

Studies by Knepper et al. (2014) and Dreyer et al. (2014) also examined outdoor jackets for PFASs. Knepper et al. (2014) purchased the garments between August 2011 and March 2012. Whereas in both studies PFHxA is identified in nearly every jacket with comparable maxima of 120 and 147 µg/kg of textile, the 6:2 FTOH pattern is different. Only in two of the 16 jackets 6:2 FTOH was detected with a maximum concentration of 186 µg/kg of fabric by Knepper et al. (2014). The chemical analysis by Dreyer et al. (2014), on the other hand, revealed 6:2 FTOH in eleven of 14 jacket samples with concentration ranging from < 300 to 8 500 µg/kg of fabric.

More recent data by Greenpeace on the content of PFHxA and 6:2 FTOH in outdoor textiles purchased in 2015 are in good agreement with the findings by (Dreyer et al., 2014) regarding a higher prevalence of these substances (Brigden et al., 2016a). In seven of eleven jackets 6:2 FTOH has been extracted from the fabric with a peak concentration of 4 600 µg/kg. PFHxA was identified in eight jackets with a maximum concentration of 546 µg/kg of textile.

When comparing both Greenpeace studies, a shift from C8 to C6 substances is observed, as shown in Figure 6.

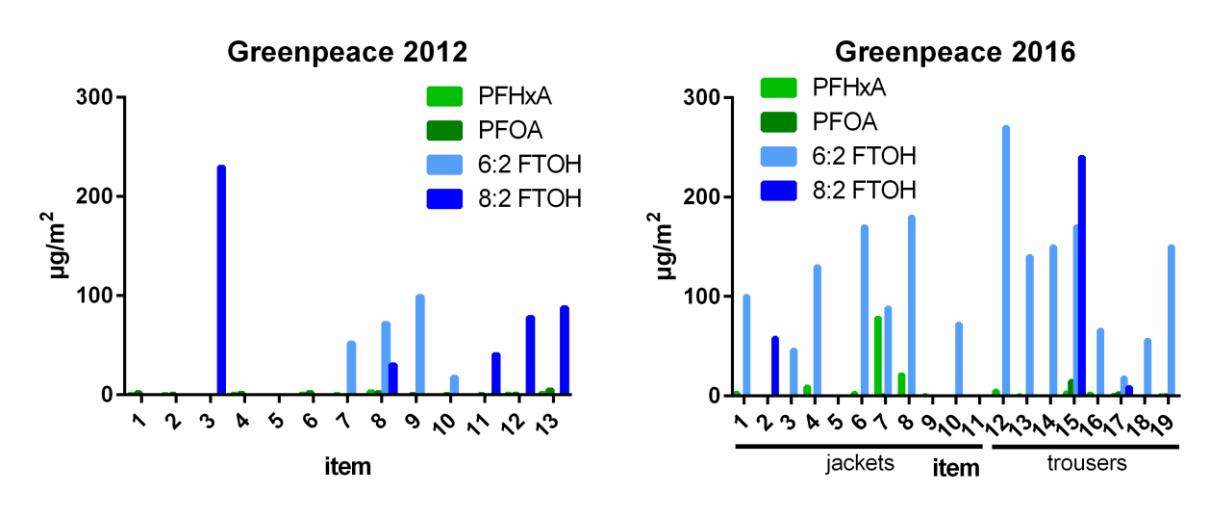


Figure 6: *Comparison of PFHxA, PFOA and fluorotelomers in outdoor clothing. Data were taken from Bridgen et al. (2016) and Santen and Kallee (2012).*

Analytical results by Borg and Ivarsson (2017) from textile samples purchased in the same year (2015), however, do not point to an increased usage of C6-perfluoralkyl substances to waterproof outdoor jackets. In their study, eight textiles samples (six jackets and two pair of shoes) collected in 2015 for a monitoring project by the Swedish Chemicals Agency have been analysed for their total organic fluorine content (TOF) and for 22 individual PFAS. The result of the targeted PFAS analysis showed that three jackets contained PFHxA albeit at much lower concentrations, nearly 30-fold less, than reported by Greenpeace. In contrast to the findings by Greenpeace, 6:2 FTOH was only identified (1400 µg/kg of textile) in one jacket. This would rather indicate a shift to PFAS free DWR alternatives.

There are few studies reporting on measurements of PFHxA or 6:2 FTOH in carpets or upholstery. Herzke et al. (2012) and Kotthoff et al. (2015b) analysed carpets purchased in 2009 in Norway and 2010 in Germany, respectively. Low levels of PFHxA were detected in some of the analysed samples with a maximal concentration of 11 µg/kg while 6:2 FTOH was detected in all carpets reaching up to 2000 µg/kg in one sample. A further study investigated PFAS in products imported to Norway from China (Vestergren et al., 2015). Several furniture textiles comprising towels, blankets, curtains and other products were investigated in addition to carpets, bath mats and rugs. Here, maximal PFHxA levels under 1 µg/m^2 were reported, but 6:2 FTOH levels were 2 - 3 orders of magnitude higher. These results confirm the general observation from the outdoor textile studies, that the fluorotelomer alcohol was also found in much higher concentrations than the corresponding fluorocarbon acid. In addition, Guo et al. (2009) analysed carpets and upholstery purchased between 2007 and 2008 in the USA. In these two product groups, maximal PFHxA levels reached 224 µg/kg and 238 µg/kg, respectively. It should be noted, that levels of C7 and C8 PFCAs in the latter study were generally higher than the C6 values, suggesting long-chain based treatment of these products.

For the estimation of environmental release of PFHxA from textiles only few studies are available. Gremmel et al. (2016) re-analysed PFAS content in outdoor jackets after three years of storage and found a decrease of volatile FTOHs and a slight increase in PFCAs. Likewise, it has also been shown that FTOHs in textiles are not significantly decreased by washing (Liu et al., 2015a).

A study investigating textiles and carpets in experimental anaerobic landfill reactors shows a release of PFHxA in leachate, suggesting that degradation of these consumer products in landfills is a source of environmental exposure (Lang et al., 2016). However, to date there is a lack of data concerning the kinetics of long-term degradation of SFPs in DWR textile coatings during the textile's use phase and concerning the migration of PFAS from the textiles into aqueous media such as sweat. Direct dermal exposure from outdoor textiles containing PFHxA is generally expected to be low for consumers during the garment's use phase, because the finishing is located on the outside of the garment.

For carpets or other household textiles, PFHxA-containing material released into house dust is the primary source for exposure, which is covered in B.9.14. For the volatile telomer 6:2 FTOH, transfer to indoor air is also to be expected. In addition, direct skin contact with carpets is very likely especially for toddlers, but data on dermal exposure of PFHxA are not available.

In conclusion, the consumers are being potentially exposed to 6:2 FTOH and PFHxA primarily via waterproofed outdoor textiles. Robust, statistically relevant and more recent marketplace data is lacking to support the working hypothesis that manufactures have substituted C8 with C6 fluorochemistry on a large scale. Depending on the study, a shift from C8 PFAS either to C6 PFAS or to fluorine-free alternatives can be assumed.

Uncertainty

For a qualitative assessment of human exposure, several uncertainties need to be considered. First of all in the listed studies only new products have been investigated. As mentioned before, 6:2 FTOH may occur as residual from the telomerisation process and PFHxA as oxidised product of the former substance. Thus, the PFAS concentrations measured in the studies represent maximal extractable levels in newly purchased textiles. These unbound residues might then be released and lead to human and environmental exposures. In addition, degradation of polymer side-chains by hydrolysis or UV light during the garments' life cycle is expected to lead to a constant release of PFAS, but systematic investigations on the release of PFHxA and 6:2 FTOH are still lacking.

The products analysed in the studies were purchased in different years ranging from 2007 to 2015. Thus, another uncertainty in the determination of human exposure is that the studies mentioned above might have contained C6 PFAS as by-product from C8-based PFAS treatment, because most products were purchased before the phase-out of C8 fluorochemistry has started. It is unknown whether C8 chemistry is substituted by non-fluorinated alternatives or by C6 chemistry. If the latter case holds true, there is also the concern that 'because some of the shorter-chain PFASs are less effective, larger quantities may be needed to provide the same performance' (Blum et al., 2015b). Thus a higher content of PFHxA might be likely when today's products are analysed. However, it cannot be concluded from the data summarized here which scenario applies. Data from the most recent studies are controversial. While C6 PFAS are reported by Brigden et al. (2016b), only low levels of PFHxA and 6:2 FTOH have been reported by Lassen et al. (2015). While the former study

investigated outdoor textiles from specialized stores the latter study focused on textiles for children which might have a different requirements concerning water and stain repellence. In general the different studies have to be compared with care since the methodology of analytical measurements is not standardized.

B.9.16 Other sources

Natural sources for PFHxA are unknown. As far as we know, PFHxA itself is not used in Europe for manufacturing products and articles. But the precursors are used in large quantities and finally are released into the European Environment. As well as in the article's matrix as in the environment these precursors may degrade and form PFHxA. Further, PFHxA may occur as an impurity in articles and products containing PFHxA precursors. As a consequence, the environmental exposure of PFHxA arises from the use and the degradation of precursors.

B.9.17 Overall environmental exposure assessment

PFHxA related substances are used in Europe in large quantities. These substances are released into air, water and soil during all life cycle steps of an article or product. The tonnages of PFHxA and of the related substances that currently and in future will be released into the environment are summarised in Table 24. PFHxA and the precursors are highly water soluble. By leaching from soil and landfills and by precipitation these substances are enriched in the water to the uppermost part. So, water is considered as the main target compartment into which PFHxA, its salts and related substances are released. The substances may be transported into remote areas by water and air.

Polymer particles are released into all environmental compartments for example by abrasion from articles. Currently, up to 120 t/a of polymers are released during the service life of articles. This amount contributes among others to microplastic.
With a calculated annual average release up to 2.55 kg/a PFHxA resulting from polymerdegradation from landfills, the release of PFHxA from polymer degradation is considerd as very low. However, polymers with perfluorinated C6 side chains are a longlasting constant source for PFHxA emissions over centuries.

For calculating environmental concentrations the default values from R16, listened in chapter B.9.2 (General Assumptions made for environmental exposure estimations) are used. Due to the high water solubility, the share accumulates in water, is assumed with 80%. Minimum values representing the northern- and maximum values the southern scenario. Based on the evaluated data, PFHxA precurcors are released into the environment of about 6 600 t/a (measured values are converted with findings using the TOP-assay – only 50 % of compounds are detectable using water or methanol as extracting solvent). Based on this value, this may lead to an annual increase of regional concentration of the precursors in European waters between 4 and 37 µg/L. But the local concentration may be much higher for example in case of firefighting operations.

However, the precursors do not accumulate for long time in the environment. The precursors degrade at ambient conditions fairly rapidely and form PFHxA. There are no natural sources

of PFHxA known and PFHxA itself is not used in the EU. So, it could be assumed that, in summary, about 1 000 to 5 000 t/a PFHxA (using different approaches like published experimental data or stoichiometrically calculated values) are currently released into the European environment as degradation product. This could result in a European PFHxA concentration of 3 – 28 µg/L water body. In contrast to the precursors PFHxA accumulates due to non-degradability. PFHxA precursors will be used in large quantities in the coming years, too. So, about 10 000 to 50 000 t PFHxA will have been released into the environment within the next 20 years without restriction. This is equal to a concentration of 28 – 279 µg/L in rivers and lakes.
However, the measured concentration in several European rivers and lakes is by magnitudes lower (in average below 10 ng/L). Due to high mobility of this substance, the amount of PFHxA reaches the surface water, is rapidely transported by the rivers into the oceans and seep into groundwater. Taking the by (Ahrens et al., 2009a) measured maximum concentration of PFHxA (9.56 ng/L) about 7 t PFHxA could be found in the German Bights surface water. Extrapolating this result to European territorial coastal surface waters, concidering an average coastline of 68 000 km, about 144 t PFHxA already have been accumulated in this water body. The coastal waters are part of a larger system of seas and oceans. There are some publication available which report the PFHxA concentration in open sea surface water (see table 48 in appendix B.4.2). Assuming the measured PFHxA-concentration in the open sea surface water is equally distributed over the whole water body from surface to bottom, in the North Atlantic Ocean about 16 500 t PFHxA, in the Mediterranean Sea about 700 t and in the Baltic Sea about 6 t PFHxA are deposited. This assumption could only be a narrow regional snapshot. By main oceanic circulation the water globally is exchanged leading on a dilution on regional scale. However, PFHxA is distributed worldwide and is transported into remote areas.

Using PFHxA, its salts and related substances further without restriction, the PFHxA concentrations will increase as well in fresh- and marine water as in groundwater. Consequently, the chronic exposure of organisms will be increased, too. The increasing concentrations of PFHxA in groundwater will effect the drinking water quality and consequentely a higher human exposure could be expected. Above that, PFHxA precursors are used as constituents in many consumer products like cosmetics or outdoor clothes leading to dermal exposure of human.

Table 24: Overall exposure assessment: Overview of manufacture of articles and products (28a), the use and environmental release of polymers (28b), PFHxA related substances (28c) and PFHxA (28d). Unit in all tables [t/a].

Table 24a Overview of manufacture of articles and products.

Sector of use	**Subsector**	**Current manufacture of products / articles**	
		min	max
1. polymers	1.1. manufacture of (acrylic-) polymers with C6 side chains	1 000	10 000
	1.2. manufacture of fluoroelastomes with APFHx	100 000	200 000
2. textiles	2.1. clothing manufactured in the EU		1 600 000
	2.2. clothing imported into the EU		4 800 000
	2.3. outdoor clothing		150 000
	2.4. occupational wear		95 000
	2.5. carpets and other textile floor coverings		200 000
	2.6. industrial textile fabrics		100 000
3. paper and card board	3.1. grease proof papers		47 000
4. extinguishing agents		11 000	12 500
5. chrome plating	5. chrome plating	no data available	
6. inks	6. inks	no data available	

Table 24b: Use and predicted environmental release of C6 polymers [t/a].

Sector of use	Subsector	Used tonnages of C6 fluoropolymers		Current release of C6 fluoropolymers		Cumulative release of C6 fluoropolymers until 2040 (no restriction)		Cumulative release of C6 fluoropolymers until 2040 (restricted)	
		min	max	min	max	min	max	min	max
1. polymers	1.1. manufacture of (acrylic-) polymers with C6 side chains	1 000	10 000	3.48	33.90	69.50	678.00	20.25	202.50
	1.2. manufacture of fluoroelastomes with APFHx	no environmental release of C6 related polymers is expected							
2. textiles	2.1. Ccothingmanufactured in the EU	3 200	8 000	25.60	64.00	512.00	1 280.00	28.80	72.00
	2.2. clothing imported into the EU	3 200	24 000	4.80	12.00	96.00	240.00	14.40	36.00
	2.3. outdoor clothing	300	750	2.31	5.78	46.20	115.50	2.61	6.53
	2.4. occupational wear	190	475	1.52	3.80	30.40	76.00	1.71	4.28
	2.5. carpets and other textile floor coverings	400	1 000	3.08	7.70	61.60	154.00	4.28	10.70
	2.6. industrial textile fabrics	300	500	2.79	6.98	55.80	139.50	15.69	39.23
3. paper and card board	3.1. grease proof papers	141	705	1.20	5.99	23.97	119.85	1.34	6.70
4. extinguishing agents		no environmental release of C6 related polymers is expected							
5. chrome plating	5. chrome plating	no environmental release of C6 related polymers is expected							

6. inks	6. inks	no environmental release of C6 related polymers is expected							
	summary:	**7 541**	**42 705**	**35**	**116**	**701**	**2 318**	**65**	**317**

Table 24c: Use and predicted environmental release of C6 precursors [t/a].

Sector of use	**Subsector**	**Used tonnages of C6 precursors**		**Current release of C6 precursors**		**Cumulative release of C6 precursors until 2040 (no restriction)**		**Cumulative release of C6 precursors until 2040 (restricted)**	
		min	max	min	max	min	max	min	max
1. polymers	1.1. manufacture of (acrylic-) polymers with C6 side chains	1 000	10 000	11.00	110.00	220.00	2 200.07	10.00	100.04
	1.2. manufacture of fluoroelastomes with APFHx	no environmental release of C6 related precursors is expected							
2. textiles	2.1. clothing manufactured in the EU	640	13 600	43.48	923.98	869.63	18 479.68	427.74	9 089.42
	2.2. clothing imported into the EU	1 920	40 800	116.04	2 465.95	2 320.90	49 319.04	1 268.81	26 962.27
	2.3. outdoor clothing	60	1 275	4.06	86.24	81.17	1 724.82	39.63	842.19
	2.4. occupational wear	38	808	2.58	54.86	51.63	1 097.23	25.11	533.63
	2.5. carpets and other textile floor coverings	34	440	2.30	29.71	45.91	594.18	22.48	290.94
	2.6. industrial textile fabrics	0	1	0.01	0.17	0.17	3.37	0.04	0.84
3. paper and card board	3.1. grease proof papers	0	470	0.00	31.81	0.05	636.27	0.02	310.33
4. extinguishing agents	4. summary	1 000	3 000	*released precursors from fire fighting foams are expressed as PFHxA due to using the TOP assay*					

5. chrome plating	5. chrome plating	100	1 000	20.00	200.00	400.00	4 000.00	68.66	686.57
6. inks	6. inks	10	100	8.02	80.20	160.41	1 604.09	13.07	130.72
	summary:	**4 670**	**68 970**	**199**	**3 812**	**3 971**	**76 239**	**1 788**	**37 279**

Table 24d: Use, impurities and predicted environmental release of PFHxA [t/a].

Sector of use	**Subsector**	**Used tonnages or impurities of PFHxA and salts**		**Current release of PFHxA its and salts**		**Cumulative release of PFHxA and its salts until 2040 (no restriction)**		**Cumulative release of PFHxA and its salts until 2040 (restricted)**	
		min	max	min	max	min	max	min	max
1. polymers	1.1. manufacture of (acrylic-) polymers with C6 side chains			0.00	0.003	0.01	0.05	0.00	0.01
	1.2. manufacture of fluoroelastomes with APFHx	10	100	0.10	1.03	2.06	20.64	0.22	2.17
2. textiles	2.1. clothing manufactured in the EU	5	874	0.34	59.35	6.76	1 187.05	3.34	583.86
	2.2. clothing imported into the EU	14	2 621	0.85	158.41	16.93	3 168.26	9.25	1 732.06
	2.3. outdoor clothing	0.45	82	0.03	5.54	0.61	110.79	0.30	54.71
	2.4. occupational wear	0.29	52	0.02	3.51	0.39	70.17	0.19	34.65
	2.5. carpets and other textile floor coverings	0.00	2.20	0.00	0.15	0.00	2.97	0.00	1.45
	2.6. industrial textile fabrics	0.00	0.03	0.001	0.004	0.01	0.08	0.00	0.02
3. paper and card board	3.1. grease proof papers	0.07	8	0.005	0.58	0.09	11.58	0.04	5.59

4. extinguishing agents	4.1 use by professional firefighting			0.02	0.52	0.35	10.94	7.32	229.83
	4.2 use by volunteer fire fighting brigades			4.60	143.84	96.60	3 020.64		
	summary extinguishing agents*			4.72	144.61	99.05	3 036.83	7.53	230.36
5. chrome plating	5. chrome plating			0.78	7.80	15.60	156.00	2.68	26.78
6. inks	6. inks			0.31	3.13	0.00	0.02	0.00	0.00
	summary:	**29**	**3 603**	**7**	**375**	**140**	**7 580**	**23**	**2 581**

* except for 4.1 and 4.2 the whole life cycle is covert

B.10 Risk characterisation

There is currently insufficient information to derive a robust predicted no effect concentration (PNEC) aswell as a predicted environmental concentration (PEC) that could be used to underpin a conclusion that risks are adequately controlled, either now or on the future. See also section1.3.7.

Annex C: Justification for action on a Union-wide basis

Based on the hazardous properties of PFHxA, its salts and PFHxA related substances a union-wide restriction is needed to minimize the release to the environment and reduce human exposure to a minimum. These considerations are described below.

Perfluorohexanoic acid (PFHxA) and its salts have a combination of hazardous properties. The substance is extremely persistent and by far exceeds the trigger of being vP. Furthermore, the substance is mobile in the aquatic environment, can be distributed easily within and between environmental compartments by aqueous media, has a long-range transport potential and the potential to enrich in plants. In addition, the substance shows adverse effects in developmental toxicity studies. Though PFHxA does fulfil the P-criterion and vP critierion and even by far exceeds these, the data on bioaccumulation and ecotoxicity are not sufficient to identify PFHxA as a PBT or vPvB substance. Nevertheless, PFHxA shows characteristics which do comply to the concerns which are put forward to reason that a safe concentration of PBT/vPvB substances in the environment cannot be established with sufficient reliability due to unpredictable and irreversible adverse effects on the environment or human health over time. For vPvB substances this applies even if no toxicity is demonstrated. This similarity is in particular founded on the extreme persistence. In addition to the extreme persistence, the mobility and long range transport potential of PFHxA leads to unpredictable and irreversible adverse effects on the environment or on human health over time. Therefore, PFHxA should be treated as a non-threshold substance for the purposes of risk assessment, similar to PBT/vPvB substances under the REACH regulation, with any release to the environment regarded as a proxy for an unacceptable risk.

A large variety of emission sources contributes to the exposure of humans and the environment to PFHxA (see chapter B.9). Several of its potential precursors as well as the ammonium salt are registered with tonnage bands from 1 to more than 1000 tonnes per annum. Use and production of these precursors are taking place in Europe. The use areas are broad and release into the environment cannot be excluded. Monitoring data for PFHxA and knowledge from other PFASs show that release into the environment is occuring.

Sources of human exposure include food, drinking water, house dust, air and dermal contact to consumer articles. Apart from the exposure via the environment, also articles are a significant source of PFHxA for direct human exposure. Relevant articles such as furniture or textile and leather care articles or cosmetics are placed on the market and used in all EU Member States. A considerable share of articles containing PFHxA or related substances is imported from outside the EU.

Therefore, any national regulatory action will not adequately manage the risks of PFHxA and related substances. Risk management measures need to be taken on a Union-wide basis.

An alternative for the restriction would be to list the substances in Annex XIV. However, this would a) enable companies to apply for an authorization, b) would make it difficult to set a threshold for unintended impurities and c) would not affect the import of articles containing these substances. In sum this could lead to ongoing emissions and therefore, to an unacceptable risk for human health and the environment. Moreover, a global regulation seems to be necessary since these substances are transported over global borders via air, water and articles. A European restriction could be the first step to achieve such a global action.

In conclusion, a restriction on PFHxA, its salts and related substances is the most appropriate way to limit the risks for human health and the environment on an EU level. Particularly import of articles containing these substances can be regulated this way.

Annex D: Baseline

Since the 1950ies perfluorinated substances and the polymers made there of became more and more important for a wide range of uses. Mainly substances with C8 perfluorinated (side-) chains were used. Above that, the use of C4 and C6 substances was also very common. Due to their hazardous properties the C8 substances have been replaced by substances with shorter perfluoroalkyl chains by manufacturers in the USA, Canada, Europe and Japan step by step since 2002. Contemporarily the global market for fluoropolymers was growing rapidly. Assuming a constant release of C6 fluorinated polymers and of PFHxA over the last 50 years, about 6 000 t of polymers and about 19 000 t PFHxA have been released into the European environment.

So, PFHxA has been investigated in environmental compartments by several authors (e.g. Benskin et al. 2012b; Ahrens et al. 2010b; Zhao et al. 2012; Gellrich et al. 2012). PFHxA already is found ubiquitously as well in fresh- and marine surface waters as in groundwater. Compared to the estimated high annual release of PFHxA, the environmental load in European rivers and lakes is fairly low with about 2 t. However, PFHxA is extremely mobile in water. About 144 t PFHxA could be detected in European territorial coastal surface waters. Considering the whole water body, in the North Atlantic about 16 500 t PFHxA could be assumed. The waters of the world oceans are linked by the great currents which transport warm water at ocean's surface like the Gulf Stream and transport cold water in the depth e.g. by the East Greenland Current. In the Arctic PFHxA is transported with the currents into deep waters and to the Antarctic. On the one hand this leads to a dilution of the PFHxA concentration in European waters, on the other hand PFHxA is transported to remote areas.

By manufacturing, formulating and the use of articles and products containing PFHxA, its salts and related substances, PFHxA already could be detected in humans (see chapter B 4.4.2). PFHxA concentrations in human serum are often reported below the limit of detection. However, higher frequencies of detection are found in urine and hair than in serum.

Without restriction about 10 000 to 50 000 t PFHxA will have been released into the environment within the next 20 years. At the moment it is very difficult to remove PFHxA from the environment. PFHxA is extremely persistent. Consequentely, the concentration of PFHxA will be increased in the environmental compartments and the exposure of organisms and humans will increase, too. Future generation will be faced with these contaminations. Effects will not only occur on the point of release of PFHxA but also far away from its point of release.

A restriction will decrease the release of PFHxA into the European environment within 20 years by two third. Supplementary mitigation measures, like the further replacement of PFHxA based products and the improvement of water cleaning methods will further reduce the release of PFHxA, its salts and related substances into the environment.

Annex E: Impact Assessment

E.1 Risk Management Options

E.1.1 Proposed option for restriction (phase out over 18 month with exemptions)

The proposed restriction is defined as a ban on the use of PFHxA, its salts and related substances. This includes a restriction on the manufacturing, placing on the market and use of PFHxA, its salts and related substances in the EU. The import of PFHxA, its salts and their related substances in articles to the EU is also included.

PFHxA is not registered under REACH and therefore most probably not intentionally used within Europe. Salts of PFHxA and related substances, however, are registered and used (see annex A.1.1). Imported articles are an emission source of intentionally used PFHxA, its salts and related substances as well. The substances are used for different purposes in the production of a large variety of mixtures and articles. Therefore, a broad restriction represents a sufficient way to emission reduction.

In terms of risk reduction capacity, a total phase out of manufacturing, use and contents in articles and mixtures (including imports) would be most effective. However, further criteria have to be considered: proportionality, implementability, enforceability and manageability /monitoring.

Proportionality: PFHxA, its salts and related substances are used in the production of a large variety of mixtures and products. For most of the uses alternatives are available and affordable. For some uses the availability of alternatives is unknown. Some uses are essential, meaning that no alternatives are available for highly important purposes, for example health or safety. For these essential uses a total ban on PFHxA, its salts and related substances is not proportionate considering that in relation to the expected emissions reduction large societal costs are to be expected.

Implementability: The proposed restriction is considered to represent an implementable option for the actors involved within the timeframe of 18 months for most uses. As described in Annex E.2 Impact Assessment for specific uses it appears that the necessary technology, techniques and alternatives are available and economically feasible. However, for some essential uses alternatives are not available. For other uses alternatives are available but a longer timeframe than 18 months is needed for the adjustment to new technology, techniques and alternatives.

Enforceability: Enforcement authorities can set up efficient supervision mechanisms to monitor industry`s compliance with the proposed restriction. Methods can be easily adapted from the methods to analyse of PFOA and longer-chain PFAS. Given that methods exist, the absence of an EU standard analytical method is not considered as a hindrance to the enforceability of the proposed restriction.

Manageability/monitoring: There are numerous analytical methods reported in the scientific literature to perfluorinated and some related substances in almost all environmental media, e.g. water, air, biota, and in humans.

Sweden has already initiated the development of a new CEN standard within the Technical committee TC248/WG26, "EC restricted substances in textiles" that specifies a test method for detection and quantification of extractable PFAS in textile articles, that includes PFHxA, its salts and related substances. Furthermore, at least in Germany, there is a norm (DIN 38407-42) for analysing PFCAs and PFSAs in water, sewage and sludge (Deutsches Institut für Normung e.V. (DIN), 2011). The method is applicable to concentrations higher than 0.01 µg L^{-1} in water (0.025 µg L^{-1} in treated sewage). Within that method unfiltrated water samples are spiked with mass-labelled internal standards and extracted with solid phase extraction. The instrumental analysis should be performed with liquid-chromatography coupled to a mass-spectrometer. A possibility to measure PFHxA related substances without knowing every single substance, is the conversion of these substances to the corresponding acids and subsequent analysis of the PFCAs, for example in water samples. Oxidation can be performed with hydroxyl radicals (Houtz and Sedlak, 2012). These radicals can be produced in a water sample by thermolysis of persulfate under basic pH conditions. Besides the availability of analytical methods a sampling strategy is needed to monitor the restriction. There are different possibilities:

- time trend monitoring
- monitoring of emissions

For both strategies it has to be kept in mind that PFHxA is persistent. In consequence, PFHxA will remain in the environment for ages even if emission to the environment is stopped immediately. In addition there will be continuing emissions from articles in use and from non-EU-countries via long-range transport. A time trend monitoring can be performed with samples from the environment, from animals or from humans. Methods and instruments available in (environmental) specimen banks could be used for such a monitoring. Reductions of emissions of PFHxA and related substances in the environment should result in decreasing PFHxA concentration in such a trend monitoring. It might be sufficient to measure PFHxA in such a trend monitoring, because the related substances will be degraded to the corresponding persistant acid in the environment. Decreasing trends in emissions will then not be directly measurable in environmental samples because time is needed for degradation. Furthermore, it has to be kept in mind that release of PFHxA from environmental sinks, like sediment, might bias time trend in some cases.

A joint approach for different enforcement activities such as inspections and testing for the occurrence of serveral regulated PFASs as PFOS, PFOA, C9-C14 PFCAs and PFHxA, its salts and related substances at the same time would lower costs. Thereby, enhancing cost effectiveness and reducing enforcement costs for PFHxA, its salts and related substances. Regarding imported acrticles, border authorities can control compliance using the RAPEX system (Rapid Exchange of Information System) to report any violation of the restriction. A time trend monitoring can be performed with samples from the environment, from animals or from humans. Methods and instruments available in (environmental) specimen banks could be used for such a monitoring.

This restriction proposal also includes recycled material and articles made from recycled materials. In the dossier we have demonstrated a concern resulting from the exposure to PFHxA, its salts and related substances. Subsequently there is a concern if recycled materials contain these substances. An exemption for recycled materials would potentially lead to higher emissions to the environment in comparison with an appropriate waste

management. Recycling of contaminated wastes contributes to environmental releases and the contaminants may again circulate through use, disposal and recycling phase of articles.

Considering all aspects, the Dossier Submitter proposes a restriction that bans all manufacturing, uses or content in articles 18 months after entry into force of the restriction except for the uses specified in Table 5 of Part 1 of the restriction dossier, for which time-limited or total exemptions are proposed. It is concluded that the following thresholds are feasible for mixtures and articles placed on the market:

- 25 ppb for for the sum of PFHxA and its salts
- 1000 ppb for the sum of PFHxA- related substances.

The proposed restriction does not cover the "second-hand" market (e.g. used textiles and textiles in the supply chain). One reason for this is that the second hand market is difficult to control, in most cases one consumer donates /sells single articles to another consumer (directly or via a second-hand store). It would not be practical to remove single articles from the market. Also, to use e.g. a jacket as long as possible before it turns into waste is a sustainable management of resources.

E.1.2 Other Union-wide risk management options than restriction

Table 25: Other Union-wide risk management options than restriction.

Other relevant Instruments	**Community wide option for risk management**
Stockholm Convention	PFHxA might be proposed as POP in the future. However, it seems to be more effective to start with the assessment of concerns on PFHxA in the frame of an SVHC identification under REACH regulation first.
Further international regulatory activities	Given PFHxA might be present in imported articles, and due to its ubiquitous presence in environmental compartments, it is important to consider initiating world-wide risk management measures.
Voluntary industry activities	Voluntary measures to be initiated by industry might cover phase out of PFHxA and related substances from certain product categories and industrial uses. Furthermore, it might comprise the education of manufacturers, downstream users and consumers regarding the proper use of articles with PFHxA and related substances during its whole life-cycle. Emissions during manufacture

	might be as far as possible prevented. However, voluntary industry activities might address only certain sectors and applications, therefore they cannot completely prevent emission of PFHxA into the environment

E.2 Impact Assessment for specific uses

Table 26: Main applications, as well as benefits, of C6 fluorinated polymers and fluorinated surfactants.

Industry	**Application**	**Property**	**Benefit**	**Fluoro-technology**
performance textiles and carpeting	interior textiles of cars /aircrafts	water, oil, stain, soil protection	improved cleanability, longer fabric life lowering overall maintenance costs	fluorinated polymer
	outdoor apparel and equipment	water, oil, stain, soil protection	durable, lifesaving protection in severe environments, longer useful garment life	fluorinated polymer
	professional protective textile	durable, high water and oil (solvent) repellency. Chemical resistance	life protection in severe environments, protection against hazardous chemicals, protection against water and liquids in a (fuel) fire.	fluorinated polymer
	non-woven (medical)	IPA repellency (isopropanol alcohol); repellency to blood, urine and other body fluids	prevention for medical work wear for the operating theatre; protection of hospital staff; departmental, ward and surgical clothing for nurses, nursing staff and doctors	fluorinated polymer

	non-woven (automotive)	water- and oil repellency; resistance to liquid chemicals (battery), diesel- and gasoline; heat resistance	protection of components in the motor area; insulation	fluorinated polymer
	carpets /home textile	water, oil, stain, soil protection, reduced dirt pickup	easy clean, longer useful life	fluorinated polymer
food packaging		oil and grease resistance	enabling paper packaging for pet food, microwave popcorn, quick service restaurant, meals; reduces potential for burns from hot oil migration through the packaging or wrap; maintains aesthetics and integrity of packaging material	fluorinated polymer
electronics	semi-conductors (etching and resist materials, cleaning fluids)	wetting and levelling to control and improved chemical etching. High purity, pure drying cleaners	ability to manufacture semi-conductors.	fluorinated surfactant
firefighting foams	airports, oil fields, fuel storage, defence applications	high efficiency oxygen starvation, faster extinguishment times, better burnback resistance	quicker extinguishing of fires, resulting in saved lives, reduced asset losses; fire-fighter safety	fluorinated surfactant

building and construction	paints, building materials protection	wetting, levelling, mold-releasing, anti-fouling	longer useful lifetime, lower repainting interval, reduced paint waste from recoat preparation	fluorinated surfactant

E.2.1 Fluoropolymers and side-chain fluorinated polymers

E.2.1.1 Overview

PFHxA, its salts and related substances are used for the production of (per-)fluorinated polymers, either as monomers or as processing aid to control the polymerisation process. Fluoropolymers provide vital performance characteristics to products or production processes. These polymers are used for several applications as finishing agents or as repellents. Therefore, fluoropolymers are used in a wide range of sectors.

Proposed restriction elements for PFHxA and related substances in fluoropolymers

Shall not be manufactured, used or placed on the market as substances on their own; shall not be used or placed on the market in:

(a) Another substance, as a constituent,
(b) A mixture,
(c) An article,

in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances.

Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction

Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3.

The concentration limit referred to in paragraph 2 shall be 150 ppm for the sum of PFHxA and its salts in fluoroelastomers used in the following usage groups: Automotive and aerospace industry. This derogation shall not apply to articles referred to in paragraph 2(c).

E.2.1.2 Use and functions

Structurally, fluorinated polymers belong to different polymer classes: side-chain fluorinated polymers (SFPs) and fluoropolymers. SFPs consist of a non-fluorinated polymer backbone with fluorinated side-chains. Non-fluorinated side-chains can be present as well. The fluorinated side-chain is typically composed of a terminal perfluoroalkyl moiety, a spacer and a linker. The backbone is attached to the fibre surface via physical or chemical bonding. Fluoropolymers such as polytetrafluoroethylene (PTFE) are used for the breathable membrane (Figure 8 (C)). They are distinguished by a carbon-only polymer backbone with fluorines directly attached to the backbone carbon atoms (Buck et al., 2011; Henry et al., 2018).

Several precursors of PFHxA are used as intermediate and as monomers for polymerisation. Most important for polymer production are numerous acrylates with a C6 perfluorinated

side chain like the registered 6:2 FT(M)A. As well the acrylate (6:2 FTA) as the metacrylate (6:2 FTMA) are registerd for 100 – 1000 t/a for use in the EU.

Fluoropolymers as such do not contain structural moieties like FTOHs and PFCAs. A potential source, however, could be residues of fluorinated processing aids. The ammonium salts of PFOA or PFNA have been historically used as fluorosurfactant in the manufacture of fluoropolymers by emulsion polymerisation (Buck et al., 2011). Many fluoropolymer manufacturers have discontinued the use of PFOA and PFNA salts as processing aids and are now using alternative fluorinated substances (Buck et al., 2011; Henry et al., 2018; Wang et al., 2013). Wang et al. (2013) mention that some producers may have used, or may use, the ammonium salt of PFHxA or a 6:2 fluorotelomer carboxylic acid (a precursor of PFHxA) as an alternative processing aid. The ammonium salt of PFHxA is an essential processing aid in the production of fluoroelastomers. Fluoroelastomers are predominantly used in highly critical combustion engine vehicles (gasoline, diesel). Their excellent heat and chemical resistance are necessary for smaller, higher performance engines necessary to meet the EU car emission standards (Euro6b). To our knowledge, fluoroelastomers are the only material combining excellent heat, oil, ozone resistance as well as fuel permeability. With the added amount of APFHx the quality of the fluoroelastomers is controlled. Fluorinated surfactants are required to achieve the intimate mixing of monomers in the ploymerisation step to complete an efficient and safe reaction. The compound is registered for 10 – 100 t/a and is imported as 50 % water solution into the EU. Depending on polymertype, the residual content of unbound APFHx is varying.

Aqueous based products on the basis of side-chain-fluorinated polymer dispersions are used to impart functional oil and water repellency when applied to textile, leather, hard surfaces or paper fabrics (industrial and consumer application). The fluorochemical finishes can be applied by padding (foulard), spraying, foam applications, exhaustions or coating. During the manufacturing of synthetic fibers a fluorochemical polymer can be added during the polymer melt process to impart oil and water repellency to the finished fibers. A large quantity of the fluoropolymers is further processed into a variety of specialized articles (fibers, tubes, sheets and tapes). Those articles are than further processed into the final products and offered for sale.

For side-chain-fluorinated polymers some information is available on uses from the public literature, too. For example textiles is one of the use areas of side-chain-fluorinated polymers (European Chemicals Agency, 2015a). Textiles are also mentioned by some registrants as one of the product categories for use of 6:2 FTMA in polymerization. Fluorinated polymers are used for making textiles water-, dirt- and stain repellent (Lacasse and Baumann, 2004). When extracting such textiles, e.g. outdoor textiles, non-polymeric fluorinated substances, beyond others, PFHxA and 6:2 FTOH, can be found (Greenpeace, 2016; Gremmel et al., 2016; Kotthoff et al., 2015a).

The fluorinated side-chains comprise an alcohol moiety which is bonded *via* ester linkage or other (e.g. urethane) linkages to the non-fluorinated polymer backbone (Figure 7). The alcohol moiety can typically be n:2 FTOHs or perfluoro-alkane sulfonamidoethanols. The former are precursors of PFCAs whereas the latter are precursors of perfluoroalkyl sulfonic acids (PFSAs). Polymer degradation and related breakage of the linkages can release the fluorinated alcohols as cleavage products. Degradation half-lives for fluorotelomer-based

SFPs in soil and water are on the time scale of decades or longer (Holmquist et al., 2016; Li et al., 2017a) However, the ester linkages could be cracked partially, so that the polymeric structure itself seems to be a source for the occurrence of FTOHs and PFCAs, too. Most relevant sources are, however, residuals from production such as unreacted monomers and derivatives thereof. Impurities from the production process could be another source.

To better understand the structural identity of these residuals, it is useful to briefly mention the two principal technologies for the manufacturing of compounds containing perfluoroalkyl chains: electrochemical fluorination and telomerisation. The former produces a mixture of branched and linear isomers, whereas the latter produces primarily or exclusively linear compounds (Buck et al., 2011). According to information from manufacturers, telomerisation is the most frequently used technology. The telomerisation process usually starts with a perfluorinated C2 parent structure (tetrafluoroethylene) which is converted to a perfluoroalkyl iodide (Knepper and Lange, 2012). The addition of tetrafluoroethylene building blocks yields a mixture of perfluoroalkyl iodides with even-numbered fluorinated carbon chains. The mixture can be further purified by distillation to obtain compounds with desired chain lengths. The addition of ethylene finally yields fluorotelomer iodides which can be further transformed to, e.g., fluorotelomer alcohols (e.g., 6:2 FTOH, 8:2 FTOH) and (meth)acrylate monomers (Figure 7).

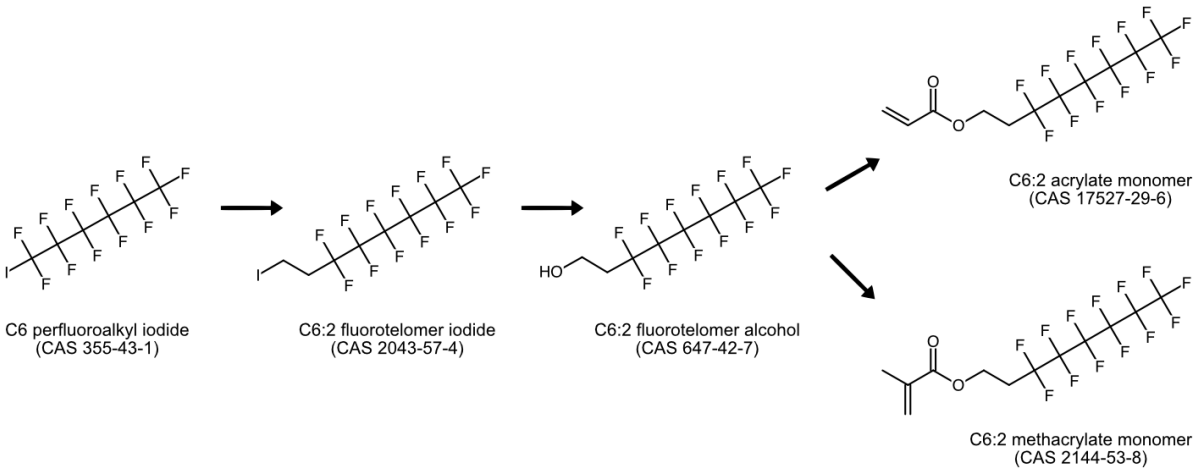


Figure 7: *Synthesis of fluorotelomer-based (meth)acrylate monomers as raw material for the manufacturing of side-chain fluorinated polymers (SFPs).*

The fluorinated (meth)acrylate monomers are copolymerized with one or more non-fluorinated acrylate monomers, and possibly other monomers. The SFPs contain, as a rule, 20 – 50 % (w/w) fluorine and are commercially available as water-based dispersions with a polymer content of 20 – 30 %.

The basic substances are manufactured in an integrated way as a production cascade where one reaction product serves as feed stock of the next stage. Alternatively at some stages the reaction products can be isolated and as such be sold to customers that perform

further processing to manufacture fluorinated compounds of higher complexity (usually fluorinated polymers or fluoropolymers).

Overall, the fluoropolymer does not seem to be a relevant source of FTOHs and PFCAs because of structural reasons. The replacement of PFCA surfactants and processing aids are removed by postpolymerisation processing (Henry et al., 2018).

E.2.1.3 Baseline

Manufacturing of polymers with perfluorinated C6 side chains is one of the most important uses of PFHxA precursors. These polymers are used in the EU in quantities from 1 000 to 10 000 t/a. Further, the ammonium salt from PFHxA is used as processing aid for manufacturing of fluoroelastomers from 10 – 100 t/a. These polymers and fluoroelastomers mainly are designed for the special needs of the customers using these products.

E.2.1.4 Economic and other impacts

According to information from consultations with stakeholders production sites for polyacrylates and polyurethane in the EU rely heavily on fluorinated compounds. One manufacturer claimed that a restriction would lead to complete reorganisation of his business and could entail a closure of the production site. The manufacturer claims that this might lead to the loss of a considerable number of jobs. However, this might be an overestimation, considering that according to publicly available information only 80 workers are employed at the production site. Further it is uncertain if and how the manufacturer could shift production to alternatives. Finally, the Dossier Submitter lacks information on whether the proposed derogations would enable the manufacturer to continue at least part of his business. Therefore, more detailed information is needed.

Another manufacturer contacted the Dossier Submitter late in the preparation process for this dossier asking for a derogation for the use of PFHxA-related substances in the production of fluoropolymers, fluorinated polymers and fluoroelastomers at his manufacturing facilities in the EU. The manufacturer did not provide case specific data on possible socio-economic consequences in case of a restriction.

If PFHxA, its salts and related substances are restricted in the future, downstream users will switch to non-fluorinated alternatives. The Dossier Submitter expects that an unknown share of this demand will be served by European manufacturers that offer fluorine-free solutions for uses considered by this restriction proposal.

One manufacturer of fluoropolymers also produces non-fluorinated products in small quantities. In sum, the Dossier Submitter has not enough information to assess whether this manufacturer or others will be able to reorganize business to the production of non-fluorinated alternatives, whether other EU-based manufacturers can take over business or whether non-EU manufacturers will serve the increasing demand. Therefore, the Dossier Submiter does not consider any job losses at the moment but considers this potential cost a major uncertainty.

The Dossier Submitter has not enough information on the manufacturers that are already producing alternatives.

Proposed exemption for the use of APFHx in the production of fluoroelastomers:

Fluoroelastomers are predominantly used in highly critical combustion engine vehicles (gasoline, diesel). Their excellent heat and chemical resistance are necessary for smaller, higher performance engines to meet the EU car emission standards. Typical products are turbo charger hoses, fuel hoses, seals and gaskets. There is another way to produce fluoroelastomers called soap-free emulsion polymerization but the resulting fluoroelastomers do not reach the same performance levels. According to information received supply shortage of fluoroelastomers that are produced with C6 polymerisation aid would lead to considerable costs: massive requalification costs and time for downstream users and a considerably reduced competitiveness of the EU car industry.

The Dossier Submitter received information that the EU market for fluoroelastomers with C6 polymerisation aids is served by two producers. One of them demonstrated that emissions from the production process are in the very low kilogram-range. No information from the competitor(s) are available but the Dossier Submitter assumes that even if other manufacturers have higher emissions, these still will be considerably below 1 t/a. Releases from articles containing fluoroelastomers into water and soil have been calculated according to the expected use in automotive and aviation applications and are expected to be 100 – 1 000 kg/a.

The Dossier Submitter estimates loss of profit of the European (C6-)fluoroelastomer manufacturers in case of a restriction in the range between 2-16 million €/a. With no more details available a central estimate of 9 million €/a is assumed. A Cost-effectiveness ratio of 2 000 - 160 000 €/kg results with a central estimate of approximately 30 000 €/kg. Additional costs for downstream users might be possible in case they have to use non-C6 fluoroelastomers. Considering CEAs from previous restriction proposals the Dossier Submitter deems that the cost are not proportionate and therefore proposes an exemption as stated in paragraph 5 of the restriction proposal.

E.2.1.5 Cost-effectiveness, affordability and proportionality to risk

Cost-effectiveness cannot be calculated for the production of fluoropolymers as possible impacts on European manufacturers are highly uncertain. Releases have been calculated for the service life of fluoropolymers produced in the EU. However, these emissions are also incorporated in the emission estimates for specific uses. Therefore, they are accounted for in the respective sections to avoid double counting.

The Dossier Submitter cannot evaluate whether demand for fluorine-free alternatives can be met by the manufacturers that are currently producing (acrylic) polymers with C6 side chains or whether distributional impacts will occur in the EU with other manufacturers taking over the demand.

With regard to the production of fluoroelastomers the Dossier Submitter recognizes the high costs in relation to potentially reduced emissions and proposes a derogation.

E.2.1.6 Impact of different transitional periods

No information has been received on the impacts of different transitional periods.

E.2.1.7 Uncertainties and sensitivity analysis

Major uncertainties have to be considered with regard to the manufacture of polymers. A manufacturer commented that it is uncertain if he can transition to fluorine-free production. Closing of a manufacturing plant is possible.

Effects of closures are uncertain at the moment. However, in case of closure it would be highly likely that current producers release an unknown number of workforces, leading to costs of temporary unemployment.

No information is available if producers of alternatives within the EU would be prepared to meet the increased demand for non-fluorinated alternatives.

With regard to the derogation for the production of fluoroelastomers one manufacturer claims that emissions from end of life vehicles are low because shredder residues will be incinerated. It is unknown to the Dossier Submitter whether this is a high-temperature incineration process. Therefore, emissions might be much higher.

The estimated number of unreported releases could be much higher. The number of articles imported into the EU containing fluoroelastomers or other products with APFHx as impurity is unknown but might be very high.

E.2.2 Semiconductor

E.2.2.1 Overview

The semiconductor industry uses PFASs as process agents for the photolithography process, etching process and furthermore, in cleaning fluids. Besides surface activity, also purity and stability of PFASs are relevant properties for semiconductor industry. Furthermore, usage of PFASs in photo-acid generators (PAGs) allows the creation of strong acids and non-diffusive, highly soluble and non-agglomerating PAG molecules (Stakeholder Consultation, 2018).

Proposed restriction elements for PFHxA and related substances in semiconductors

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3. Paragraphs 1 and 2 shall not apply to photolithography or etch processes in semiconductor industry until seven years after entry into force of the restriction.

E.2.2.2 Use and functions

Four fundamental processes are involved when manufacturing semiconductors: Implant, deposition, etch/polish and photolithography. PFOS was used for Photo-resist and anti-reflective coatings for semiconductors, as etching agent for compound semi-conductors and ceramic filters, photo masks in the semiconductor and liquid crystal display industries (UNEP, 2016). The industry eliminated PFOS and is eliminating PFOA and related substances. As replacement short-chain PFCAs and PFSAs are used. They are used in photoresists and antireflective coatings in the photolithography processes in semiconductor manufacturing (Stakeholder Consultation, 2018).

Photoresists are light-sensitive materials that allow transferring a pattern from a photo mask to a waver. In the photoresist coating process several critical issues exist: coverage over uneven surfaces, consistent coating thickness, controlling pattern defects and particle contamination. Short-chain PFASs are used as ingredients in photoresists as surfactants to achieve uniformity and change the absorption and refractive index. A photo-acid generator (PAG) is contained in the photoresist, which decomposes by light into an acid. As a strong acid is preferred fluorinated substituents are used which increase the acidity of the acid. This is because PFASs are able to trap the hydrogen atoms liberated in the photolysis process. Additonally, the highly non-polar tail of PFASs, allows the molecule to stay in place when exposure occurs (Stakeholder Consultation, 2018).

Anti-Reflective Coatings (ARCs) reduce the reflectivity of the photoresist coating, e.g. by being spun onto the wafer prior to the resist coating stopping reflections from underlying layers. PFASs are used in ARCs chemical formulations to improve film forming properties and adjust the refractive index.

Furthermore, fluoropolymers are used in the etching process and in cleaning fluids in semiconductor manufacturing. In the etching process they are used due to their stability and their low surface tension for wetting and leveling to control and improve chemical etching. Fluoropolymers are used in cleaning processes as they provide purity as pure drying cleaners which is relevant to avoid trace contaminants in the production of the microchips.

E.2.2.3 Baseline

Brooke et al. (2004) estimated a consumption of PFOS-related substances to be 470 kg/a for the year 2002 for the semiconductor industry in the EU (Brooke et al., 2004). Today the overall amount of PFASs used by semiconductor industry is assumed to be < 10 t/a (Stakeholder Consultation, 2018).

E.2.2.4 Uses, functions and alternatives

As non-fluorinated alternatives for both photo-lithography (photoresists and ARC) and etching (etching agent) processes the following substances were identified during the assessment of alternatives for PFOS: amyl acetate, anisole, *n*-butyl acetate, ethyl lactate, methyl-3-methoxypropionate and propylene glycol methyl ether acetate (UNEP, 2018a).

In 2010 IBM announced the invention of a fluorine free photo acid generator, which is used in photoresists and the holding of several respective patents using this PAG (IBM, 2010). However, it is unclear if such products are used at the moment.

One objective in the semiconductor industry is the continuation of scaling which leads to different challenges e.g. in the lithography process (Wojtecki et al., 2018). Therefore, new methods are developed such as selective area atomic layer deposition which bypasses the lithography step (Elinoff, 2018). Innovations exist that enable usage of latter at scale relevant for semiconductor industry (Staff, 2018)

E.2.2.5 Economic and other impacts

Short-chain perfluorinated substances are used in very small quantities as ingredients at low concentrations in photoresist and ARCs chemical formulations in semiconductor photolithography. Short-chain perfluorinated substances are not becoming part of the final product (the microchip). They are purely used as a manufacturing chemical in very small quantities, estimated to be < 10 t/a.

A fluorocarbon surfactant /surface modifier is much preferred to available alternatives because the known alternatives all contain silicon. Etching and ashing photoresist (subsequent steps in production of semiconductor wafers) convert the silicon to silicon dioxide, which is a difficult residue to remove and interferes with product quality.

No single "drop-in" replacement is possible for all semiconductor applications where substitutes exist. Every use has to be re-engineered to see, if a replacement material will meet the technology requirements. Moreover, even within the semiconductor industry technologies are not consistent. Alternatives that work for one application, or one company, will not necessarily work for another application or another company. A company use of PFAS is in many areas of photoresists specific to their individual process.

This substitution process takes also time and can only be done once the well-defined chemical structure, that is seen as the alternative, has been identified (hence, only after the step of an identification of a clear chemical alternative on a chemical level, real feasibility testing can be initiated). It is assumed that this process will take more than five years. If no such substitute is found to be available, R & D will have to look for alternative chemistry or processes and the time period needed for an invention cannot be estimated.

Currently the semiconductor industry does not see an option to substitute the fluorine chemistry from their processes immediately. If uses in the manufacturing of semiconductors are included in the scope of the restriction severe economic impacts are expected. Detailed information on impacts for European industry could not be obtained during the consultation or from research. Some general information is available: Global revenue of the semiconductor industry amounted to around 470 billion US $ in 2018. The share of Europe based manufacturers is estimated to be roughly nine percent.[16] However, it is unknown to the Dossier Submitter how many articles from European manufacturers are produced within the EU.

It is important to consider that PFHxA-related substances are used as manufacturing chemicals and are not present in the final articles. Therefore, if production is no longer possible in the EU it is expected that production will take place outside the EU and articles will be imported. The benefit of a restriction would be < 10 t/a emissions avoided.

In summary we propose a time limited derogation for seven years for semiconductors. Alternatives are not available at the moment but industry informed during the stakeholder consultation that efforts are undertaken to identify fluorine-free alternatives and to integrate them into production processes. The dossier submitter is aware that use quantities and emissions are comparatively low in comparison to the economic impacts that are possible when EU manufacturing would no longer be possible. Therefore, the Dossier Submitter expects that manufacturers will provide more information on detailed substitution plans in the public consultation in case the seven years are believed by them to be too short to realize substitution.

E.2.2.6 Cost-effectiveness, affordability and proportionality to risk

Cost estimates could not be derived. Therefore, it was not possible to calculate cost-effectiveness. The reduction of emissions is expected to be less than 10 t/a. The yearly revenue of Europe based manufacturers is estimated to be 42 billion US $. Even considering that part of the production (and therefore part of the emissions) takes place outside the EU it is highly likely that the societal costs resulting from profit losses, the closure of manufacturing sites and release of workforce result in a very high cost-effectiveness ratio that indicates unproportionately high costs of a restriction.

Stakeholders emphasized the high societal cost in case no alternative was available. They did not comment on the affordability of the substitution process in general.

E.2.2.7 Impact of different transitional periods

Industry needs the appropriate amount of time to transition to fluorine-free production. A transitional period of less than seven years would probably lead to a discontinuation of production and high costs.

A longer transitional period might be necessary for manufacturers to implement alternative manufacturing processes without PFHxA-related substances. However, the Dossier

[16] https://www.zvei.org/fileadmin/user_upload/Presse_und_Medien/Pressebereich/2018-89_Deutscher_Halbleitermarkt/2018-12_Pressekonferenz_Fachgruppe_Halbleiter_ZVEI.pdf (last access: 13.12.2019).

Submitter expects that manufacturers present detailed substitution plans in case a different transitional period is required.

E.2.2.8 Uncertainties and sensitivity analysis

Substitution depends on feasibility testing that needs more than five years. If these tests fail during the substitution process alternatives need to be identified which would result in much more time needed for substitution.

In general, the Dossier Submitter received information that the semiconductor industry is already investing in R&D activities to substitute fluorine-free substances. Therefore, no additional cost for substitution processes have to be calculated. But it might be possible that a restriction with a time-limited derogation results in the need to invest considerably larger resources than expected, leading to costs that can be attributed to this restriction.

E.2.3 Fire-fighting foams

E.2.3.1 Overview

Fire extinguisher based on foams are used for class B fires (flammable liquids) as well as in special cases for class A fires (combustible materials). Socio-economic impacts of a regulatory action under REACH on the use of PFHxA and related substances in fire fighting foams are studied for five broad categories of uses:

- Aviation: Fluorinated fire-fighting foams are used in stationary fire extinguishing systems within buildings on the airport grounds as well as by the plant fire brigades to extinguish hydrocarbon fuel fires (de Vries, 2014).

- Petrochemical industry: Fluorinated fire-fighting foams are used in oil and gas platforms, raffineries and fuel depots for e.g. in cases of mineral oil fires. They are used in stationary and non-stationary systems (IPEN 2018/POPRC-14, 2018; Stakeholder Consultation, 2018).

- Defence applications: Fluorinated fire-fighting foams are used for fire fighting of class B fires in seagoing military units, fuel depots and airports. Also, for training purposes regarding fire-fighting on ships fire-fighting foams are used (information received by the Federal Ministry of Defence (Germany)).

- Other industrial uses: Fluorinated fire-fighting foams are used by plant fire brigades to protect e.g. production and in stationary fire extinguishing systems in warehouses e.g. in automotive industry in cases of fire of stored flammable liquids or tires (Stakeholder Consultation, 2018).

- Other uses: Hand-held fire extinguishers: Fluorinated fire-fighting foams are used in hand-held fire extinguishers for different operation sites such as indoor areas in public sectors or private sectors. They are used for Class B as well as Class A fires (MINIMAX, 2019).

The joint stocks of such firefighting foams of the German armed forces, of larger airports, of refineries, municipal fire departments and chemical industrial fire departments were estimated with about 12 500 t (personal communication Blunk,

University of Cologne 2017). This is sufficient to prepare firefighting foams with fluorosurfactants for more than six years (assuming no changes in demand within the next years). Due to the enormous costs of AFFFs, it could be expected that this stock will be used until the use of perfluorinated surfactants will be forbidden in extinguishing agents.

Proposed restriction elements for PFHxA and related substances in fire-fighting foams

Shall not be manufactured, used or placed on the market as substances on their own;
Shall not be used or placed on the market in:

(a) another substance, as a constituent,
(b) a mixture,
(c) an article

in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances.

Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction
Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3.
Paragraphs 1 and 2 shall not apply to concentrated fire-fighting foam mixtures, which were placed on the market before [date – 18 months after the entry into force of this Regulation] and are used or are to be used in the production of other fire-fighting foam mixtures, until five years after entry into force of the restriction.
This shall not apply to:

(a) use of fire-fighting foam for training;
(b) use of fire-fighting foam for testing unless all releases are contained.

Furthermore, Paragraphs 1 and 2 shall not apply to concentrated fire-fighting foam mixtures for defence applications – as long as no successful transition to military operable fluorine free foams can be achieved:

- for seagoing units, air traffic facilities and storage of fuel
- for training purposes provided that emissions occur in enclosed areas and wastewater is collected and disposed of safely

Additionally, Paragraphs 1 and 2 shall not apply to concentrated fire-fighting foam mixtures until twelve years after entry into force of the restriction for:

- for cases of class B fires in storage tanks with a surface area above 500 m^2.

(a) By (entry into force + 6 years), the Commission shall re-evaluate paragraph 6 in the light of new scientific information, including the availability of alternatives for articles referred to in paragraph 6 modify this entry accordingly. Additionally, from (entry into force + 12 months), a natural or legal person benefitting from the derogation in paragraph 6 shall provide by 31 January of each calendar year a report to the competent authority in the Member State concerned containing:
(a) efforts on substitution of fire-fighting foams that contain PFHxA, its salts and PFHxA-related substances;
(b) used quantities in the previous year of fire-fighting foams that contain PFHxA, its salts and PFHxA-related substances per sector specifying:
    (i) share n training and in operation
    (ii) information on whether emission was contained, collected and disposed safely or emitted into the environment.

Member States shall forward the data to the Commission by 31 March every year.

E.2.3.2 Use and functions

Different fire-fighting foams exist. Fire-fighting foams can be assigned to protein foams (P) and synthetic foams (S) as well as to their respective alcohol-resistant (AR) versions: P(AR) and S(AR), which are fluorine-free and the following foams which are fluorinated fire-fighting foams: Aqueous film-forming foams (AFFF, AFFF (AR)), fluorprotein foams (FP (AR)) and film-forming fluoroprotein foams (FFFP, AR-FFFP).
The listed fluorinated fire-fighting foams are often referred to as Class-B-foams, although they might be used for other classes of fires, e.g. Class-A, as well. In contrast to Class-B-foams these foams are not listed in EN 1568 as they are not developed to extinguish Class-B fires. They are chemically considered to be part of the synthetic foams (S) and are therefore considered as fluorine free fire-fighting foams. (CHEMGUARD, 2013; De Vries and Holemann, 2001; DIN EN 1658, 2018; Fire Fighting Foam Coalition (FFFC), 2016; Zwirner, 2010)

FP, FP(AR), P and P(AR) are not able to provide a film-forming effect on flammable liquids (Ulrich et al., 2018). However, users often state foams as AFFF but refer to it as a group which includes FFFP, FP and respective AR species, as AFFF and AFFF (AR) play the predominate role in fire fighting compared to fluorprotein foams. Due to latter and the scarce information on FFFP and FP in the Stakeholder Consultation and in literature, the next paragraphs concentrate on AFFF and do not include fluoroprotein foams. However, it is not always transparent which definition was applied in respective studies and some of the listed points may also apply to fluoroprotein foams.

Fluorinated fire-fighting foams for extinguishing hydrocarbon-based fuel fires include fluorosurfactants to reduce the surface tension of the aqueous solution. The AFFF concentrates consist of water, surfactants, solvents and additives. The fluorinated surfactants contained in AFFF lower the surface tension and allow the formation of an aqueous film between fuel and foam, thereby cooling the surface, acting as a vapor barrier, allowing a fast spreading of the foam on the fuel and preventing re-ignition. Furthermore, fuel shedding is prevented as the oleophobicity of the fluorinated foam reduces the fuel contamination of the foam thereby preventing flammable foam (Ahrens et al., 2015; Kempisty et al., 2018; Laundess et al., 2011; Pabon and Corpart, 2002; Stakeholder Consultation, 2018).
AFFF are especially used for hydrocarbon fuel fires occurring in defence, industrial, aviation and municipal applications, but can also be used in firefighting trainings, in households and in public buildings. Different concentration ranges of fluorosurfactants in foam concentrates are reported, e.g. 0.6 – 1.5 wt% of total weight (Kempisty et al., 2018) or 1.5- 6.5 wt% (Moody and Field, 2000).

The composition of AFFF is divers and the structure of used fluorinated surfactants used varies (D'Agostino and Mabury, 2014). In recent years a shift from long-chain PFASs to short-chain PFASs used in AFFF formulations could be observed (Houtz et al., 2016) due to several regulations regarding long-chain PFCAs, PFSAs and their precursors. Most fire-fighting foams are now manufactured with fluorochemicals /fluorotelomers based on a perfluorohexane (C6) chain (UNEP, 2016). Several short-chain alternatives used in AFFF are known, e.g. fluorotelomer surfactants like 6:2 fluorotelomer sulfonamide alkylbetaine

(Moe et al., 2012), 6:2 fluorotelomer sulfonamide aminoxide (Jensen and Leffers, 2008)and 6:2 fluorotelomer thioamidosulfonate (Harding-Marjanovic et al., 2015).

However, the chemical structures of the fluorosurfactants are often trade secrets and many substances are difficult to analyze. (Dauchy et al., 2017) oxidized samples of fire-fighting foams to transform PFCA-related substances into the end-stage products. Thereby allowing conclusions regarding precursor concentrations in AFFF. PFHxA was detected in all three tested foams exceeding the concentration predicted based on prior analysis of precursor substances in the given samples. The highest concentration of PFHxA in an AFFF being 578 570 µg /L.

PFHxA can also be found in AFFF as unintended by-product (Cortina and Korzeniowski, 2008); (Favreau et al., 2017)). A chemical analysis of PFASs in Class-B-foams on the Swedish market in 2014 detected PFHxA in all seven foams showing the highest concentration of the analysed PFCAs for PFHxA (up to 14 000 µg/kg) (Swedish Chemicals Agency, 2015a).

In conclusion, a shift from long-chain to short-chain chemistry in AFFF could be observed in recent years with new fluorosurfactants being mainly based on a perfluorohexane (C6) chain, therefore being potential precursors for PFHxA. Some structures are known precursors for PFHxA, while further unidentified PFHxA-precursors are used as fluorosurfactants as well. Furthermore, PFHxA itself can be contained as impurity in aqueous fire-fighting foams. The application of fire-fighting foams will in most cases lead to considerable amounts released to the environment as it was shown by measured concentrations in the environment after such events.

E.2.3.3 Baseline

For professional firefighting an annual use of fluoro-surfactant containing firefighting foam concentrate of about 12 500 t was estimated in Europe. Surfactants placed on the market in the area of firefighting foams are estimated to be in the range of 1 500 – 3 000 t/a.[17] Products that require these compounds are the AFFF and AR-AFFF products. Preliminary results from an ongoing study by the European Commission and ECHA (European Commission DG Environment and European Chemicals Agency, 2019) suggest a market split as follows: Military 29%, civil aviation 16%, municipal fire services 14%, petroleum refineries 20%, petrochemical manufacturing 21%. Not included are handheld and mountable fire extinguishers and uses in other industrial manufacturing sites. The Dossier Submitter assumes that for example manufacturing sites storing large amounts of plastics use AFFF in parts (e.g. automotive industry). Further the Dossier Submitter received information that suggests that the market share for municipal fire services is considerably higher than assumed in the study.

[17] At the time of writing this restriction dossier the joint project by EU and ECHA on the use of PFAS in fire-fighting foam was still ongoing. Preliminary data suggests that the estimations used for this restriction proposal are plausible, i.e. of the same order of magnitude as what can be expected to be calculated by EU/ECHA.

Within the last years a shift from AFFF to FFF occurred. Some airports already substituted AFFF with FFF. Personal information from an alternatives supplier suggests that substitution processes are also taking place in industrial manufacturing sites. On the one hand the information suggests a decrease in the use of PFHxA-related substances in fire-fighting foams. On the other hand, it is expected that foam containing PFOA-related substances needs to be replaced when the PFOA-related requirements from the Stockholm Convention are implemented in the EU. This will lead to an increased demand for AFFF with PFHxA-related substances.Considering the divergent trends, the Dossier Submitter expects a stable demand for AFFF in the future for the non-restriction scenario.

E.2.3.4 Uses, functions and alternatives

As already described several classes of fires exist in which fire-fighting foams are used. However, only in cases of fires with incinerated, non-polar liquids with an even liquid surface and an intensity and quantity not allowing the use of synthetic fire-fighting foams (S) the use of AFFF might be considered (Keutel and Koch, 2016; Ulrich et al., 2018). A Best practice guidance for Use of Class-B fire fighting foams published by FFFC (2016) states that the use should be limited to cases in which a significant flammable liquid hazard is present and only after investigating whether non-fluorinated techniques can achieve the required extinguishment and burn-back resistance. Furthermore, training foams not containing fluorosurfactants should be used in training situations. Surrogate liquid test methods without fluorosurfactants should be used for testing fixed systems and vehicle foam proportioning systems.

In recent years several fluorine-free fire fighting foams meet the requirements of Class-B standard fire fighting performance certifications (see Table 6 in UNEP/POP/POPRC.14/6) as alternatives to AFFF were developed. A project by the New York State Pollution Prevention Institute (Winnebeck, 2018) identified over 100 fluorine-free Class-B foams from 25 manufacturers.

Non-fluorinated alternatives are given in Table 27 and are e.g.:

- Hydrocarbon based foams,
- protein based foams,
- foams based on other detergents such as alkylsulfates.

Table 27: Examples for non-fluorinated foams.

	Substances /Product	**Manufacturer**	**Use**	**Reference**
Hydrocarbon based foams	2-6 % hexylene glycol (CAS No: 107-41-5, EC 203489-0); hydrolysed protein [70 – 80 %], metallic salt: $NaCl+MgCl_2$ [8 – 15 %]; $FeSO_4*7\ H_2O$ [0 – 2 %] /PROFOAM 806G	Gepro Group		(UNEP, 2018a)
	RE-HEALING	Solberg	foam concentrates (for class-B fires of hydrocarbon based burning material and fires of polar solvents, also useable for class-A fires)	(UNEP, 2018a)
Protein based foams	Sthamex F-15	Dr.STHAMER	synthetic foam concentrates *(*officially approved in accordance with DIN EN 1568 for use as low, medium and high expansion foam for class A + B fires*, mainly used for training, but also has some marine uses)*	(Sthamer, 2018; UNEP, 2016)

Other Foams	sodium decyl sulfate (142-87-0), alkylpolyglycoside (132778-08-6) /trainol	Angus Fire	training foam concentrate	safety data sheet (ANGUS FIRE, 2018)
	Orchidex BlueFoam 3x3	Orchidee	foam concentrate for class A and class B fires	(Orchidee, 2019)
	Freedol	3F	different applications e.g. in industrial plants	data sheet (3F, 2019)

However, this is a non-exhaustive list and the market for fluorine free foams is fast moving regarding new developments, as stated by an expert at the ECHA Stakeholders' Workshop on firefighting foams (2019).

FFFC (2016) stated, that the use of class-B foams should be limited to institutions such as: airport operations, storage tanks, terminals and petroleum /chemical processing, highway and rail transportation, marine and defence applications, industrial facilities and some power generating facilities where situations may arise in which a significant flammable liquid hazard is given. Several establishments of the named industries shifted successfully from the use of AFFF to fluorine-free fire fighting foams (see Table 28) showing the applicability of the developed alternatives.

Table 28: Examples for applications of non-fluorinated foams.

Place	Country	Area	Industry	Reference
Auckland	New Zealand	(major hub) airport	aviation	(IPEN 2018/POPRC-14, 2018)
Copenhagen	Denmark	airport	aviation	
Dubai	United Arab Emirates	(major hub) airport	aviation	
Edinburgh	Great Britain	(major hub) airport	aviation	
Gatwick	Great Britain	(major hub) airport	aviation	
London Heathrow	Great Britain	(major hub) airport	aviation	
Stuttgart	Germany	(major hub) airport	aviation	
Åre Östersund	Schweden	airport	aviation	(Goldenman, 2019)
Göteborg/Landvetter	Schweden	airport	aviation	
Kiruna	Schweden	airport	aviation	
Luleå	Schweden	airport	aviation	
Malmö	Schweden	airport	aviation	
Ronneby	Schweden	airport	aviation	

Stockholm/Arlanda	Schweden	airport	aviation	
Stockholm/Bromma	Schweden	airport	aviation	
Umeå	Schweden	airport	aviation	
Visby	Schweden	airport	aviation	
23 (out of 260) capital and major region airports	Australia	airport	aviation	(UNEP, 2018a)
Cologne /Bonn	Germany	airport	aviation	(de Vries, 2014)
40 off shore installations	Norway	off shore installation	petrochemical industry	(Ystanes, 2019)
Danish Armed Force			military	(Goldenman, 2019)
Royal Danish Air Force			military	-
Billund	Denmark	airport		-
Paris Charles De Gaulle	France	airport	aviation	(Ross, 2019)
Paris Orly	France	airport	aviation	-
Oslo	Norway	airport	aviation	-
Dubai	United Arab Emirates	airport	aviation	-
Dortmund	Germany	airport	aviation	-
Allgau	Germany	airport	aviation	-
Lyon	France	airport	aviation	-
Helsinki	Finland	airport	aviation	-
Lisbon	Portugal	airport	aviation	-
Leeds /Bradford	Great Britain	airport	aviation	-
London City	Great Britain	airport	aviation	-
Bristol	Great Britain	airport	aviation	-
Brussels	Belgium	airport	aviation	-
Manchester	Great Britain	airport	aviation	-
Stansted	Great Britain	airport	aviation	-
East Midlands	Great Britain	airport	aviation	-
Blackpool	Great Britain	airport	aviation	-
Bristol	Great Britain	airport	aviation	-
Newquay	Great Britain	airport	aviation	-

Furthermore, LASTFIRE tested six C6 pure AFFF and two fluorine-free fire fighting foams on large-scale tanks. It was concluded that no 'drop in' replacement for previously used AFFF formulations by the new generation foams exist, independent from whether or not they contain fluorosurfactants. It was suggested that the performance capability of the alternative foams is specific to a formulation and the type of application equipment which is used (Ramsden, 2018).

At the ECHA Stakeholders' Workshop on firefighting foams (2019) it was stated by several experts that for the successful transition from AFFF to fluorine foams several factors

besides replacement of the product to a fluorine free foam concentrate have to be taken into account such as application rate, application technique, equipment, training, etc. It was also stated, that requirements for fire fighting foams are based upon fluorine containing foams but that known standards are already reviewed in regard of adaptions to test fluorine free foams.

E.2.3.5 Economic and other impacts

AFFFs are used in several classes of fires and by several different actors. Main users according to information received by the Dossier Submitter are airport rescue and firefighting, industrial firefighting, petrochemical industry firefighting, defence applications firefighting and private users. Temporary derogations from the restriction on PFHxA-related substances are proposed for certain uses in the petrochemical industry and for defence uses. Alternatives are currently not available for some uses in the petrochemical industry, which results in unacceptable risks for human health and the environment. The Dossier Submitter expects that alternatives for the derogated uses will become available within twelve years for the derogated uses in the petrochemical industry. While some armed forces already transitioned to fluorine free foams and report positive experiences with these foams, other armed forces reported challenges regarding a complete transition due to missing alternatives in the defence sector. An exemption shall therefore apply as long as a transition due to missing alternatives is not possible.

According to information received during further consultation and through publicly available information substitution is possible in most areas except the uses proposed for a derogation.

The Dossier Submitter could not calculate total impacts of the proposed restriction. However, stakeholders provided extensive comments and additional information was obtained from publicly available resources. The Dossier Submitter interprets the information he received at the stakeholder workshop and from the accompanying document with preliminary results (European Commission DG Environment and European Chemicals Agency, 2019) in a way that the EU/ECHA faces similar problems with regard to information gathering. On the other hand, it seems that the costs described qualitatively and quantitatively in the following are mostly complete. Final results from the EU/ECHA project are expected to be available later in 2020 and might present more reliable information to assess the costs of this restriction proposal. Relevant costs for users of fire fighting foams arise from the following substitution activities which are described in more detail in chapter 2.5.1.3.

- Price differences for fluorine-free fire fighting foams,
- procurement costs for replacement with fluorine-free fire fighting foams,
- incineration cost for replaced AFFF,
- cleaning of existing fire fighting installations and vehicles,
- adjustments to existing extinguishing infrastructure,
- administrative issues, training with alternative foam,
- handheld fire extinguishers.

The dossier submitter is not aware of data on hand held fire extinguishers in use in the EU. But considering that in Germany roughly 600 000 hand held fire extinguishers containing

AFFF are placed on the market per year[18] it is possible that in Germany 6 - 12 million and EU-wide 40 - 80 million devices are in use. Only an unknown share of the extinguishers will be affected by the restriction. For devices in private use a significant share of users will probably not comply with obligations resulting from this restriction (because of lack of awareness and enforcement).

Calculation of avoided emissions

Surfactants placed on the market in the area of firefighting foams are estimated to contain PFHxA-related substances in the range of 1 000 – 3 000 t/a. 4.6 to 144.4 t/a PFHxA (chemically bound in precursors) are released with extinguishing agents by professional and skilled workers into the European environment. Fire-fighting foams will not be incinerated during an event of fire. As a worst-case estimate, 100 % of the remaining AFFF will be emitted into the environment. Lacking further information, the median of the emissions estimate will be used as a central estimate. Considering that emissions will continue as a direct consequence of the proposed derogations avoided emissions are estimated to be approximately 1 450 t over 20 years.

E.2.3.6 Cost-effectiveness, affordability and proportionality to risk

It is not possible to calculate cost-effectiveness because important details on costs like the amount of fire-fighting equipment installations affected and the cost for cleaning are unknown. It is not known whether affordability could be an issue. Obviously larger airports, some manufacturers and the defence sector in general can afford the costs associated with substitution to FFF. No information is available if SME, smaller airports or municipal firefighting would be financially prepared to afford substitution. However, the Dossier Submitter takes into consideration that some SME might face difficulties when forced to replace or clean-up their fire-fighting installations. As well it might be possible that smaller professional firefighting units still use very old equipment that is not suited for the use of FFF. Hence, such units would have to replace equipment to be able to replace AFFF.

It is not possible to determine whether a restriction would be proportionate. Costs are high, especially for the replacement of existing foam.

On the other hand, emissions of PFHxA into the environment of up to 2 800 t (central estimate 1 450 t) could be avoided over 20 years.

E.2.3.7 Impact of different transitional periods

Longer transition periods most certainly would reduce the cost of substitution substantially. More firefighting vehicles and stationary extinguishing systems would meet their regular end of service life. Replacement of this equipment and the switch to non-fluorinated FFF could be combined, thereby realizing a reduction of the total cost.

On the other hand, the Dossier Submitter considers that a longer transitional period results in ongoing high emissions of PFHxA-related substances directly into the environment.

[18] Personal communication with one stakeholder (28 May 2019). Information is based on data from bvfa - Bundesverband Technischer Brandschutz e. V.

Considering the large stock of AFFF a longer transition period for AFFF already on the market is not justified.

E.2.3.8 Uncertainties and sensitivity analysis

The major uncertainties are the largely unknown costs discussed in the impact assessment.

Further major uncertainties are:

- The impact of the ban of the use of PFOA-stocks resulting from the Stockholm convention.

- Whereas most AFFF agents are compatible and different brands can be mixed in the same equipment, fluorine-free foams are generally not compatible and cannot be mixed with other types of foam agents. Mixing the foams may especially cause issues for fixed fire protection systems and defence applications.

- The availability of alternatives for firefighting in cases of class B fires in storage tanks with a surface area above 500 m^2 is uncertain.

E.2.4 Printing inks

E.2.4.1 Overview

Adding fluorinated surface-active substances to inkjets improves the working of modern printers as well as enhancing picture quality with different media.

Proposed restriction elements for PFHxA and related substances in printing inks

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA-related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3. Paragraphs 1 and 2 shall not apply to latex printing inks until seven years after entry into force of the restriction.

E.2.4.2 Use and function

The surface active fluorinated substance improves surface wetting during the printing process (UNEP, 2012b). During stakeholder consultation it was confirmed that C6 based short-chain fluorinated surfactants are used in some water-based inkjet inks and latex inks. The main function is the reduction of the water surface tension, when applied on nonporous substrates. In absence of a surfactant the mixture would tend to form large unequal drops that would lead to a non-uniform surface coverage of the inks (Stakeholder Consultation, 2018).

E.2.4.3 Baseline

There is little data on the volumes of PFHxA related substances used in inks. But results from the consultation with industry indicate that short chain PFAS are still commonly used in printing inks applications.

E.2.4.4 Uses, functions and alternatives

Various non-fluorinated surfactants were tested. Only the C6-based fluorinated surfactants provided the required performance, but research on non-fluorinated alternatives surfactants is continued. Alternative technologies are solvent based or UV-curable mixtures (Stakeholder Consultation, 2018).

E.2.4.5 Economic and other impacts

Very little information could be gathered on the availability of alternative substances to be used in water-based printing inks. According to industry, fluorinated products are used in applications that require exceptional technical performance such as industrial coatings. In many coatings siloxanes are commonly used instead, also because fluorine-based additives are comparatively expensive. It has been reported that C4 PFAS have partially replaced the long-chain PFAS. The dossier submitter therefore believes that alternatives are available.
Considering the lack of additional information, a calculation of substitution costs was not possible but the following aspects have been considered:

- Information from industry suggests that printing inks are mainly produced outside the EU.
- The worst case estimate for emissions of PFHxA-related substances is slightly above 10 t/a.
- Companies already undertake R&D irrespective of this restriction proposal. Therefore, these costs must not be counted as direct impact from the restriction proposal.
- Siloxanes and C4 PFAS have partially replaced longer chain PFAS. The dossier submitter assumes that this group of substances can be used as direct substitute.
- Industry stated that slightly higher costs for the substitute substances in latex printing inks are expected.

<u>Latex printing inks</u>
For latex printing inks the dossier submitter proposes a temporary exemption. During the stakeholder consultation information was submitted that PFHxA-related substances are used in latex printing inks. One manufacturer claimed that a simple "drop in" substitution is not possible and a more extensive reformulation will be necessary to develop competitive products. The manufacturer estimated the time needed for substitution with five to ten years. Considering that research for substitution according to information submitted has already started the dossier submitter assumes that alternatives will be available in 2024.
However, printers in use have to be equipped with the current generation of printing inks. These printers are expected to have a seven to ten-year service life. Hence, printing inks for the current printer generation need to be available after 2024 to avoid early

replacement of the printers. The proposed exemption ensures that printer hardware can be used until the expected service life expires. Therefore, impacts from early replacement are not expected.

E.2.4.6 Cost-effectiveness, affordability and proportionality to risk

The Dossier Submitter expects the restriction to be cost-effective. Manufacturing most probably takes place outside the EU meaning that distributional consequences would not affect European companies and workers. Stakeholders did not indicate that prices for inks would be affected. Most likely the largest effect of a restriction would be the early obsolescence of the current printer generation. The temporary derogation ensures that printers for latex inks are in service for another seven to ten years, i.e. the expected service life.

E.2.4.7 Impact of different transitional periods

As explained a shorter transitional period would lead to a shortened service life of printers and therefore considerable cost which would most likely be unproportionate.

E.2.4.8 Uncertainties and sensitivity analysis

Functional losses are not expected but according to scarce information from the stakeholder consultation possible.

E.2.5 Chrome plating

E.2.5.1 Overview

Identification of PFOS as persistent organic pollutant (POP) and the inclusion in Annex B of the POP regulation (EC No 850/2004) led to the substitution of PFOS with 6:2 fluorotelomer sulfonate (6:2 FTS also known as H4-PFOS) in chrome plating processes (UNEP, 2018a).

6:2 FTS degrades to PFHxA under environmental conditions (see chapter B.4.1.2). Furthermore, for 6:2 FTS itself not for all toxicological hazards sufficient data are available. Hence, a comprehensive assessment is not possible.

6:2 FTS is used in hard chrome plating processes as well as decorative chrome plating processes as surfactant to lower the surface tension of the plating solution. The differences between both chrome plating processes are reflected in thickness, hardness and deposition of the chrome layer on the plated object.

Aim of hard chrome /functional chrome plating (layer thickness > 0.2 mm) is to provide e.g. hardness, corrosion and wear resistance, lubricity and high resistance against chemicals. Hard metal plated parts are used e.g. in automotive industry, aircraft construction, shipbuilding and engineering like hydraulic cylinders and rods, railroad wheel bearings and couplers, moulds for the plastic and rubber industry (Blepp et al., 2017; UNEP, 2018a).

Decorative chrome plating is used for decorative surface finish. The thin layer of metal (layer thickness 0.05 - 0.5 µm) provides properties like aesthetically pleasing appearance

or non-tarnishing and is used e.g. in sanitary industry, kitchen appliances, car and truck pumpers or motorcycle parts (Blepp et al., 2017; UNEP, 2018a).

A further electroplating process is the electroplating of plastics in combination with decorative chrome plating.

Proposed restriction elements for PFHxA and related substances for chrome plating

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction. Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3. Paragraphs 1 and 2 shall not apply to hard chrome plating until five years after the entry into force of the restriction.

E.2.5.2 Use and functions

PFASs (e.g. 6:2 FTS) are used as wetting agents for numerous wet-chemical processes of surface finishing due to their properties with regard to process safety (Blepp et al. 2017). The wetting agents are used for chrome baths to lower the surface tension of the plating solution. The surfactants are also used to decrease aerosol emissions especially to reduce emissions of chromium VI (carcinogen) to the air (UNEP, 2018a; Willand et al., 2019). Due to reducing the surface tension, process gas bubbles become smaller and rise more slowly compared to larger bubbles. When the bubbles burst at the surface, mist is less likely to be emitted into the air because of the reduced kinetic energy of the slower bubbles (UNEP, 2017).

Fluorinated surfactants are only used in metal plating with chromium (VI) (Blepp et al., 2017; UNEP, 2018a).

For the process of plastic electroplating, firstly the plastics must be made electrically conductive. Therefore, microscopic pores are etched into the plastic surface by treatment with very strong oxidizing etchants. Mostly, a highly concentrated chromo-sulfuric acid solution is used as etchant. For achieving wettability of the hydrophobic plastic surface, a stable surfactant has to be added to the chromo-sulfuric acid (Blepp et al., 2017). As an alternative for PFOS predominantly polyfluorinated wetting agents (e.g. with 6:2 FTS) are used today (Willand et al., 2019).

E.2.5.3 Baseline

Based on an extrapolation approximately 150 t/a 6:2 FTS are used for chrome plating in Germany (Willand et al., 2019). This extrapolation has high uncertainties as only 40 of ~1 400 companies have been taken into account. Extrapolated to the EU, a consumption of 600 – 1 000 t/a is estimated.

E.2.5.4 Alternatives

Fluorinated alternatives could have similar risks to the environment like PFOS or 6:2 FTS (degradation to a substance with environmental concern). Therefore, these substances should not be used to avoid regrettable substitution.

Fluorine-free substances /products are not considered equally effective to fluorinated surfactants. Furthermore, additional risks with respect to safety, process stability and device preservation are mentioned by German electroplating industry association (UNEP, 2018a). Nevertheless, these substances have been partly used successfully in bright (decorative) chrome electrolytes (Blepp et al., 2017). The use in hard chrome plating is also possible, but according to the current state of knowledge the substances should be used on a case-by-case basis. Furthermore, fluorine-free surfactants oxidatively decomposed very rapidly in the process solutions and chromium (III) compounds are formed. This impairs the functional efficiency of the process solution (Blepp, et al., 2017).

Fluorine-free wetting agents contain higher concentrations on active substance (fluorine-free 1 – 50 %; 6:2 FTS 1 – 10 %). Reasons for this are, for example: a) these alternative substances reduce surface tension only at higher concentrations and b) higher consumption due to more or less rapid oxidation. Fluorine-free products often require a higher technical effort compared to the previous application with PFOS. In contrast to fluorinated products the fluorine-free products often have to be added diluted and in smaller dosages throughout the day. To achieve comparable surface tensions higher amounts of wetting agents are necessary (Willand et al., 2019).

As part of the assessment of alternatives for PFOS in chrome plating processes it was confirmed that non-fluorinated surfactants seem feasible for decorative as well as hard chrome plating (UNEP, 2019)

No surfactants (either fluorine-free or fluorinated) are necessary in closed coating reactors (UNEP 2018; Blepp et al., 2017). Chromic acid aerosols which are emitted to room air are significantly reduced. This is especially a technical alternative for hard chrome plating. Nevertheless, attention should be given due to explosion hazard of produced hydrogen gas (H_2) (UNEP, 2017). Due to highly diversified chrome plating processes it is impossible to describe a universal closed loop process technology for all of the various uses and process combinations (Blepp, et al., 2017).

For plastic electroplating non-fluorinated surfactants, which are not toxic and easily biodegradable, can be used successfully in the etching process if the production line is very constant. As a precondition, the plastic goods have to be dipped into the surfactant liquid before the etching process (UNEP, 2015). Successfully tested alternative immersion techniques include acidic permanganate solutions, nitric acid and trichloroacetic acid mixtures. The following disadvantaged were pointed out: problems with wastewater treatment due to organohalogen compounds; problems when searching for suitable rack insulation; risk of formation of nitrous gases during the use of nitric acid, and problems with the formation of manganese dioxide and fire safety issues when using permanganate solutions (Blepp, et al., 2017). Potassium permanganate, one of the alternatives, is harmonised classified as Repr. 2 (H361d).

Further fluorine-free alternatives and alternative processes are listed in Table 29.

Table 29: Examples for fluorine-free alternatives and alternative processes for chrome plating (UNEP, 2016; UNEP, 2018a; Willand et al., 2019).

Alternative	Hard chrome plating	Decorative chrome plating	Additional information	Reference
alkane sulfonates	x	x	not resistant to hard chrome plating; less effective in decorative chrome plating disadvantage: considerable data gaps of their chemical composition, hence environmental hazards cannot be assessed; general group of alkylsulfonates: commonly used degradable substances	(UNEP, 2016; UNEP, 2018a)
amine, C12-C14 alkyl, ethoxylated (CAS-No. 61791-14-8)	x	x	disadvantage: potential hazardous to the aquatic environment based on notified classifications in C&L inventory (impacts in mixtures unclear – specific amounts not known) self classification for human health endpoints: Acute Tox 4 (H302), Skin Corr 1B, Eye Irrit 2	(Willand et al., 2019)
oleo amine ethoxylates (e.g. mixtures with (Z)-octadec-9-enylamine, ethoxylated CAS-No. 26635-93-8)	x	x	disadvantage: (Z)-Octadec-9-enylamine, ethoxylated itself is potential hazardous to the aquatic environment based on notified classifications in C&L inventory (impacts in mixtures unclear – specific amounts not known) self classification for human health endpoints: Acute Tox 4 (H302), Skin Irrit 2 or Skin Corr 1B, Eye Irrit 2	(UNEP, 2018a; Willand et al., 2019)
3-[dodecyl(dimethyl)ammonio]propan-1-sulfonat (CAS-No. 14933-08-5)		x	self classification for human health endpoints: Acute Tox 4 (H302), Acute Tox 4 (H312), Skin Irrit 2 or Skin Corr 1B, Eye Irrit 2 or Eye Dam 1, STOT SE 3 (lungs)	(Willand et al., 2019)
paraffin oils, sulfochlorinated, saponified (CAS-No. 68188-18-1	x	x	disadvantage: potential hazardous to the aquatic environment based on notified classifications in C&L inventory (impacts in mixtures unclear – specific amounts not known)	(Willand et al., 2019)

			self classification for human health endpoints: Acute Tox 4 (H302), Skin Irrit 2, Eye Irrit 2	
other non-fluorinated alternatives	x	x	disadvantage: no information on chemical identity	(UNEP, 2018a)
physical covers (netting, balls) for metal plating baths (chromium (VI))	x	x	e.g. mesh or blankets (composite mesh pads) placed on top of bath or add-on air pollution control devices (packed bed scrubbers): advantage: high efficiency in removing chromium (VI) aerosols (> 98 %) (UNEP, 2016); no adverse health and environmental effects from control devices themselves; no factors limiting the accessibility e.g. PTFE coated balls on top of bath disadvantage: PTFE coated balls will not reduce chromium emission from the bath (onthe contrary: increasing chromium emission compared to using no mist suppressant)	(UNEP, 2016; UNEP, 2018a)
add-on air pollution control devices	x	x	e.g. packed bed scrubbers	(UNEP, 2018a)
novel plating processes	x	x	e.g. HVOF (high velocity oxygen fuel) process: advantages: process is globally available and is considered effective (high deposition efficiency and good quality finish) and with low costs; disadvantage: requiring high temperature application: layers may be more porous and less resistant to corrosion	(UNEP, 2018a)
chromium (III) plating		x	advantage: process does not require the use of fluorinated mist suppressants or wetting agents; disadvantage: potential for conversion of Cr(III) to Cr(VI) during plating process is unclear; potential contamination with other metals; potential formation of complexing agent	(UNEP, 2018a; Willand et al., 2019)

closed coating reactors	x	x	advantage: no fluorinated wetting agent necessary; limited aerosol emission to room air disadvantage: attention to possible explosion hazard	(UNEP, 2018a)

E.2.5.5 Economic and other impacts

For plastic electroplating non-fluorinated and non-toxic surfactants are available if the production line is very constant. As a precondition, the plastic goods have to be dipped into the surfactant liquid before the etching process (UNEP, 2015).

Fluorine-free substances /products are not considered equally effective to fluorinated surfactants. Furthermore, additional risks with respect to safety, process stability and device preservation are mentioned by German electroplating industry association (UNEP 2018). Nevertheless, these substances have been used successfully in bright (decorative) chrome electrolytes (Blepp et al., 2017).

The use in hard chrome plating is also possible but still under investigation.

An economic assessment for PFOS has been undertaken. Based on the price alone this was inconclusive. Some alternatives may be cheaper and some may be more expensive. This was related to PFOS and not 6:2 FTS. However, the POP Review Committee concluded: "Non-fluorinated surfactants are used during the production process for hard metal plating and decorative metal plating. Although they are degraded in the chromium electrolyte or etching bath and must be constantly dosed, the costs are not higher than using fluorinated surfactants" (UNEP/POPS/POPRC.12/INF/15/Rev.1).

For decorative plating a shift to other electrolytes that are Cr(III) based is an available alternative. This would mean that the demand on surfactants and process fluids is considerably lower, and that PFAS are not required.

It has to be considered that in contrast to fluorinated products the fluorine-free products often have to be added diluted and in smaller dosages throughout the day. To achieve comparable surface tensions higher amounts of wetting agents are necessary (Willand et al. unpublished). Therefore, it is possible that production processes need to be changed.

If an alternative is used where the goods have to be dipped into the surfactant liquid an additional bath has to be installed into the production facility. This means additional cost for the procurement of equipment as well as cost related to a reorganization of the production facility for some companies.

The information that is available at the moment is not sufficiently concise to derive a cost estimate. Therefore, the following information was taken into account to consider the economic impacts qualitatively:

- PFHxA-related substances are used in large quantities in the EU (estimated 800 t/a)

- It is estimated that a large share of the quantities used are emitted into the environment. The Dossier Submitter estimates that without a restriction nearly 3 500 t of PFHxA related substances will be emitted to water in the EU until 2040.
- Alternatives are available and used for decorative chrome plating and plastic electroplating.
- Alternatives for hard metal plating have been identified but not tested sufficiently by the industry.
- Of the various alternatives available some seem to have issues regarding performance, health and environmental impacts.
- Some alternatives proposed cannot be used without additional cost. For example, control devices for air flow, additional baths or additional waste water treatment could be needed. It is possible that manufacturing routines have to be changed.
- The chrome plating industry is characterized by heterogeneity and a large share of small and medium enterprises.
- It is not possible to derive a realistic restriction scenario for this diversified industry.
- The automobile industry is an important customer of hard metal plated parts and relies on these products.
- PFHxA-related substances are not present in the chromium-plated article. Therefore, no impacts are expected for imported articles.

Considering the scarce information, the Dossier Submitter proposes a temporary five-year exemption from the restriction for hard metal plating. The information suggests that an immediate substitution of substances falling under this restriction proposal is not possible. The European manufacturers of hard chromium plated articles would no longer be able to participate in the market and most likely their products would be replaced by imported articles. This could lead to supply shortages for downstream users who, like the automotive industry, depend on these products heavily. Five years also is realistic to install the necessary production processes for continued manufacturing in the EU.

For decorative chrome plating and plastic electroplating alternatives are available and scarce information suggests that the cost of substitution is affordable.

E.2.5.6 Uncertainties and sensitivity analysis

The information on further costs is highly uncertain: Implementation costs might be a heavy burden especially for the large number of SMEs in the market. The Dossier Submitter expects that the impacted industries will present further information if necessary during the public consultation for this restriction proposal.

No transitional periods have been proposed for decorative chrome plating and plastic electroplating. As alternatives are available longer transitional periods are not seen as proportionate. For hard chrome plating a transitional period of less than five years would lead to high economic costs in case alternatives could not be installed successfully in that time period.

E.2.6 Building material

Fluorinated substances are used in paints to improve flow, wetting, and levelling. The highly fluorinated substances are used to reduce surface tension in paints so that the surface on which the paint is applied is wetted. Fluorinated surfactants can yield in higher stability or resilience of foams for the formation of low-density concrete building blocks or adjustment of surface tension for better wetting behavior of paints. Due to the good wetting property, fluorinated surfactants are also used as additives in adhesives and glues. Some sectors of building industry directly incorporate fluoropolymers as a construction material.

Proposed restriction elements for PFHxA and related substances for building material

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction. Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3.

Compared with other wetting agents, such as silicones, PFASs are more effective in reducing surface tension which ultimately improves paint adhesion. It is primarily in water-based paints where these properties are required. Here, PFASs can be present at concentrations of about one percent. However, this figure is unreliable; in most cases there may be concentrations around 0.05 percent (European Chemicals Agency, 2018a).

Suppliers in the paint industry are of the opinion that surface-active fluorinated substances are generally significantly more expensive than alternative surface-active substances. They are therefore used only if such a low surface tension is required that this cannot be achieved with a fluorine-free alternative (UNEP, 2013).

The Swedish Chemicals Agency investigated a number of polymers and polymer appearing in raw materials in inventoried databases of paints and adhesives (Swedish Chemicals Agency, 2015b). These include perfluorinated and polyfluorinated (meth)acryl polymers, as well as several complex compounded side-chain fluorinated polymers (copolymers) which have not been categorized. Relevant for this restriction proposal are the following raw materials: silicones /siloxanes (C2-14), alkylammonium compounds (C4-7) and a smaller number of alkyl thiols (C4-20), phosphorus compounds (C6), (meth)acrylates (C6). Poly /perfluorinated (meth)acryl polymers (C-16), polyfluorinated silicones /siloxanes (C6-14), and poly /perfluorinated alkyl alcohols (C8-14) are used on the global market for printing inks.

On behalf of the German Environment Agency various building materials were investigated for per- and polyfluoroalkyl substances (Janousek et al., 2019; Knepper and Janousek, 2019). Prior to the analysis of the building materials a literature research on the use of PFASs in building materials was carried out. PFASs are used in coatings to achieve water, oil or dirt repellent properties and protect building materials from weather influence.

Fluorinated surfactants can yield in higher stability or resilience of foams for the formation of low-density concrete building blocks or adjustment of surface tension for better wetting behavior of paints. Due to the good wetting property, fluorinated surfactants are also used as additives in adhesives and glues (e.g. for production of derived timber products like oriented strand boards (OSB)). Some sectors of building industry directly incorporate fluoropolymers as a construction material. Application of polymers in building industry often involves ethylene tetrafluoroethylene (ETFE), which can be adopted for lightweight building shells (ETFE cushions), transparent roofing systems, greenhouses, covering of photovoltaic panels, or simply facade materials. Main superior properties of ETFE over glass or other conventional building materials are low dirt pick-up, corrosion protection, UV-light transparency, superior weight to surface ratio to glass builds, anti-fouling properties and long-lasting colour retention.

During the project selected building materials (total samples = 23) were analysed for various per- and polyfluorinated substances (e.g. PFHxA, 6:2 FTOH and 6:2 FTS). The samples included coatings, paints, lacquers, stain, foils (e.g. façade material), roofing material for flat roofs as well as sealants and glues. All samples were collected between October 2016 and August 2017 and have been analyzed as soon as possible. The following limits of quantification were determined: for 6:2 FTOH 40 µg/kg, for PFHxA and 6:2 FTS 2 µg/kg. C6 based PFASs were only detected in coatings (n= 3 of 4). Concentrations of PFHxA ranged from < 2 µg/kg to 360 µg/kg (aqueous and methanol extracts). 6:2 FTOH and 6:2 FTS were detected in one sample with a concentration of 1 700 µg/kg and 2.9 µg/kg respectively. Furthermore, 6:2 FTOH was detected in two further samples which had to be diluted. 6:2 FTOH concentrations were 520 mg/L and 4 300 mg/L. Due to high dilution factors, concentrations should be considered as approximative values. However, both, peak shape and retention time that were observed in dilutions matched standards. Nevertheless, since the used sample preparation technique was disadvantageous for volatile compounds, FTOH concentrations might be higher (Janousek et al., 2019; Knepper and Janousek, 2019).

Bečanová et al. investigated building materials including oriented strand board (OSB) and wood (n = 14), insulation materials (n = 16), mounting and sealant foam (n = 6), facade materials (n = 5), polystyrene (n = 5) and air conditioner components (n = 5) with the following resulting concentrations of PFHxA: OSB and wood: < 0.23 – 3.14 µg/kg (detected in twelve samples); insulation materials: < 0.23 – 5.79 µg/kg (detected in six samples). In all other samples PFHxA concentrations were below the limit of quantification of 0.23 µg/kg) (Bečanová et al., 2016).

During information collection one company reported the use of C6 fluorotelomer as oil and water repellent in special glass for construction (external glazing and interior decorative glass) as well as for the solar sector (Stakeholder Consultation, 2018). For water repellency the use of fluorine-free alternatives is possible.

Economic Impacts:

The tonnage range for this application area is unknown. Sufficient information on specific uses is not available. But it is assumed that Coatings with fluorosurfactants especially are used outdoors. So, a direct release of perfluorinated surfactants from the sector building and construction into the environment is considered as very likely in significant amounts.

C4 or C6 PFAS have been introduced in this area as substitutes for the formerly used C8 substances. They are used in some special applications where water-based mixtures are intended to be applied to very non-porous surfaces like e.g. plastic films. Here the main function in the mixtures is the reduction of the water surface tension when the mixture is applied on nonporous substrates.

There is little data on the volumes of PFHxA related substances used in paints. Comments from stakeholders indicate that short chain PFAS are still commonly used in paint applications (paints and varnishes). Suppliers in the paint industry commented that surface-active fluorinated substances are generally significantly more expensive than alternative surface-active substances. They are only used if a very low surface tension is required which cannot be achieved with a fluorine-free alternative (UNEP, 2013).

The concentration of the fluorinated substances in the paint can be up to 1 %, depending on the specific application. However, in most cases it is considered to be much lower, e.g. within the range of 0.05 %.There is little data on the volumes of PFHxA-related substances used in paint. Results from consultation for the preparation of the restriction proposal on PFOA with industry indicated that short-chain PFASs were already commonly used in paint applications. For that proposal it was estimated that PFOA-related substances were used (in 2015) in paints and inks within the range of 50 - 100 t/a within the EU. Considering that before the phase-out of PFOA, C6 substances were already in use and having received also information from industry that PFOA-related substances were substituted in the meantime at least partially with C6-substances, the Dossier Submitter estimates the same amount of use for PFHxA related substances for the purpose of this restriction proposal: within the range of 50-100 t/a. This estimate is highly uncertain.

One company reported the use of C6 fluorotelomer as oil and water repellent in special glass for construction (external glazing and interior decorative glass) as well as for the solar sector.

For water repellency the use of fluorine-free alternatives is possible.

Considering that fluorinated substances are more expensive fluorine-free alternatives would be cost effective and available if only the water-repellent properties are needed and considered.

Stakeholders submitted information that dirt and oil repellent properties have considerable benefits: longer useful lifetime, lower repairing interval, reduced paint waste from recoat preparation. It might also be possible that the protective properties of anticorrosive paints can be enhanced by perfluorinated urethanes. No information is available on the magnitude of such effects. But it is possible that some uses would be affected considerably, for example maintenance intervals of constructions where maintenance and refurbishing is difficult in general.

Without further information the Dossier Submitter proposes a restriction on PFHxA-related substances in building materials. Benefits include lower-priced products and cessation of direct emissions into the environment from outdoor applications. However, costs might be considerable as well, when dirt and oil repellent properties are missing.

E.2.7 Photographic applications

C6-based fluorinated surfactants are used in small tonnages in photographic equipment or in coatings when manufacturing conventional photographic films (Stakeholder Consultation, 2018). These substances are applied for coating printing plates, coating of photographic layers for various application (e.g. for medical applications) and for production of conductive screen inks and coating formulations. In these applications the substances are used as surfactants, as static control agents, as dirt repellents during coating operations and as friction control agents.

Proposed restriction elements for PFHxA and related substances for photographic applications

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction. Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3. Paragraphs 1 and 2 shall not apply to photographic coatings applied to films until five years after entry into force of the restriction.

In the draft report on the assessment of alternatives to perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (UNEP, 2018a) no C6 based fluorinated surfactants are mentioned as alternative for PFOS in the photo imaging sector. However, I&P Europe indicated that detailed information on alternatives in imaging products cannot be provided because it is considered as confidential business information. I&P Europe indicated that the search towards alternatives for C8 based substances typically involved a "preferred replacement hierarchy" favouring non-fluorinated hydrocarbon alternatives, followed by non-perfluorinated substances, further followed by per-fluorinated substances with shorter chain lengths (C3 or C4).

During stakeholder consultation it was commented that for some specific applications suitable non-fluorinated alternatives have not been found. Substances to be used in photographic applications require specific properties, e.g. lack photoactivity or colloidal stability (Stakeholder Consultation, 2018).

Nevertheless, at thirteenth meeting of the Persistent Organic Pollutants Review Committee (POPRC.13), representatives of the European photographic industry provided information that for specific photographic applications (photographic coatings applied to paper and for use in printing plates) non-fluorinated alternatives and the move to digital imaging have successfully replaced the use of PFOA and PFOA-related substances. These alternatives and alternative techniques should also be useable for the applications with C6-based fluorinated surfactants (UNEP, 2018b).

Economic Impacts:

According to information received during the consultation for the PFOA restriction proposal remaining products are mainly used by professional or hobby photographers, in medical or defence applications. Digital techniques will completely replace traditional photographic film within the coming ten years. Owing to this strongly decreasing market demand and the significant investment that would be needed to switch to alternatives (0.5 - 1 million € for a single photographic material), it is likely that the manufacture of the photographic film could cease in response to the proposed restriction. It is reasonable to assume that cost would be high compared to the volumes of PFHxA and PFHxA-related substances used given the probability that no traditional photographic film might be available to consumers /downstream users anymore. The dossier submitter assumes that this business will phase out within the next years. Therefore, an exemption for five years after entry into force of the restriction is justified after which no more production is expected anyway.

E.2.8 Fragrance and flavour industries

During the public consultation regarding the SVHC-dossier for PFHxA, it was noted that PFHxA, its salts and related substances may be in use in fragrance and flavour industries. Fragrances are one of the key factors in consumer preference of cosmetic, home care or personal care products. In the past few decades, beside natural-, synthetic fragrance compounds have become ubiquitous components of consumer products. Fragrances are mostly apolar molecules with low water solubility and in the absence of substantial amounts of cosolvents such as ethanol, surfactants are needed to solubilize them in water-based applications. At equilibrium the solutes are distributed between the aqueous phase and the hydrophobic pseudo-phase formed by the micelles, respectively (Fieber et al., 2018). Microencapsulation has been widely used to encapsulate various core materials to protect them from the outside environment and provide long-lasting releases in the use of the products. Perfume oil, as an odor supplier is encapsulated to form perfume oil-filled microcapsules. These capsules have to be resistant against to several chemicals, like those essential oils containing high active unsaturated bonds on the structure such as clove oil, Litsea cubeba oil and lemongrass oil. Further, emulsifiers are necessary to stabilize oil droplets (He et al., 2018). Products made by PFHxA, its salts and precursors have properties that are essential for handling of fragrance and odour componds in products and articles, such as they are surface-active and inert to different chemicals. However, the use of PFHxA, its salts and related substances in this field of use is not clear so far.

E.2.9 Mixtures for Consumer Use

E.2.9.1 Overview

PFAS are used in various mixtures intended for end-use by consumers. These include impregnating agents, ski or floor wax, cleaning products, car care and polishes (Jensen et al., 2008; KEMI, 2015; Knepper et al., 2014; Posner et al., 2013). Only limited information is available regarding the use of PFHxA related substances in these products. However, information is available that suggests availability of alternatives.

Proposed restriction elements for PFHxA and related substances in mixtures for consumer use.

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction. Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3.

E.2.9.2 Concentrations of PFHxA and precursors in consumer mixtures

PFAS are used in various mixtures intended for end-use by consumers. These include (water)proofing agents, ski or floor wax, cleaning products, car care and polishes (Jensen et al., 2008; KEMI, 2015; Knepper et al., 2014; Posner et al., 2013). Some sources indicate a use of potential PFHxA precursor substances in relevant products. For example, 6:2 fluorotelomer silanes or siloxanes (e.g. CAS No 51851-37-7 and 85857-17-6) are known to be used in nanofilm spray products on surface coatings with non-stick properties, which are applied to surfaces such as bathroom tiles, floors, windows and textiles (Kjølholt et al., 2015; NICNAS, 2016; Wang et al., 2013). According to the restriction proposal for TFDA's[19] in consumer products for spray application (RAC/SEAC, 2017), the *"…parent TDFAs will most likely predominantly [be] degraded/transformed to PFHxA".*

While the composition of the mixtures for consumer use (hereafter referred to as "consumer mixtures") is difficult to uncover due to lack of information in SDS and due to business confidentiality (BfR, 2014; Knepper et al., 2014), several studies have analysed the composition and contents of PFAS in these products. Historically, these investigations focused on PFOA, PFOS and potential precursors; however, several authors also reported on shorter chain PFAS content in consumer mixtures.

For this restriction proposal the openly available literature was evaluated for reported levels of PFHxA in consumer mixtures.

The literature search included the keywords "perfluoroalkyl", "PFAS" and "perfluorohexanoic acid" /"PFHxA" in combination with relevant products as "impregnating agents", "waterproofing agents", "paints" and "consumer products" in general. The retrieved sources were manually filtered for relevance for this restriction proposal. The evaluation also included likely PFHxA related substances (see section B.1.1). Among those, only 6:2 FTOH was reported in the available sources.

[19] (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol tri-O-(alkyl) derivatives

Herzke et al. (Herzke et al., 2012; Herzke et al., 2009) analyzed consumer products and preparations collected in Norway with supplemental samples from Sweden. A number of per- and polyfluorinated substances was analysed. PFHxA was found in two of five waterproofing agents and lubricants (23 and 25.6 µg/L), 6:2 FTOH in three of these products (523, 1 750 and 13 250 µg/L). In the three paints analysed, neither PFHxA nor 6:2 FTOH was found.

Fiedler et al. (2010) investigated impregnating agents, cleaning agents, lubricants /corrosion prevention agents, "conditioners" for wood or leather and other products. All products were sprays produced for private households and were samples from the German market (except one product from Brazil). Fluorotelomer alcohol 6:2 FTOH was detected in four of nine impregnating agents (max value 2.1 µg/mL) and two of four cleaning agents (72 and 148 µg/mL), PFHxA was not reported.

In a project regarding proofing products and technology, Knepper (Knepper et al., 2014) investigated five consumer impregnating agents. In two of five products PFHxA (0.1 and 0.13 µg/mL) and 6:2 FTOH (16.4 and 225 µg/mL) were found.

In a work by Liu et al. (2014b) investigating the increase or decrease of PFCAs in US household products a number of relevant liquid products was investigated. Including earlier results (Guo et al., 2009) in products purchased from 2007 - 2011 PFHxA was found in six of 13 carpets and fabric care liquids /foams (18.9 – 195 ng/g) and in four of eight "floor waxes and stone/wood sealants" (7.19 – 1 540 ng/g). In another study published by Liu and coworkers (Liu et al., 2015a) 6:2 FTOH was found in two of three carpet and fabric care liquids /foams (3 280 and 105 000 ng/g) and in one of five "floor waxes and stone/wood sealants" (754 ng/g).

In a study aiming at gathering more information on the use and the incidence of per- and polyfluorinated substances in every-day consumer products, Blom and Hanssen (2015) focused on shorter chain length polyfluorinated substances. While PFHxA was not detected, 6:2 FTOH was found in seven products from different categories (50 – 100 % of tested products) with concentrations of 0.114 mg/L (lubricant) to 0.741 mg/L (glider /glidewax for skis). In addition the phosphate esters 6:2 PAP and 6:2 diPAP were included in the analysis but were not detected in the consumer mixtures.

Kotthoff and coworkers analysed a number of consumer mixtures purchased in Germany for different PFCA and FTOH (Kotthoff et al., 2015b). Three "Nanosprays" and impregnating sprays were investigated for PFHxA (max. 14.1 µg/kg, median 6.9 µg/kg) and 13 for 6:2 FTOH (max 440 000 µg/kg, median 1 900 µg/kg). In addition 13 ski waxes were analysed for PFHxA (max. 1 737.1 µg/kg, median 17.9 µg/kg).

Borg and Ivarsson (2017) have focused on relevant consumer product types identified in the study from Blom and Hanssen (2015). The products were randomly selected from a number of Swedish retail stores. In several product types, including e.g. car wax, PFHxA and FTOH could be detected and quantified (PFHxA: 6/12 samples, 0.54 - 5.6 µg/L; 6:2 FTOH: 4/12 samples, 1 834 – 120 300 µg/L).

In a work including a relatively large number of samples Favreau et al. (2017) have reported on PFHxA in 7/60 proofing products (0.1 – 0.6 mg/kg, average 0.3 mg/kg). No PFHxA was reported in cleansers (n = 24), polishes (n = 18) or other products (n = 23).

In the same study 6:2 FTOH was quantified in 30 impregnating agents (2 - 1 840 mg/kg, average: 194; median 2 mg/kg), in one cleanser (4 mg/kg) and one polish (26 mg/kg).

The available results, recalculated to µg/kg and µg/L respectively, are given in Table 30.

Table 30: Reported concentrations of PFHxA and 6:2 FTOH in consumer mixtures.

Reference	**Products**	**PFHxA**					**6:2 FTOH**				
		N	**Detects**	**Max.**	**Min.**	**Median**	**N**	**Detects**	**Max.**	**Min.**	**Median**
Favreau 2017			LOQ 0.5 ng/mL	**µg/kg**				LOQ 10 ng/mL	**µg/kg**		
	impregnation products	60	7	600	100	(300 „average“)	60	30	1 840 000	2 000	(194 000 "average")
	cleansers	24	0	-	-	-	24	1	4 000	-	-
	polishes	18	0	-	-	-	18	1	26 000	-	-
	others	23	2	0.4	0.2	-	23	0	-	-	-
Borg 2017			LOD /LOQ not rep.	**µg/L**				LOD /LOQ not rep.	**µg/L**		
	rinse aid	2	0	-	-	-	2	0	-	-	-
	waterproof shoe treatment	2	1	2.5	-	-	2	1	120 300	-	-
	waterproof textile treatment	2	2	3.6	2.3	-	2	1	43 070	-	-

	waterproof textile /leather treatment	1	0	-	-	-	1	1	12 340	-	-
	shoe wax	1	1	4.7	-	-	1	0	-	-	-
	floor polish	1	1	5.3	-	-	1	1	1 834	-	-
	furniture polish	1	0	-	-	-	1	0	-	-	-
	car wax	2	1	0.54	-	-	2	0	-	-	-
Liu 2015								LOD 331 µg/g	**µg/kg**		
	carpet care liquid	n.a.	-	-	-	-	3	2	105 000	3 280	-
	household carpet /fabric-care liquids and foams	n.a.	-	-	-	-	2	0	-	-	-
	floor waxes and stone /wood sealants	n.a.	-	-	-	-	5	1	754	-	-

Kotthoff 2015			LOQ 0.5 µg/kg	**µg/kg**				LOQ up to 20 000 µg/kg	**µg/kg**		
	cleaning agents	6	0	-	-	-	3	n.r.	38 700	n.r.	3 800
	nanosprays and Impregnating sprays	3	n.r.	14.1	n.r.	6.9	13	n.r.	440 000	n.r.	1 900
	ski waxes	13	n.r.	1 737.1	n.r.	17.9	0	-	-	-	-
	wood glue	1	0	-	-	-	0	-	-	-	-
Bloom 2015			LOD 0.1 µg/L	**µg/L**				LOD 0.0001 µg/L	**µg/L**		
	car polish	2	0	-	-	-	2	1	263	-	-
	dishwasher liquid	2	0	-	-	-	2	1	391	-	-
	waterproofing product, shoes	2	0	-	-	-	2	1	2 410	-	-
	waterproofing product, textiles	2	0	-	-	-	2	1	259 000	-	-

			LOD 0.1 µg/kg	**µg/kg**				LOD 0.0001 µg/kg	**µg/kg**	
	glider for skis	1 to 2	0	-	-	-	1 to 2	1	741	-	-
	ski wax	1	0	-	-	-	1	1	623	-	-
	lubricant for bicycles	1	0	-	-	-	1	1	114	-	-
Liu 2014				**µg/kg**							
	household carpet /fabric-care liquids and foams	13	6	195	18.9	0	n. a.	-	-	-	-
	floor waxes and stone /wood sealants	8	4	48.3	15.3	21.4	n. a.	-	-	-	-
Knepper 2014			LOD 0.001 µg/mL	**µg/L**				LOD 0.01 µg/mL	**µg/L**		
	impregnation agents	5	2	130	100	-	5	2	225 000	16 400	

Herzke 2012, Herzke 2009			LOD /LOQ not rep.	**µg/L**				LOD/LOQ not rep.	**µg/L**	
	waterproofing agents	5	2	25.6	23	-	5	3	13 250	535	1 750*
	paint	3	0	-	-	-	3	0	-	-	-
Fiedler 2010				**µg/L**				LOQ 0.3 µg/mL	**µg/L**	
	impregnating agents	n. a.	-	-	-	-	9	4	2 100	600	1 250*
	conditioners for wood and leather	n. a.	-	-	-	-	4	0	-	-	-
	lubricants /corrosion inhibition agents	n. a.	-	-	-	-	4	2	148	72	-
	cleaning agents	n. a.	-	-	-	-	6	0	-	-	-

n.a.: not analysed; n.r.: not reported; LOD: limit of detection; LOQ: limit of quantification

Uncertainty

The overall number of data on PFHxA contents in mixtures for consumer use is very limited compared to the number of products on the European market that, due to their function, could potentially contain PFHxA. The available studies report PFHxA in various product types, with the highest concetrations found in ski waxes and in proofing products.

While the studies focused on products where PFAS can be expected due to their function, the number of samples for a single product type was below 20, and the number of detects within these samples was even smaller (up to 7). Robust statistical distributions can not be derived on this basis and even the maximum values found may not represent realistic worst cases.

In addition, the reported studies differ in their sampling strategies and analytical methods. This makes it difficult to compare their results. The reported concentrations range over four orders of magnitude. This may be the result of analytical difficulties othe diversity of the samples.

Taken to together the differences between the samples, the low number of samples with comparable product types and methods, and the lack of data for many products and countries, the database seems to be explorative, giving indications on orders of magnitude rather than the present distributions of PFHxA concentrations in European consumer products. Due to the ongoing changes in PFAS uses, it is not possible to deduce future concentrations of PFHxA in consumer products from these data.

E.2.9.3 Baseline

Information on current and future uses of PFHxA related substances in mixtures for consumer use is highly uncertain.

Currently, the Dossier Submitter can only refer to uncertain and incomplete information regarding the market for mixtures for consumer use. The studies that are summarized in Annex ‘E.2.9 Mixtures for Consumer Use’ suggest that products are available with and without shorter chain PFAS content. Publicly available information (e.g. from nordic ecolabel certification “Nordic Swan”) indicates that fluorinated as well as fluorine-free products are available to consumers for impregnating agents, ski or floor wax, cleaning products, car care and polishes. It remains unclear what the respective market-shares are and whether quantities will change in the future.

From the scarce information available it can only be assumed that use quantities and emissions are not negligible. The only respondent in the Dossier Submitter’s stakeholder consultation is present on the majority of the European markets but has no dominant market share.

Regarding emissions the DS assumes that a large share of quantities used will be emitted into the environment.

E.2.9.4 Uses, functions and alternatives

Additional information regarding specific uses and functions is not available. The manufacturer who responded indicates that substitution of fluorinated substances, technically and economically, is possible but would require some efforts. The area where they think that substitution could be possible the easiest is the impregnation of leather and textiles.

Publicly available information also suggests that alternatives are already available. A broad range of fluorine-free impregnating agents, ski and floor waxes and cleaning agents are on the market. There also seem to be manufacturers producing both fluorinated and fluorine-free products.

E.2.9.5 Economic and other impacts

Information on current and future use of PFHxA related substances in mixtures for consumer use is highly uncertain. No information on quantities produced within and outside the EU could be uncovered. Only one manufacturer in the field took the opportunity to present information on uses of PFHxA and related substances. The manufacturer produces under established brand names cleaning and care products for private consumers as well as bulk for professional building cleaning.

This company reported that it produces mixtures that contain or are produced with fluorinated substances as well as fluorine free alternative products. The production costs when fluorinated substances are used compared to their non-fluorinated alternatives, are "somewhat higher costs than fluorine free alternatives (11-25 %)".

Besides this information, the Dossier Submitter can only refer to publicly available information and to cursory market research on the availability of alternatives. This publicly available information indicates that fluorinated as well as fluorine-free products are available to consumers for impregnating agents, ski or floor wax, cleaning products, car care and polishes. Fluorinated and non-fluorinated products are generally in a comparable price range. Several manufacturers produce fluorinated products as well as non-fluorinated alternatives. It is unknown what the respective market-shares are and if quantities will change in the future.

According to an older study from Kemi (Swedish Chemicals Agency, 2006) cleaning products, polishes and other mixtures for consumer use are widely used and are directly released into wastewater and water purification plants. They argue that in spite of the low concentrations used in products, emissions to the environment can be significant.

Fluorinated compounds are not added to the products for their cleaning characteristics but because they provide good spreading properties and an even surface (Swedish Chemicals Agency, 2006).

Additional information regarding specific uses and functions is not available.

Direct economic impacts for manufacturers and consumers are expected to be low. Alternatives seem to be available on the market from a number of manufacturers. As mentioned above, one stakeholder reported that non-fluorinated alternatives are slightly less costly than fluorinated mixtures. This information is highly uncertain as it is based on information from one manufacturer only, who produces some of the products falling under the category of mixtures for consumer use.

Impacts resulting from reduced or lost functionality of the mixtures are possible. For example, fluorine-free impregnating agents and floor polish might be less effective in protecting textiles and floors against oil and grease stains leading to a reduced service life or a loss of consumer-friendly cleaning properties. Fluorine-free ski waxes are less effective in optimizing the sliding properties of skiers. Such impacts cannot be further qualified or quantified by the Dossier Submitter. But it is assumed that not monetarizing reduced functionality leads to an underestimation of substitution cost.

In absence of more detailed information the Dossier Submitter argues that a restriction on the use of PFHxA, its salts and related substances in mixtures for consumer use will be proportionate. Alternatives are most likely less costly and already available on the market. Emissions most likely will be directly released into soil and wastewater: However, information is scarce on the possible impacts of functional losses and in addition it is possible that the Dossier Submitter is unaware of essential uses in specialized products.

E.2.9.6 Cost-effectiveness, affordability and proportionality to risk

The dossier submitter expects the restriction to be cost-effective. Alternatives are available in a similar price-range and therefore no additional costs are expected.

The restriction therefore is affordable and proportionate to the risk. It might even be possible that manufacturers are in a position to manufacture less expensive when the costs for non-fluorinated substances are lower as indicated by one stakeholder.

E.2.9.7 Impact of different transitional periods

Alternatives are already available on the market. Transition for users still using PFHxA-related substances should be possible in a short timeframe. Therefore, a longer transitional period has no effect on affordability.

E.2.9.8 Uncertainties and sensitivity analysis

Most of the information presented on PFHxA in mixtures for consumer use is highly uncertain.

- Products with and without PFHxA-related substances are available on the market for mixtures for consumer use.
- Highly certain is that the available fluorine-free products are direct alternatives to fluorinated products.
- Information regarding the substitution cost is highly uncertain, especially with regard to products like car polish and ski waxes. It might be possible that at least some reformulation processes are costly.

- Information regarding quantities produced in Europe and imported quantities is not available.
- Emission quantities are unknown but non-negligible.
- Functional losses have not been considered for the discussion on cost-effectiveness.

E.2.10 Cosmetic Products

E.2.10.1 Overview

PFAS are used in various cosmetic products. PFHxA concentrations have been reported in concentrations up to 6 500 µg/kg. PFAS serve as emulsifiers and surfactants and are added to cosmetic products for binding, bulking and skin /hair conditioning purposes. Studies suggest that PFAS are used in higher concentrations only in some product groups. Market research indicates that PFAS-free alternatives are available for all cosmetic products.

Proposed restriction elements for PFHxA and related substances for cosmetic products

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction. Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3.

E.2.10.2 Use and functions

A search of CosIng, a database hosted by the European Commission, identified more than 70 perfluorinated cosmetic ingredients. According to the database, substances like polyfluoroalkyl phosphonic acids (PAPs) serve as emulsifiers and surfactants. Other PFAS (e.g. perfluorinated polymers, ethers and esters) are added to cosmetic products for binding, bulking and skin /hair conditioning purposes. According to a recent study from the Danish Environmental Protection Agency, 0.7 % (78 out of 11108) cosmetic products had declared contents of fluoroalkyl substances or other fluorinated compounds (Brinch et al., 2018).

There are only a few studies aiming to determine the PFHxA content in cosmetic products, whereas no studies report on FTOH 6:2 concentrations. It is to note that product selection in all three studies focused on products with declared PFAS content. A recent study from the Danish EPA found PFHxA concentrations in 15 of 18 products, whereas a study conducted in Sweden detected PFHxA in ten of 31 products (Brinch et al., 2018; Schultes et al., 2018). An older study from Japan sampled cosmetic products in 2009 and 2011 (Fujii et al., 2013). In this study sunscreens were analyzed, too, and 18 of 23 products

contained detectable levels of PFHxA. In all three studies high levels (> 1 mg/kg) of PFHxA were detected in foundations, which are leave-on applications with direct and prolonged skin contact. Thus, it is reasonable to assume that cosmetic products contribute to human exposure in some cases, when high PFHxA containing products are used on a daily basis. The exact origin of the detected PFHxA is not known; however, both impurities in and degradation products of intentionally added PFAS seem plausible explanations. Indeed, foundations with high PFHxA levels also contained more than 100-fold higher PAP concentrations in the Swedish study. In addition, there is no data on the stability of PFAS such as PAP during dermal application under real-life conditions involving solar UV light radiation, skin bacterial metabolism, and skin metabolism.

Table 31: Reported concentrations of PFHxA in cosmetic products.

Data source	**PFHxA**		**µg/kg**		
Brinch et al. (2018)[a]	samples (n)	positive samples	max.	min.	median
all products	18	15	3 340.0	n.d.	4.9
facial scrub	1	1	6.3	5.4	5.9
BB /CC creams	3	3	397.0	12.0	16.5
body lotions	2	2	24.0	4.5	14.2
cream /lotion	2	2	2.6	1.1	2.1
eyeliner	1	0	n.d.	n.d.	n.d.
foundations	4	3	3 340.0	n.d.	178.5
concealer	1	1	1 940.0	1 930.0	1 935.0
highlighter	1	1	18.0	17.0	17.5
hair spray	1	0	n.d.	n.d.	n.d.
powder	1	1	34.0	30.0	32.0
eye shadow	1	1	5.5	5.4	5.5
Schultes et al. (2018)					
all products	31	10	4 640	< 3.35	< 3.35
cremes	7	0			
foundations	9	4	4 640	< 3.35	< 3.35
pencil	1	0			

powders	12	6	447	< 3.35	3.62
shaving Creme	2	0			
Fujii et al. (2013)					
all products	23	18	6 500	< 1.9	350
foundations	9	8	2 100	< 1.9	410
manicure	3	3	140	4.7	24
lip rouge	2	0	< 5.7	< 3.8	
sunscreen (milk)[b]	6	5	6 500	< 4.6	2 800
sunscreen (foundations)	3	2	350	< 2.3	180

[a] two individual products were analyzed per sample
[b] four different lots of a specific sunscreen milk were analyzed

E.2.10.3 Baseline

No information on use quantities and emissions is available. The highest concentrations of PFAS have been found in foundations, concealers and sun screen. Emissions from these uses are at least partly emitted directly into environment and wastewater.

E.2.10.4 Uses, functions and alternatives

Market research indicates that PFAS-free alternatives are available for all cosmetic products: Some large producers have announced a phase-out of all PFAS from their products: L'Oréal, H&M, Lumene, the Body Shop, Isadora and Kicks. L'Oréal announced in 2018 that the reformulation processes are completed for all their trademarks (Chemical Watch, 2018).

The Danish retailer Coop eliminated all cosmetics containing PFAS from their product range.

E.2.10.5 Economic and other impacts

No cosmetics producer submitted information during the stakeholder consultation. However, the phase-out activities by the mentioned companies suggest that affordable alternatives are available and functional losses of products are not to be expected. It can be assumed that alternatives are available for the whole scope of cosmetics on the market. For example, L'Oréal is the world's largest cosmetics company and serving various market segments with different brands (e.g. mass, professional, luxury, and active cosmetics markets).

E.2.10.6 Cost-effectiveness, affordability and proportionality to risk

Cost effectivenes cannot be demonstrated due to the lack of data. However, the voluntary phase-out activities demonstrate that the transition to a PFAS-free production is affordable and therefore the Dossier Submitter proposes to restrict the use of PFHxA-related substances in cosmetic products.

E.2.10.7 Impact of different transitional periods

The Dossier Submitter has no information on possible impacts of a longer transitional period.

E.2.10.8 Uncertainties and sensitivity analysis

Uncertainties regarding functional losses are minor. The manufacturers that phase-out PFAS from their products serve large parts of the cosmetics market and have alternatives available for all their products.

Some uncertainties remain regarding the affordability of a restriction on PFHxA-related substances. Obviously, some large companies are in a position to reformulate their products at reasonable costs. However, according to information from the restriction proposals on microplastics and D4, D5 and D6 several participants on the cosmetic market are small and medium enterprises. No information is available how these companies would be affected by a restriction on PFHxA-related substances. Uncertainties remain on whether such companies are prepared to reformulate at affordable costs, i.e. whether scientific expertise and financial resources are always available to substitute their products without functional losses.

E.2.11 Textiles

E.2.11.1 Overview

Proposed restriction elements for PFHxA and related substances in mixtures for textiles

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3. Paragraphs 1 and 2 shall not apply to personal protective equipment intended to protect users against risks as specified in Regulation (EU) 2016/425 of the European Parliament and of the Council, Annex I, Risk Category III (a), (c), (d), (e), (f)[20] Paragraph 1 and 2 shall not apply to non-woven medical textiles Paragraph 1 and 2 shall not apply to impregnation agents for re-impregnating of articles referred to in paragraph 9(b) (personal protective equipment) From (entry into force + 12 months), a natural or legal person placing an article specified in paragraph 9(b), 9(c) or 9(d) on the market for the first time and benefitting from the derogation therein shall provide by 31 Januar of each calender year a report to the competent authority in the Member State concerned containing: (a) the identity of the substance(s) used in the previous year; (b) the quantity of PFHxA, its salts and PFHxA-related substances used in the previous year. Member States shall forward the data to the Commission by 31 March every year.

The occurrence of fluorotelomer alcohols (FTOHs) and PFCAs in textiles is (primarily) related to the DWR finishing that imparts water, oil and stain resistance to the textile. DWR finishing finds important application in functional clothing such as performance outdoor textiles, which provide weather protection and body moisture management to the wearer (Schellenberger et al., 2018). This is achieved by a multi-layered fabric system, in which a water-repellent outer fabric is combined with a waterproof breathable membrane inside (Figure 8 (A)).

[20] Regulation (EU) 2016/425 of the European Parliament and of the Council of 9 March 2016 on personal protective equipment and repealing Council Directive 89/686/EEC. Category III includes risks that may cause very serious consequences such as death or irreversible damage to health. The categories mentioned above relate to the following: III(a) substances and mixtures which are hazardous to health, III(c) harmful biological agents, III(d) ionising radiation, III(e) high-temperature environments the effects of which are comparable to those of an air temperature of at least 100 °C, III(f) low-temperature environments the effects of which are comparable to those of an air temperature of – 50 °C or less.

E2.11.2 Use and functions

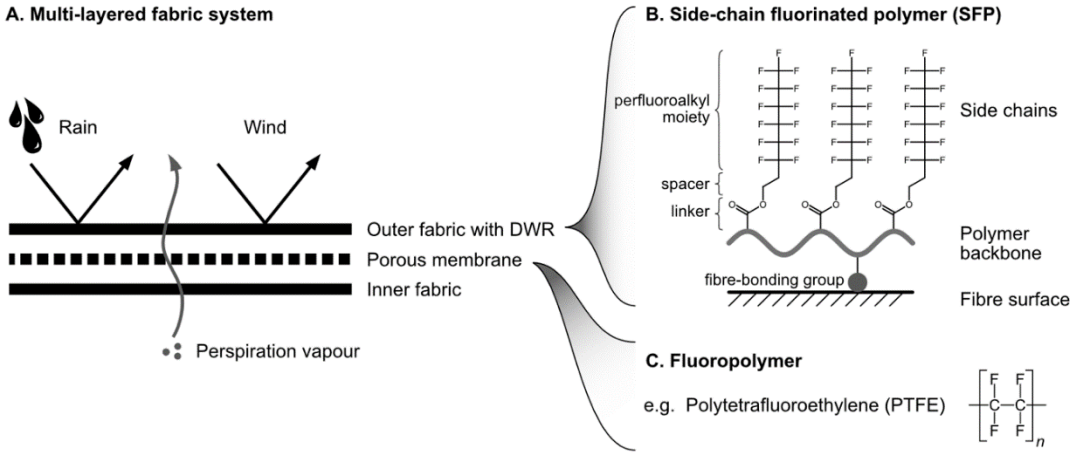


Figure 8: *Schematic representation of a multi-layered waterproof and breathable fabric used in performance outdoor textiles (A) as well as general structure of a side-chain fluorinated polymer (B) for durable water repellent (DWR) finishing and a fluoropolymer (C) for a vapour permeable porous membrane. Adapted from Holmquist et al. (2016).*

Both the DWR finishing and the breathable membrane can be made of fluorinated polymers (Figure 8 (C)).

Table 32: Reported concentrations of 6:2 FTOH and PFHxA in textiles. Values given as µg/m² were converted to µg/kg on the basis of 1 m² of fabric weight equals 100 g.

Data source	samples (n)	Positive samples	**µg/kg**			samples (n)	Positive samples	**µg/kg**		
Outdoor textiles										
			Max.	Min.	Median			Max.	Min.	Median
Santen and Kallee (2012)	**6:2 FTOH**	LOD/LOQ not rep				**PFHxA**	LOD/LOQ not rep			
outdoor clothing jackets (12) trousers (1) purchased 2012	13	jackets (6)	3 520	176		13	jackets (8)	32	3	
Brigden et al. (2016b)	**6:2 FTOH**	LOD/LOQ not rep				**PFHxA**	LOD/LOQ not rep			
Hiking & camping equipment purchased 2015	29	21				29	19			

jackets (11)		jackets (7)	4 600	270			jackets (8)	546	1.2	
trousers (8)		trousers (7)	1 500	400			trousers (6)	27.8	1.8	
footwear (7)		footwear (6)	1 300	470			footwear (4)	18.8	0.5	
sleeping bags (2)		sleeping bags (1)	1 100				sleeping bags (1)	18.6	n/a	
gloves (1)		gloves (0)		n/a			gloves (0)			
Kotthoff et al. (2015b)	**6:2 FTOH**	LOQ 0.3 - 0.8 µg/m^2				**PFHxA**	LOQ 0.5 µg/m^2			
outdoor textiles (5) purchased 2010	**4**	outdoor textiles (4)	158	65		19	outdoor textiles (3)	171		15
leather (13)							leather (13)	45		
gloves (3)		gloves (1)	90	82			gloves (3)	26		13
Borg and Ivarsson (2017)	**6:2 FTOH**	LOD/LOQ not rep				**PFHxA**	LOD/LOQ not rep			
jackets (6) purchased 2015	8	jacket (1)	1 405	<LOD		8	jacket (3)	11.6	0.33	
shoes (2)		shoes (0)	<LOD	<LOD			shoes (0)	<LOD	<LOD	

Lassen et al. (2015)	**6:2 FTOH**	LOD 0.6 µg/m^2				**PFHxA**	LOD 0.001 µg/m^2			
children's clothing snowsuits (5) purchased: not reported	15* (22)	snowsuits (3)	41	0.2			snowsuits (3)	9.9	0.0	
jacket (4)		jacket (1)	2.5	n/a			jacket (1)	0.5	n/a	
softshell suits (2)		softshell suits (1)	6.1	n/a			softshell suits (1)	32.6	n/a	
rain suits (4)		rain suits (3)	4.8	4.4			rain suits (3)	2.2	0.1	
gloves/mittens (3)		gloves/mittens (3)	830	17.3			gloves/mittens (3)	5.4	0.7	
infant sleeping bags (4)		infant sleeping bags (4)	61.9	8.3			infant sleeping bags (4)	2.5	0.0	
Knepper et al. (2014)	**6:2 FTOH**	LOQ 0.2 µg/m^2				**PFHxA**	LOQ 0.02 µg/m^2			
jackets purchased 2011-2012	16	2	186	< LOQ		16	13	147	0.1	

Gremmel et al. (2016)	**6:2 FTOH**					**PFHxA**				
jackets (15) purchased 2011-2012	11	< LOQ				13	13	147	0.1	
Dreyer et al. (2014)	**6:2 FTOH**	LOD/LOQ not rep				**PFHxA**	LOD/LOQ not rep			
outdoor jackets (14) purchased: not rep.	16	jackets (11)	8 500	~ 300		16	jackets (12)	120	2	
gloves (2)		gloves (2)	11 900	306			gloves (1)	12.5	2	
BVL (2018b)						**PFHxA**	LOD 1 µg/kg			
underwear purchased 2010–2014						48	48	60.9	1.5	4.3
outerwear						4	3	9.7	<LOD	2.3
gloves						5	2	3.7	<LOD	<LOD
other products						32	13	19.2	<LOD	<LOD

Other Textiles										
			Max.	Min.	Median			Max.	Min.	Median
Herzke et al. (2012)	**6:2 FTOH**	LOD/LOQ not rep				**PFHxA**	LOD/LOQ not rep			
carpet (2) purchased 2009	4	carpet (2)	2 200	170		carpet (1)	carpet (1)	11		
table cloth (2)		table cloth (2)	191	540						
Kotthoff et al. (2015b)	**6:2 FTOH**	LOQ 0.3 - 0.8 µg/m^2				**PFHxA**	LOQ 0.5 µg/m^2			
carpet (14) purchased 2010	8	8	21.2	?		6	2	0.8	<LOQ	<LOQ
Guo et al. (2009)	**6:2 FTOH**					**PFHxA**	LOD 0.05 µg/kg			
pre-treated carpet (9) purchased 2007/2008						23	3	224	<LOQ	<LOQ

treated home textiles and upholstery (14)							9	238	<LOQ	2.96
Vestergren et al. (2015)	**6:2 FTOH**	LOD 0.5 µg/m^2				**PFHxA**	LOD 0.005 µg/m^2			
furniture textiles (27) purchased 2012-2013	36	14	3 737	<LOD	5.50	36	10	8.12	<LOD	<LOD
carpets/mats (9)		6	744	<LOD	252.0		5	1.53	<LOD	0.14

On behalf of the German Environment Agency various industrial fabrics (total samples = 28) were investigated for per- and polyfluoroalkyl substances like PFHxA, 6:2 FTOH and 6:2 FTS (Janousek et al., 2019; Knepper and Janousek, 2019). The samples included seat covers (furniture upholstering, bus /train seat upholstering, car seat upholstering; n = 11), covers for truck trailers (n = 3), covers for maritime applications (e.g. boat cover, seat cover, bimini tops; n = 5), awnings and tarpaulins (e.g. marquee awning, party tent; n = 9). All samples were collected between October 2016 and August 2017 and have been analyzed as soon as possible. The following LOQs were determined: for 6:2 FTOH 40 µg/kg, for PFHxA and 6:2 FTS 2 µg/kg. PFHxA was found in one seat cover, two maritime covers and five marquee awnings. Concentrations of PFHxA ranged from 2.4 – 15 µg/kg (average 7.7 µg/kg) in aqueous extracts and 2.6 - 18 µg/kg (average 9.9 µg/kg). 6:2 FTOH was found in one seat cover, one tarpaulin for truck trailers, two maritime covers and three marquee awnings with concentrations ranging from 40 to 790 µg/kg (average 350 µg/kg). 6:2 FTS was not detected above the LOQ in any of the samples.

E.2.11.3 Baseline

Information on relevant uses and their quantities in the textile sector is scarce. The Dossier Submitter obtained only some basic information: In 2015 1.6 million t of clothing were manufactured in the EU and 4.8 million t were imported into the EU (Rijkswaterstaat, 2017). From the total 6.4 million t of clothing a share of about 95 000 t of occupational wear and about 150 000 t of outdoor clothing are assumed. In 2018 about 200 000 t of textile floor coverings were used in Europe.

For 95 % of the on the European market available textiles production steps are outsourced abroad partially or even entirely. So, emissions of PFHxA, its salts and related substances via manufacture of textile fibers and fabrics are considered as very low in Europe. Otherwise, the abroad use and finally the content of the perfluorinated substances is difficult to predict (Greenpeace, 2012) but should be kept in mind when discussing proportionality of a restriction.

The Dossier submitter estimates (see B.9.5 Textiles that the use of PFAS remains constant in the future. Without a restriction, constant releases of PFHxA-related substances from textiles amount to 162 – 3 420 t/a. Accordingly, emissions over 20 years are expected to add up to 3 240 – 68 400 t. Additionally releases of C6 fluoropolymers of approximately 36 – 91 t/a (724 – 1 814 t over 20 years) need to be considered. These numbers are highly uncertain.

Estimates for the releases from major sub-uses are as follows:

Table 33: Releases from use in textiles.

Subsector	**Release of C6 fluoropolymers (min – max t/a)**	**Release of C6-related substances (min – max t/a)**
clothing and textiles except outdoor and occupational	26.6 – 66.5	152.9 – 3 249.2
outdoor clothing	2.3 – 5.8	4.1 – 86.2
occupational wear	1.4 – 3.7	2.6 -54.6
carpets and other textile floor coverings	3.1 -7.7	2.3 – 29.7
industrial textile fabrics	2.8 – 7.0	0 – 0.1

E.2.11.4 Uses, functions and alternatives

To identify alternative technologies a literature search was performed. The focus was on coating technologies which allow fabrication of water-, oil- and dirt-repellent textiles and fabrics.

According to present knowledge, no alternatives allow an encompassing replacement with a performance of equivalent quality. Especially development of alternatives for properties such as oil and dirt repellency are challenging.

For DWR a progress in development of alternatives can be observed. Several chemical processes are available, which show comparable results for water repellency. An example is shown in Figure 10. In the field of industrial textiles, which are designed and produced for professional uses and have to withstand harsher conditions, limitations exist.

Information on durability of textiles faced with physical and chemical stress (e.g. rain, washing, abrasion) are scarce in the screened literature. Also, regarding the renewability of coatings, the stability and the wear comfort of textiles limited information are available. Furthermore, it cannot be determined whether the identified alternatives can be used in the same manner as the PFASs based substances for textiles, leather, carpets and impregnation sprays.

Information in more detail on coating technologies, processing chemicals and substance identity of *active ingredients*, are confidential and therefore not available.

Following technologies were identified (non-exhaustive list):

1. Paraffin-based repellent.
2. Silicon-based repellent.
3. Dendrimer-based repellent.
4. Polyurethane-based repellent.
5. Stearic acid – melamine repellent (melamine resin).
6. Stearamidomethylpyridinium chloride.
7. Nanomaterial-based repellent.

Some examples of fluorine-free DWR alternatives are shown in Figure 9.

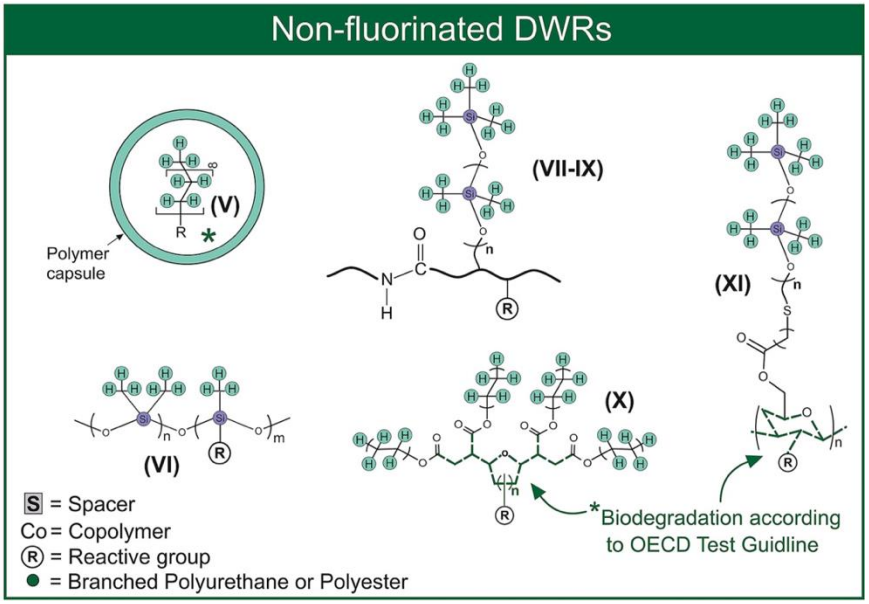


Figure 9: *Simplified structures of non-fluorinated durable water repellents (DWRs) (Schellenberger et al., 2019). The examples comprise an encapsulated wax-based polymer (V), a polymer based on polydimethylsiloxane (VI), silicone functionalized polyurethane (VII–IX), a fatty acid-modified saccharide (X), and a silicone-modified saccharide (XI). Licensed under Creative Commons Attribution-NonCommercial-No Derivatives License (CC BY NC ND).*

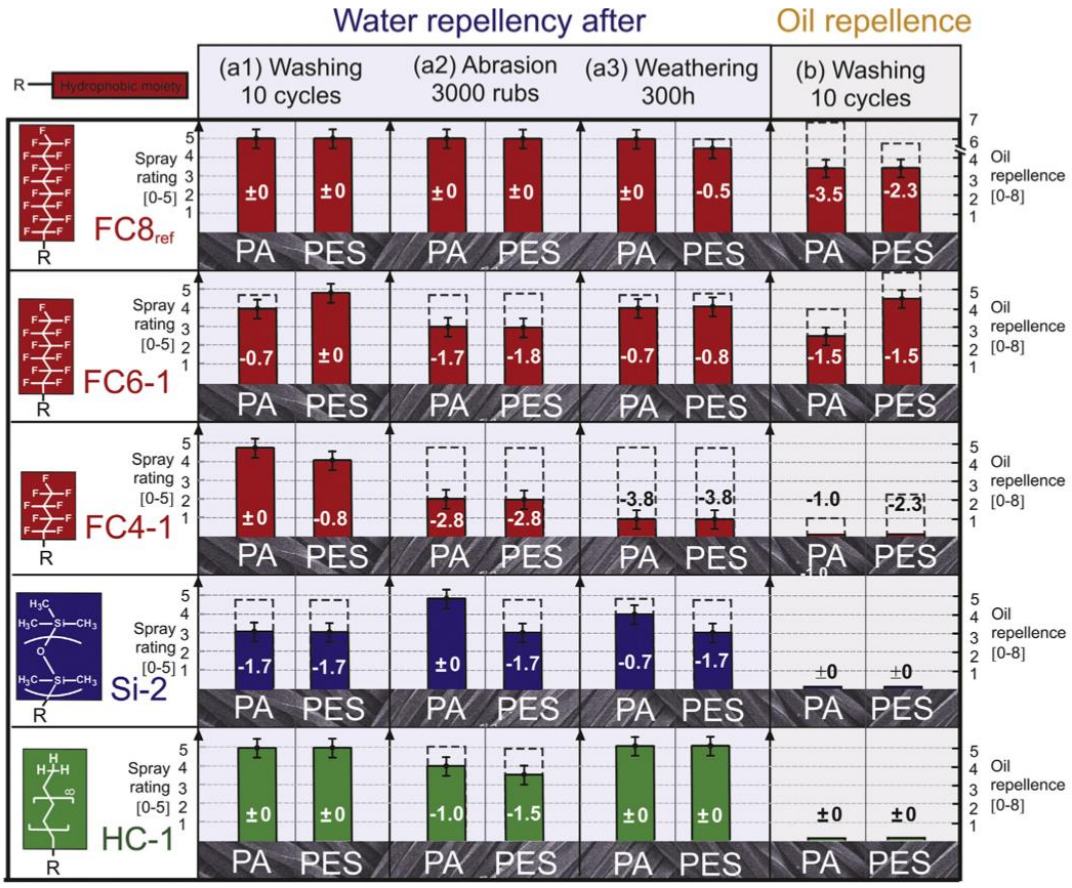


Figure 10: *Results of durability tests for fluorinated and non-fluorinated DWRs applied on polyamide (PA) and polyester (PES) fabrics (Schellenberger et al., 2018). The fluorinated DWRs comprised a C8-based side-chain fluorinated polymer (SFP) as reference ($FC8_{ref}$), C6- and C4-based SFPs (FC6-1, FC4-1), a silicone-based DRW, and an encapsulated wax-based polymer (HC-1). Water repellency was tested after ten washing cycles, abrasion tests and artificial weathering. Oil repellency was tested after ten washing cycles. Reprinted from Chemosphere, 193, S. Schellenberger,P. Gillgard,A. Stare,A. Hanning,O. Levenstam,S. Roos,I.T. Cousins, Facing the rain after the phase out: Performance evaluation of alternative fluorinated and non-fluorinated durable water repellents for outdoor fabrics, 675-684, Copyright (2018), with permission from Elsevier.*

E.2.11.5 Economic and other impacts

According to the consulted industry substitution is possible for water repellence. There is a general trend in the sportswear and outdoor industry to phase out PFAS-related substances and move to fluorine-free alternatives, due to increasing pressure from the public to phase out hazardous substances. This demonstrates that substitution is technically feasible. Alternatives are available that can be used without specific new investments (unchanged machinery). For applications, "where repellence against oil, alcohol and oil-based dirt is not required, the alternatives are considered to provide

acceptable properties at costs at the same level as the costs of using the PFAS-based agents (MIDWOR-LIFE, 2017).

Alternatives to provide similar oil and dirt repellence properties are not available. Two categories of use have been identified as essential uses where these properties are needed. Substitution could lead to unacceptable health risks for users, most likely leading to high social costs. Therefore, for two categories of use exemptions are proposed by the Dossier Submitter:

- Personal protective equipment intended to protect users against risks as specified in regulation (EU) 2016/425 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, Annex I, Risk Category III (a), (c), (d), (e), (f).[21]
- Non-woven medical textiles.

Both applications directly relate to risks that may cause serious consequences to health. During the consultation no information on possible alternatives has been received. Although no information on the risk reduction capacity of personal protective equipment is available, the Dossier Submitter assumes that the cost of not granting an exemption would exceed the benefit of emissions reduction which are estimated to be in the range of 2 - 4 t C6-fluoropolymers and 25 – 533 t PFHxA-related substances for derogated personal protective equipment over 20 years. For non-woven medical textiles emission estimates are not available.

In the medical sector repellency to bodily fluids is necessary to avoid the transmission of diseases. In other sectors (e.g. defence, firefighting, oil and gas industry) repellency towards non-polar stains is also part of the hazard management (Schellenberger et al., 2019).

[21] REGULATION (EU) 2016/425 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCILof 9 March 2016 on personal protective equipment and repealing Council Directive 89/686/EEC. Category III includes risks that may cause very serious consequences such as death or irreversible damage to health. The categories mentioned above relate to the following: III(a) substances and mixtures which are hazardous to health, III(c) harmful biological agents, III(d) ionising radiation, III(e) high-temperature environments the effects of which are comparable to those of an air temperature of at least 100 °C, III(f) low-temperature environments the effects of which are comparable to those of an air temperature of – 50 °C or less.

Non-woven medical textiles are used in the following applications:[22]

- Personal health care/hygienic products: Bedding, clothing, surgical gowns, cloths, wipes surgical curves, surgical hosiery, diapers, etc.
- Non-implantable material or medical dressings & auxiliaries: Wound dressing, bandage, plasters, gauge, lint wadding, etc.
- Implantable materials: Sutures, vascular grafts, artificial ligaments, and artificial joints.
- Extra corporal devices: Artificial kidneys, liver & lungs, etc.

The nonwovens are used for the given applications in different forms.

Owing to the vast number of textile and leather products and applications, in which PFHxA-related substances are used, it is not possible to give a robust estimate of substitution costs, which is representative for the entire industry. The socio-economic impact on the companies that provided information varies with their role in the supply chain but also with their product portfolio.

A constant cost per unit has been estimated based on industry information from the consultation and review of publicly available information. Respondents confirmed that treatment with PFHxA-related substances in general is more expensive than with non-fluorinated alternatives. Information from the MIDWOR-project (see above) suggests that existing machinery can be used unchanged (MIDWOR-LIFE, 2017).

Considering the various applications and the confidentiality of price information it was not possible to identify generalizable market prices. However, the Dossier Submitter estimates that industry will not face higher cost when substituting from PFHxA-related substances to fluorine-free substances. The non-fluorinated substances in general are cheaper. However, considering the information from industry that it might be possible that for some treatments slightly higher use volumes are needed, unchanged costs are assumed

Some information from industry claims that certain functional properties will not be available for end-users any longer when articles are not treated with fluorinated substances. Especially the loss of stain and oil repellent properties might lead to higher cost for textile cleaning and a reduced service life for textiles. Further, stakeholders argued that reduced water-repellent properties lead to loss of comfort for example for outdoor textiles. However, the Dossier Submitter could not obtain generalizable information on economic effects of such performance losses. On the contrary, in a recent consumer survey on important purchasing factors to consumers of outdoor apparel, 'green' chemical use was three times more important as purchasing factor than stain resistancy. The latter has been named as purchasing factor only by five percent of the survey respondents. 57 % of respondents did not consider repellency to oil, soil or dirt essential to the garment (Schellenberger et al., 2019). In a study on PFAS coatings in school uniforms in the United Kingdom, the author concludes that no reduction in wash frequency is associated with stain

[22] The Indian Textile Journal, 2008: Application of nonwovens in medical field, http://indiantextilejournal.com/articles/FAdetails.asp?id=1452 (last access: 13.12.2019).

resistant finishes and that no reduction in purchase frequency is associated with stain resistant finishes (Dinsmore, 2018).

In summary there are indications that functional properties with regard to stain repellency are not valued as highly by consumers as is claimed by industry. An unknown number of consumers might even prefer not having to pay for these properties when buying new clothes. Nevertheless, it seems plausible to consider that the loss of stain and oil repellency leads to a reduced service life of some articles. The severity of this impact is unknown, but substitution costs will be underestimated when not considering the cost of functional losses.

E.2.11.6 Cost-effectiveness, affordability and proportionality to risk

No additional costs are expected. Production processes remain unchanged and the alternatives are available in a similar price-range. However, it might be possible that for some unknown niche applications functional losses are relevant. The Dossier Submitter identified two broad categories of uses that would be affected severely from a restriction, where the functional losses would potentially lead to high social costs. Therefore, derogations have been proposed. A yearly reporting requirement has been proposed for the derogated uses. Information on the derogated use quantities is scarce and monitoring future use quantities will lead to sufficient information if further EU action is required. The costs associated with this proposed requirement are expected similar to the proposal for the restriction on microplastics to be comparatively low.

E.2.11.7 Impact of different transitional periods.

Alternatives are available and affordable. Therefore, a longer transitional period is not required.

E.2.11.8 Uncertainties and sensitivity analysis

Owing to the vast number of textile and leather products and applications, in which PFHxA-related substances are used, it is not possible to give a robust estimate of substitution costs, which is representative for the entire industry. The socio-economic impact on the companies that provided information varies with their role in the supply chain but also with their product portfolio.

Minor uncertainties have to be considered with regard to the reporting requirement. It is expected that significant quantities are imported into the EU and the Dossier Submitter is not certain whether the exporters are prepared to deliver the required information. Production of the derogated articles might happen in several stages outside the EU and it might be difficult for the exporter to obtain complete information on quantities and identity of the relevant PFHxA-related substances through the supply chain.

E.2.12 Food contact materials

E.2.12.1 Overview

For the use in food contact materials (FCM) PFHxA and related substances possess valuable properties. They are chemically stable, heat resistant as well as water- and oil-repelling. In addition they are cost-effective, because low amounts are sufficient to achieve the desired effect (Begley et al., 2005; UBA, 2018).

Proposed restriction elements for PFHxA and related substances in mixtures for FCMs

Shall not be manufactured, used or placed on the market as substances on their own; Shall not be used or placed on the market in: (a) Another substance, as a constituent, (b) A mixture, (c) An article, in a concentration equal to or above 25 ppb for the sum of PFHxA and its salts or 1 000 ppb for the sum of PFHxA- related substances. Paragraphs 1 and 2 shall apply 18 months from entry into force of the restriction. Paragraph 2(c) shall not apply to articles placed on the market before the date referred to in paragraph 3.

E.2.12.2 Use and functions

For the use in FCMs PFHxA-related substances possess valuable properties. They are chemically stable, heat resistant as well as water- and oil-repelling. In addition they are cost-effective because low amounts are sufficient to achieve the desired effect (Begley et al., 2005; UBA, 2018).

For this restriction proposal the openly available literature was evaluated for reported data on PFHxA levels in or PFHxA release from FCM. The evaluation also included PFHxA related substances. The search was performed in February of 2019 with the terms "PFHxA" OR "Perfluorohexanoic" AND "food contact material" in Pubmed, Scopus, SciFinder, Web of Science and Science Direct. Moreover, the CAS numbers of known fluorotelomers were used for research purposes in the above mentioned search engines. Furthermore, the databases of ECHA and EFSA were browsed for helpful data.

Applied substances

The German Federal Institute for Risk Assessment (BfR) received no application for inclusion of PFHxA in the "BfR-Recommendations on food contact materials" (https://bfr.ble.de/kse/faces/DBEmpfehlung_en.jsp?filter=clear), but for the respective precursor compounds. The most important precursor compounds are 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanole (6:2 FTOH, CAS 647-42-7), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylacrylate (6:2 FTAC, CAS 17527-29-6) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctylmethacrylate (6:2 FTMA, CAS 2144-53-8). Starting with these, a large variety of polymers can be synthesised using acrylates, alkenes, divinylbenzene or other compounds as comonomers (Jensen et al., 2008; Liu et al., 2014a;

UBA, 2018; Zhang et al., 2016a). However, a recent report by RIVM (National Institute for Public Health and Environment, Netherlands) shows, that FCM may contain PFHxA (Bokkers et al., 2019).

6:2 FTOH, 6:2 FTAC, 6:2 FTMA and several reaction products and (mixed) polymers are listed in the "BfR-Recommendations on food contact materials" (BfR), especially in the recommendation XXXVI "Paper and Board for Food Contact" (BfR, 2017a) and XXXVI/2 "Paper and Paperboard for Baking Purposes" (BfR, 2017b). Before listing, possible health risks arising from the migration of the substances from the paper into food and food simulants were assessed by the BfR on the basis of toxicological and analytical data according to the EFSA Note for Guidance (EFSA Panel on Food Contact Materials et al., 2008). If the migration is ≤ 50 µg/kg food, the EFSA accepts a reduced data set, consisting of two genotoxicity studies. Analytical studies demonstrated low migration of the respective fluorinated substances or migration below the detection limit. Accordingly, BfR´s risk assessment was based exclusively on genotoxicity studies indicating the absence of genotoxicity. Therein it was concluded, that the resulting migration of very low amounts of these substances (and of PFHxA) is of no risk to human health. However, meanwhile there are additional data suggesting reprotoxic actions of PFHxA in rats.

Typical articles and applications

The most important application field is the production of paper and board for the packaging and preparation of food. The PFHxA related substances are used in the paper pulp as well as for surface refining. They are applied to create water- and grease- /oil-repellent paper products, which can be used at higher temperatures without burning and adherence to food or other materials. Typical articles are baking paper, packaging for pet food, packing of take away food, table cloths, microwave popcorn bags, cupcake forms and sandwich papers (Blom and Hanssen, 2015; Borg and Ivarsson, 2017; Jensen et al., 2008; UBA, 2018).

In addition, perfluorinated substances are used as emulsifiers during the production of temperature resistant polymer coating systems (e.g. polytetrafluoroethylene) for frying, cooking and baking utensils. For this application mainly PFOA was used. In course of the regulatory measures for PFOA a change to perfluorinated compounds with shorter C-chains is expected and already occurs – not only in the field of temperature resistant polymer coating systems but also for FCM from paper and board (Liu et al., 2014a; Ritter, 2010; Sinclair et al., 2007; UNEP, 2012a; Wang et al., 2013). As a consequence, the incidence of PFHxA and its precursors in FCM might increase in future times. Currently, BfR has no information on the total amount of PFHxA used for FCM or the consumption volume of PFHxA containing FCM-products.

Content and release of PFHxA and related substances in /from food contact materials

Overall, there are only few data available on the content and release of PFHxA and its precursor molecules in /from food contact materials. Among the latter, only 6:2 FTOH was reported in the available sources. In the BfR recommendations XXXVI "Paper and Board for Food Contact" (BfR, 2017a) and XXXVI/2 "Paper and Paperboard for Baking Purposes" (BfR, 2017b) mixed polymers containing C_6-perfluorinated PFHxA precursor compounds are listed, which are typically used for surface refining and coating of FCM from paper and board. The

recommended maximum content of these polymers in the final FCM varies between 0.16 % and 1.2 % (based on the dry fibres weight). Thereby, the recommended maximum fluorine content of the polymers applied varies between 35 % and 54 % (weight/weight).

In a report from 2019, the Dutch National Institute for Public Health and the Environment (RIVM) published a summary of existing literature and data on PFAS in food contact materials (Bokkers et al., 2019). It is reported, that PFHxA and precursors are detectable in various product types of FCM sampled in different countries. Thereby, food contact papers seem to form the category of products that is affected most frequently.

In a study of 2015, the extractable amount of different PFAS, including PFHxA, was analysed in consumer products (Kotthoff et al., 2015b). In 27 % of the paper-based food contact materials tested, PFHxA was detected and quantified with a median of 1.4 µg/kg FCM and a maximum of 182.8 µg/kg FCM. On request of the BfR, the BVL provided data from migration tests for PFHxA to the BfR (BVL). From 2010 to 2017, articles that are intended to come into contact with food (packaging paper /boards and kitchen aids) were analysed for the release of PFHxA. In 6.4 % of the samples (eight out of 126), release of PFHxA was detected and quantified. The median migration was 6.6 µg/kg FCM and the maximum was 250 µg/kg FCM.

Consumer products (food contact papers and baking forms) sampled in Norway and Sweden were analysed for the release of per- and polyfluorinated substances (Blom and Hanssen, 2015; Borg and Ivarsson, 2017). Taken the respective studies together, a release of PFHxA was detected in five samples out of 17 (29.4 %), whereas 6:2 FTOH was released from twelve samples (70.6 %). PFHxA migration was only detected in FCM from paper. The median content of all detects was 0.43 µg/m^2 article surface and the maximum content of all detects was 38.9 µg/m^2 article surface. 6:2 FTOH was detected in food contact papers as well as baking forms. The median content of all detects was 5.85 µg/m^2 article surface and the maximum detect was 76.4 µg/m^2 article surface, which would result in a median content of 0.35 µg 6:2 FTOH/kg food and a maximum content of 4.6 µg 6:2 FTOH/kg food.

In a study from 2014, PFHxA was found in icecream cups, fast food wrappers and microwave popcorn bags at contents ranging from 19 to 341 µg/kg FCM (Zafeiraki et al., 2014). 42 samples were analysed and even if values are not assigned to individual samples, data indicate that in the majority of samples (> 80 %) PFHxA was not detectable (LOD = 0.94 µg/kg). In a further study, data on PFHxA amounts in microwave popcorn bags from different countries were published by (Zabaleta et al.). The median PFHxA content, excluding samples with non-detectable PFHxA amounts, was 3 µg/kg FCM. The maximum level was 811 µg/kg FCM. Another publication on the presence of PFAS in FCM reports detectable amounts of PFHxA in wrapping papers. In six out of twelve samples, PFHxA was quantifiable at contents up to 1.1 ng/m^2 article surface (Surma et al., 2015).

Regarding migration of PFHxA from FCM into food and food simulants, scientific literature is scarce. A summary is given by the report of RIVM (Bokkers et al., 2019), thereby indicating that PFHxA as well as 6:2 FTOH can migrate into food simulants, particularly when containing alcohol.

Yuan et al. (2016) published data on the occurrence and migration of PFAS and FTOHs with regard to FCM. Various commercial paper-made food contact products from China and USA were analysed. Both PFHxA and 6:2 FTOH were detectable and were shown to migrate into food simulants within short durations (15 min) and high temperatures (cooling down from

100 °C). Thereby, migration efficiency increases with rising alcohol content of the food simulant. Paper bowls containing 3.9 µg/m^2 PFHxA were analysed for PFHxA migration efficiency. Depending on the type of food simulant, migration efficiency is reported to be approximately 5 % for water increasing to about 30 % for 50 % ethanol (EtOH). Migration of PFHxA into oil was not detectable. Using a conversion factor of 6 dm^2/kg food, as applied for plastic FCM according to (EU) No 10/2011, the resulting PFHxA content in food ranges between 11.7 ng/kg food (migration $efficiency_{water}$ = 5 %) and 70.2 ng/kg food (migration $efficiency_{50\ \%\ EtOH}$ = 30 %). However, it should be noted that the experimental design of the respective study is not consistent with DIN standards for migration tests of paper/board FCMs as for example required for inclusion on BfR-Recommendation XXXVI. Consequently, the derived migration values are only a rough estimate and only applicable for the specified test conditions. The content of 6:2 FTOH in the paper bowls was 71 µg/m^2. Migration efficiency ranged from 0.24 % (water) to 13 % (50 % EtOH) and was 1.07 % for oil. According to the requirements of (EU) No 10/2011, the calculated amount of 6:2 FTOH in 1 kg food ranges between 10.2 ng/kg food (migration $efficiency_{water}$ = 0.24 %) and 553.8 ng/kg food (migration $efficiency_{50\ \%\ EtOH}$ = 13 %).

Another study (Xu et al., 2013) investigated PFAS in commercial food contact papers that were treated with polyfluoroalkyl phosphate (PAP) or di-perfluoro-alkyloxy-amino-acid (PAA) surfactants. Beside other PFAS, PFHxA was determined in papers treated with both flourochemicals at mean contents of 717 µg/kg (PAA) and 870 µg/kg (PAP). PFHxA migration into food simulants was shown to depend on contact duration, temperature and type of simulant. PFHxA migration efficiency values into oil ranged between 5 % to 10 %. The addition of an emulsifier to oil resulted in increased migration efficiencies up to about 20 %. PFHxA migration into EtOH was determined with efficiency up to 100 %. Compared to reported values from Yuan et al. (2016), data presented by Xu et al. (2013) suggest that the method of flourochemical addition /incorporation into the FCM significantly affects the content of PFAS in the FCM as well as their release into food simulants. Thereby, the release of PFAS from flourochemicals that are applied as coating can reach 100 % in the presence of EtOH. Due to deviations from standard test conditions and procedures, the comparability to existing data is not given. Hence, a conversion of the PFHxA content into a PFHxA exposure by migration into food is not useful. Noteworthy, there are no per- or polyfluorinated substances listed as surfactants in current BfR recommendations.

E.2.12.3 Baseline

Evaluating Data from UN comtrade database about 47 000 t of grease proofe paper were used in Europe in 2018. According to industries, the content of side-chain fluorinated polymers is about 0.3 – 1.5 %, depending on the specific purpose of the treated material (stakeholder consultation). The Dossier Submitter estimates that 24 – 120 t C& fluoropolymers and 0 – 636 t of PFHxA-related substances will be emitted over 20 years without the proposed restriction.

E.2.12.4 Alternatives for uses in food contact materials

The production of water- and oil- /grease-repellent paper and board products is predominantly based on fluorine technology (UBA, 2018). Apart from that, water repelling properties can be achieved (amongst others) by applying the following techniques (BfR, 2017a; BfR, 2017b; UNEP, 2012a):

- Plastics (films, melts, solutions, laquers, dispersions), e.g. polyacrylates or polyvinylalcohols with fatty alcohol sidechains, polyamides, modified polyethylenterephthalates and others,
- silicon oils /resins or silicon elastomers,
- paraffins, microcrystalline waxes, low-molecular polyolefins and polyterpenes,
- chromium-, aluminium-, calcium-, sodium- or potassium-salts of saturated straight fatty acids.

According to information from industry alternatives for PFHxA and related substances that provide similar oil- /grease-repelling properties (for FCM from paper and board as well as other materials) are scarce or less effective (UBA, 2018). This is even truer when stability at higher temperatures is needed – e.g. as packaging material in contact with hot foods or during baking or frying. Application of perfluorinated substances with shorter carbon chains (e.g. C_4-compounds such as PFBA, PFBS or FTOH 4:2) is possible as well as application of structurally different perfluorinated substances such as linear or cyclic perfluoropolyethers (PFPEs) and their salts and phosphoric acid esters as well as polyethersulfones (Sheng et al., 2018; UNEP, 2012a; Wang et al., 2013; Zhang et al., 2016a). Application of perfluorinated silanes is also described (Paxson et al., 2014), even if less stable polymer films may be formed. Recent data (Bokkers et al., 2019) indicate, that in course of the substitution of the C_6-perfluorinated substances with C_4-perfluorinated substances it might be necessary to apply higher amounts of the respective substance in order to achieve the desired properties of the FCM. Hence the overall amount of perflourinated subtances used during production of FCM might increase in course of the substitution of the C_6-technology, which would not be desirable from an environmental point of view.

Some articles for baking and frying, such as cupcake forms or baking "papers", can be made from silicone rather than coated paper board. Potential risk might arise from the migration of cyclic oligomers into food and ambient air (Fromme et al., 2019; Zhang et al., 2012), since some of the substances are suspected reprotoxicants (Greve et al., 2014) and identified as substances of very high concern due to PBT and vPvB properties[23].

For food packaging, specially adapted nano-cellulose-particles could be added to the pulp during paper production or used as surface refining agents to achieve water- and oil-repelling properties (Li et al., 2015). But until now, concepts for the assessment of the risks of the possible migration of the nanomaterials into food are still discussed controversially in the EU.

Alternatively, plastics or products containing a plastic layer in contact with the food could be used as packaging materials instead of paper and board. In course of the strategy of the EU to reduce plastics, this might not be desirable.

[23] [23] see Candidates list, entries for:
EC No. 209-136-7 (https://echa.europa.eu/de/candidate-list-table/-/dislist/details/0b0236e18263bf5e),
EC No. 208-764-9 (https://echa.europa.eu/de/candidate-list-table/-/dislist/details/0b0236e18263c05e),
EC No. 208-762-8 (https://echa.europa.eu/de/candidate-list-table/-/dislist/details/0b0236e1826466a3).

E.2.12.5 Economic and other impacts

Information on the use of fluorinated substances is very scarce. Several requests to discuss the issue of a potential restriction were not answered by paper producers. The following information are based on information from two substance importers /manufacturers.

Typical features relevant for paper applications are (food contact material):

- Oil and grease resistance and durability.
- Packaging materials for durable products: Oil repellence i.e. of pet food.
- Reduced potential for burns from hot oil migration.
- Maintains integrity and aesthetics of packaging material.

The two respondents claim that potential alternatives for paper applications do not reach an equivalent performance. On the other hand, the information collection as well as publicly available information demonstrate that some fast food companies already are substituting all fluorinated compounds from their packaging material. So most likely partial substitution processes are taking place and at least some alternatives for substitution are available in the field of short-term use and avoidance of oil migration.

As discussed in E.2.12.2 Use and functions few data are available on the content and release of PFHxA and related substances in/from FCM. Studies report that varying percentages of fluorinated products have been detected for different categories of fast food packaging. According to a summary of existing literature and data on PFAS in FCM PFHxA and precursors are detectable in various product types of FCM sampled in different countries. Food contact papers seem to form the category of products that is affected most frequently (Bokkers et al., 2019).

In general, the literature suggest use of PFAS in FCM but on the other hand it also suggest that FCM from the same product categories are available with and without PFAS. Therefore, it seems reasonable to assume that alternatives are available for certain uses and that therefore PFAS are not essential for all applications.

In a recent report on PFAS in paper and board for food contact (Trier, 2017) the authors claim that non-fluorinated alternatives "are available and functional for all uses of paper and board" and that market research demonstrates that "these are cost neutral for retailers and hence most likely for manufacturers".

The authors argue that Danish retailer COOP successfully substituted PFAS-containing FCM with non-fluorinated alternatives in their own brands in a cost-effective way: "COOP estimates that substitution to non-fluorinated alternatives is not more expensive than the fluorinated coatings, and is aiming to expand the phase-out of non-fluorinated alternatives to all of COOP Nordic" (Trier, 2017).

However, the authors suggest that there might be some additional cost in the production process of natural greaseproof paper because its content of dry solids is low compared to paper containing PFAS which leads to slower machine speed. In order to be able to estimate whether this leads to a substantial need for new machinery in the industry it would be necessary to obtain information that is not available to the dossier submitter, for example information on the number of machines available in the EU and their utilized capacity.

The Danish Ministry of Environment and Food announced in September 2019 that Denmark intends to ban the use of all PFAS in paper and cardboard used in FCM by July 2020.[24] The ministry states that alternatives with similar greaseproof and water-repellent properties are available. It is not known to the Dossier Submitter whether the Danish authorities have gathered any additional information on impacts of this proposed ban or whether they relied on information available.

In the Dossier Submitters view the information available is not fully sufficient to conclude on the availability of alternatives in FCM in general. The information that alternatives are on the market is uncertain in parts and might miss important uses. On the other hand, manufacturers and importers have not specified and/or justified essential uses. The Dossier Submitter therefore proposes a broad restriction on PFAS in paper and board without exemptions and assumes that manufacturers and users comment in the forthcoming public consultation in case essential uses without alternatives need to be considered.

The information on the affected quantities is very uncertain. The Dossier Submitter estimates that the restriction will result in an emission reduction of 23 – 113 t C6 fluoropolymers and 0 – 326 t PFHxA-related substances over 20 years.

To estimate the substitution costs the Dossier Submitter uses the information from the literature, i.e. that substitution is cost neutral. However, it is uncertain whether additional machinery is needed when fluorinated products are replaced by natural greaseproof paper.

Although it is only a comparatively small market within the EU, the Dossier Submitter expects that some manufacturers will start to develop alternatives for the Danish market.

Data from UN COMTRADE and Eurostat suggest that EU manufacturers export large quantities of greaseproof paper to non-EU countries. The Dossier Submitter has no information on quantities affected by this restriction proposal. No information is available on the share of the quantities that is re-imported as part of finished products. Further it is not possible to make assumptions whether the demand from non-EU buyers will change when greaseproof papers are coated with alternative materials. Therefore, exports represent a major uncertainty for the Dossier Submitters assumption that the restriction will have small impacts on paper manufacturing in the EU.
However, unless additional information to the contrary is provided during the public consultation in the restriction process we assume that economic impacts of a restriction are small.

E.2.12.6 Cost-effectiveness, affordability and proportionality to risk

The available information suggests that substitution costs are very small. According to some Information from the literature and from Danish authorities affordable alternatives are available for all uses. Although this information is uncertain in parts, the Dossier Submitter expects this restriction to be proportionate considering a central estimate for emission reductions of 68 t C6 fluoropolymers and 163 t PFHxA-related substances.

[24]Miljø- og Fødevareministeriet, 2019: Fødevareministeren er klar til at forbyde fluorstoffer (https://mfvm.dk/nyheder/nyhed/nyhed/foedevareministeren-er-klar-til-at-forbyde-fluorstoffer/ (last access: 13.12.2019).)

E.2.12.7 Impact of different transitional periods

The Dossier Submitter has not identified essential uses that require longer transitional periods. According to the Danish authorities substitution is possible within less than a year. However, the Danish ban affects only a comparatively small market. Therefore, the proposed transitional period of 18 months is reasonable to implement the restriction on the larger EU-market.

E.2.12.8 Uncertainties and sensitivity analysis

The information that alternatives are available for all uses is uncertain. Manufacturers and importers claim that alternatives are not available for all uses. On the other hand, there is strong evidence that alternatives are available for many uses (as exemplified by the substitution process in the Danish retail market).

Therefore, one main uncertainty with regard to the restriction of PFHxA-related substances in FCM is the potential for functional losses. In case the alternatives are less greaseproof products could be less durable with reduced shelf-life. The potential for burns from hot oil migration and the potential for soiling could be increased. However, no information is available on the likelihood or potential magnitude of such effects.

Some potential alternatives have or might have undesirable impacts. Substitution with siloxanes, plastics or C4-perfluorinated substances could be regrettable substitutions. No information is available which substitution strategies would be pursued by the impacted industries in case of a restriction.

The impact on exporters is a major uncertainty. Large quantities of greaseproof paper are exported from the EU to other countries. The Dossier Submitter could not obtain information on potential effects of a restriction.

E.6 Other impacts, practicability and monitorability

Social and wider economic impacts:
The proposed restriction is not expected to have major effects on employment because for the vast majority of uses alternatives are available that are implementable at a reasonable cost. For most of the articles concerned the use of PFHxA, its salts and related products is only one step in the production process. Alternatives have been identified for most uses. Some of the alternatives do not provide all the functions that are resulting from the application of fluorinated substances. However, for consumer articles oil and stain repellency is just one additional function of the product. Consumers still have incentives to buy them for their remaining properties. For most of the identified uses alternatives are available and affordable. It is expected that production processes will not be interrupted. For some uses derogations have been proposed because alternatives are not available at the moment. For these industries (i.e. chrome metal plating and semiconductors) major employment effects could be expected when no derogation is granted. Because PFHxA-related substances are only used in manufacturing and are not present in the final product it would be reasonable to expect that parts of the production would be replaced by imported articles.

For other uses imported articles and mixtures will also be covered by the restriction. Relocation of production facilities to countries outside the EU are not a likely response by the industry concerned.

In sum, closing down of business, relocation of business activities and employment effects are not expected. One uncertainty in this regard is the manufacturing of fluoropolymers. Production facilities affected will need restructuring for alternative production purposes. Manufacturers have not provided sufficient information to substantiate the claim that a shutdown of some manufacturing plants is the most probable outcome of a restriction. Therefore, this scenario is only considered an uncertainty for the sensitivity analysis.

Distributional impacts:
Distributional impacts are difficult to predict. It might be possible that in some sectors first movers that are already developing and marketing fluorine-free alternatives take over market shares from other market actors. However, stakeholder consultation and market review suggest that most companies affected are actively pursuing research on alternatives.

Any cost of the proposed restriction to EU and non-EU businesses are likely to be passed on along the supply chain. Most of the costs will consist of functional losses. As has been demonstrated monetary cost effects will be negligible considering the fact that non-fluorinated products are less expensive than fluorinated products. Some properties of the products will be lost or reduced. Consumers could value these functional losses as decreased convenience or functionality.

However, in general no explicit information on distributional effects of the proposed restriction surfaced in the preparation of this report.

E.7 Practicality and monitorability

Implementability: The proposed restriction is considered to represent an implementable option for the actors involved within the timeframe of 18 months for most uses. As described in Annex E.2 it appears that the necessary technology, techniques and alternatives are available and economically feasible. However, for some essential uses alternatives are not available. For other uses alternatives are available but a longer timeframe than 18 months is needed for the adjustment to new technology, techniques and alternatives.

Enforceability: Enforcement authorities can set up efficient supervision mechanisms to monitor industry`s compliance with the proposed restriction. Methods can be easily adapted from the methods to analyse of PFOA and longer-chain PFASs. Given that methods exist, the absence of an EU standard analytical method is not considered as a hindrance to the enforceability of the proposed restriction.

Manageability/Monitorability: There are numerous analytical methods reported in the scientific literature to determine easy extractable perfluorinated carboxylic and sulfonic acids of different chain length, including PFHxA. The methods are applicable as well to linear as to branched isomers. The majority of these methods focusses on water analysis (ground water, surface water, drinking water and sewage). However, it is possible to detect the perfluorinated acids in almost all environmental compartments besides water, e.g. sediment, soil, air, biota and humans by conveying the perfluorinated substances into a watery solution. The following steps are in general the same: the perfluorinated substances are enriched by solid phase extraction at a weak polymeric anion exchanger. The exchanger is rinsed with water and /or other solvents. Finally, the adsorbed substances are eluted from the solid phase with ammonised methanol. The substances are analysed with gas or liquid chromatography methods coupled with mass spectrometry. By comparing the resulting signals with the signals from internal standards are running together with the samples, the perfluorinated carboxylic and sulfonic acids could be characterised and quantified.
There are already exist standardised and international accepted methods like the ISO method ISO 25101:2009E or the German DIN norm DIN 38407-42 for analysing PFCAs and PFSAs. The detection limits already reach concentrations in water down to 0.001 ppb.

However, a vast variety of PFHxA-related substances is used in different applications instead of direct use of PFHxA. Many of these substances are unknown. The substance properties are as variable as the amount of substances. So, it is very difficult to extract and to characterise or even quantify every single PFHxA-related substance. Very often perfluorinated side chains are linked via an ester-bond to another molecule e.g. to acrylates or alcohols. A possibility to measure PFHxA-related substances without knowing every single substance, is the conversion of these substances to the corresponding perfluorinated acid or alcohol and a subsequent analysis of the substance derivatives.
Houtz and Sedlak 2012 proposed an oxidation of the related substances with hydroxyl radicals to gain corresponding PFCAs (Houtz and Sedlak, 2012). These can be produced in a water sample by thermolysis of persulfate under basic pH conditions (TOP-assay). The TOP-assay was further developed e.g. by Dauchy et al. (Dauchy et al., 2017). DAIKIN presented a method of degrading fluorotelomer monomers and polymers to the respective alcohol by severing the ester-bond by heating the sample (DAIKIN, 2019). However, it is important to know, the results gained with the methods mentioned above, are summarising many PFHxA-

related substances at once. These methods are not feasible for characterisation of a single definite substance related to PFHxA. Furthermore, it should be considered that these methods may lead to an overestimation of PFHxA released into the environment. The ester-bond is fairly inert, especially to biological degradation. So, the amount of PFHxA released into the environment arising by natural degradation processes, e.g. from polymers with perfluorinated side chains, may be much lower than the analysis results are indicating.
This uncertainty is important to keep in mind in investigating the content of PFHxA-related substances in products and articles. Mainly polymers with perfluorinated side chains are used for treatment of products and articles. Although, there are already several methods provided by industries, the examining of products and articles is still a challenge. However, Sweden has already initiated the development of a new CEN (European Committee for Standardization) standard within the technical committee TC248/WG26, "EC restricted substances in textiles" that specifies a test method for detection and quantification of extractable perfluorinated and polyfluorinated substances in textile articles that includes PFHxA, its salts and related substances.
An overview of some methods for extracting and analysing of PFHxA, its salts and precursors is shown in Table 73 "Overview of methods for extracting and analysing PFHxA, its salts and related substances as well in environmental compartments as in products and articles" in the appendix E.1.

Besides the availability of analytical methods, a sampling strategy is needed to monitor the restriction. There are different possibilities:
- Time trend monitoring,
- monitoring of releases.

For both strategies it has to be kept in mind that PFHxA is persistent, which will remain in the environment for ages even if release to the environment is stopped immediately. In addition, there will be continuing releases from articles in use and from long-range transport from non-EU-countries. A time trend monitoring can be performed with samples from the environment, from animals or from humans. Methods and instruments available in (environmental) specimen banks could be used for such a monitoring. Reductions of releases of PFHxA and related substances in the environment should result in decreasing PFHxA concentration in such a trend monitoring. It might be sufficient to measure PFHxA in such a trend monitoring, because the related substance will be degraded to the corresponding persistent acid in the environment. Decreasing trends in releases will then not be directly measurable in environmental samples, because time is needed for degradation.

A joint approach for different enforcement activities such as inspections and testing for the occurrence of several regulated PFASs as PFOS, PFOA, C9-C14 PFCAs and PFHxA, its salts and related substances at the same time would lower costs. Thereby, enhancing cost effectiveness and reducing enforcement costs for PFHxA, its salts and related substances. Regarding imported articles, border authorities can control compliance using the RAPEX system (Rapid Exchange of Information System) to report any violation of the restriction. A time trend monitoring can be performed with samples from the environment, from animals or from humans. Methods and instruments available in (environmental) specimen banks could be used for such a monitoring.

This restriction proposal also includes recycled material and articles made from recycled materials. In the dossier the Dossier Submitter has demonstrated a concern resulting from the exposure to PFHxA, its salts and related substances. Subsequently, there is a concern if

recycled materials contain these substances. An exemption for recycled materials would potentially lead to higher releases to the environment in comparison with an appropriate waste management. Recycling of contaminated wastes contributes to environmental releases and the contaminants may again circulate through use, disposal and recycling phase of articles.

The proposed restriction does not cover the "second-hand" market (e.g. used textiles and textiles in the supply chain). One reason for this is that the second-hand market is difficult to control, in most cases one consumer donates/sells single articles to another consumer (directly or via a second-hand store). It would not be practical to remove single articles from the market. Furthermore, to use e.g. a jacket as long as possible before it turns into waste is a sustainable management of resources.

E.8 Proportionality

The restriction proposal for microplastics[25] states the following on proportionality: "In order to assess the proportionality of the proposed restriction, the comparison of the cost-effectiveness with the cost-effectiveness of former measures to avoid PBT(-like) substances can provide some indication. A recent study has looked into this issue more closely. It concludes that, although cost estimates of previously adopted actions do not allow deriving a value for society's willingness to pay to reduce PBT presence, use, and emissions, roughly speaking, the available evidence suggested that measures costing less than 1 000 € per kilogram PBT use or emission reduction would usually not be rejected for reasons of disproportionate costs, whereas for measures with costs above €50 000 per kilogram PBT such a rejection is likely (Oosterhuis et al., 2017).

When looking at the data it is obvious that there is a large grey area where it is unclear whether society is willing to spend the amount needed for reduction of emissions. Much higher costs than 1 000 € per kg have been spent in the past to reduce or avoid PBT substances implying that there is a large range of cost-effectiveness that can be considered proportionate."

The willingness to pay for emission reductions for other fluorinated substances and substance groups could be considered as relevant comparison points. This restriction proposal examines substances with properties similar to the specific properties of PFOA, PFOS and C9-C14 PFAS. However, those restrictions might not be totally adequate points of reference in the Dossier Submitter's view. For those substances short-chain PFAS were considered as the most likely substitute and substitution costs were calculated on the basis of that assumption. However, short-chain PFAS were considered only as less hazardous to a small degree.

This restriction proposal, however, assumes that PFAS will be replaced by non-fluorinated alternatives where it is assumed that hazard and risk will be reduced to a larger degree. In the Dossier Submitter's view, the risk reduction capacity of this restriction proposal is larger,

[25] https://echa.europa.eu/de/restrictions-under-consideration/-/substance-rev/22921/term (last access: 13.12.2019).

resulting in the assumption that society's willingness to pay should be expected to be larger than for previous regulatory measures on fluorinated substances.

Looking only at the costs where monetization is possible with the limited information that is available the restriction is proportionate. For most uses identified here are low costs due to the fact that non-fluorinated alternatives are expected to be less expensive than the restricted substances. However, the Dossier Submitter has identified uses where he expects significant substitution costs that cannot be quantified. Further it has to be considered that functional losses can be considered a cost to society that also cannot be monetized by the Dossier Submitter.

Subjectively valued attributes like loss of convenience or modified physical attributes of a product might impact the cost-effectiveness of this restriction. Examples would be textiles with reduced water repellency, cosmetics that are more difficult to apply evenly or paint coatings that are soiled faster. Other functional losses might lead to impacts that theoretically have market values, but crucial information is missing. Examples include reduced service life of textiles when stain and oil repellency functions are missing or higher repairing intervals for constructions. The Dossier Submitter is not aware of any studies or statistics that provide an informative basis to estimate the magnitude of such effects.

Cost-effectiveness estimates highly depend on the assumptions on substitution costs as well as on emission factors. The data basis to derive cost as well as emission estimates is very limited. The costs are underestimated.

When considering the information and evidence available the Dossier Submitter finds it plausible that the missing costs will not be so considerable that the restriction is unproportionate. However, the DS considers large uncertainties regarding the uses for fire fighting foams, photographic applications, printing inks and chrome plating:

- Fire fighting foams: The costs for replacement of old foams and cleaning of equipment are expected to be very high.
- Photographic applications: phase-out of traditional photographic maybe takes longer than five years.
- Printing inks: Alternatives might not be available as soon as expected by the Dossier Submitter, meaning that the market for latex printing inks cannot be served.
- Chrome Plating: Loss of business to non-EU manufacturers is possible. Restructuring of the manufacturing plants might be expensive considering that a few thousand manufacturing plants in Europe could be affected.

The Dossier Submitter expects these industries to present additional information during public consultation in case that cost effectiveness of the proposed restriction has been overestimated.

Annex F: Assumptions, uncertainties and sensitivities of the measured data on PFHxA in consumer products, house dust and food

The presented measured data on concentrations of PFHxA and some of its precursors have been compiled in order to demonstrate the presence of PFHxA in potential sources of consumer exposure and to give rough indications on the level of contamination that has been reported in recent years. They have not been further validated and analyzed in order to deduce model parameters or distributions for quantitative assessments of external consumer exposure to PFHxA. Nevertheless, some limitations of the presented data shall be discussed here.

The presented data were compiled from samples taken in the recent years. They give some indications regarding present concentrations, although there is some uncertainty on their representativeness for the present time, due to the continuous changes in PFAS uses. However, they do not allow extrapolations to PFHxA concentrations in the coming years, which would be important in the context of the proposed restriction:

PFHxA is not intentionally added to the sources discussed here, but it is an impurity or degradation product of other substances. The technological and unintentional processes by which PFHxA reaches the sources differ, and they are submitted to changes. Historically, PFHxA could appear as technological byproduct of C8-chemistry from electrochemical fluorination. As C8-chemistry and electrochemical fluorination is still used in Asia, and the restriction of PFOA in articles is not binding before 4 July 2020, they still may be relevant for the measured data presented here. This is especially true for the food data, which may reflect environmental contaminations from the past, and for the house dust data, which may reflect contaminations from articles that were bought in former years and/ or imported from Asia.

While the importance of electrochemical fluorination as a source of PFHxA contamination is expected to diminish in the future, the importance of PFHxA precursors from C6-chemistry is expected to rise. These precursors differ according to their technical functions in different products and articles, and their market share in these functions is subject to changes depending on technological progress, worldwide regulatory risk management and availability of alternatives. This future development is highly uncertain, and so are the future PFHxA concentrations in consumer products and articles, house dust and food. They cannot be extrapolated from the presented data.

In case that the transition from C8 to C6 chemistry in consumer products and articles was ongoing at present, the PFHxA concentrations could rise in consumer products due to increased use of PFHxA precursors. PFHxA-concentrations could also rise, if a higher quantity of C6-precursors would be needed for a certain function. The PFHxA concentrations in consumer products may be limited by the nature of the technical production processes, but the level of these limits is unknown.

Concentrations in food (and in drinking water and also, possibly and to a lesser degree, in house dust), may reflect long-term accumulation of PFHxA in environmental media. Due to the persistence of the substance, they may rise over a (long) time, and, in contrast to consumer products, an upper limit for the resulting concentrations cannot be foreseen. In addition, concentrations in food (and in drinking water) could be affected by local

contaminations of water and /or soil. The probability for such "hot spots" would increase with the prevalence of PFHxA-precursors in technological processes in the EU.

All other limitations of the presented data are less relevant than the uncertainty regarding the future development of the concentrations:

The overall number of analyzed samples is limited compared to the number of product types and food items in the different regions of the EU. With few exceptions, the studies are limited to products and food items in a single country and far away from representativeness for the European countries and markets.

Moreover, the samples within the studies differ regarding influencing factors like product type (i.e. composition, function), food items and location (i.e. potential contamination /accumulation). It should be noted that if the number of analyses for a certain product type is low, the observed maximum value may still underestimate the concentration in a realistic worst case.

In addition, the reported studies differ in their sampling strategies and analytical methods, and also in the level of documentation of this information. The analytic procedures for detection of PFHxA are complex, and for most materials there is no harmonized method, neither for sampling nor for analysis. This makes it difficult to compare the results.

Taken together the differences within the samples, the low number of samples with comparable conditions and methods, and the lack of data for many product or food types and countries, the database seems to be explorative, giving indications on some orders of magnitude rather than the present distributions of PFHxA concentrations in European consumer products, food and house dust.

Many studies report a high number of non-detects for PFHxA, and the detected concentrations within a study often show considerable variation over several orders of magnitude. This may be the result of analytical difficulties in combination with the diversity of the samples. Analytical difficulties will produce underestimations as well as overestimations. The diversity of the samples should be compared to the expected diversity of the real products in order to decide, whether the observed upper range covers the realistic worst cases.

Assumptions relevant for the socio-economic analysis of the individual sectors in the scope of the restriction proposal are detailed in their respective sector-specific assessment presented in Annex E. The main uncertainties in the analysis are due to knowledge gaps regarding the tonnages of PFHxA, its salts and related substances affected by the proposed restriction and where relevant, the availability and or functionality of alternatives.
The information on amounts of PFHxA, its salts and related substances used in the EU and imported in articles is limited. Therefore, only rough estimates are possible. Limited data is available on amounts used and on environmental emissions, especially from downstream user sites. Therefore, only rough emission estimates are presented in this restriction proposal. The risk assessment of PFHxA is complicated by several uncertainties in relation to toxicity, potential for accumulation in organisms, fate and exposure. These uncertainties are described in the respective sections of this report. Not much is known about fate and especially about what areas function as sinks for PFHxA. The non-threshold-based approach to risk assessment

(and the minimisation approach to risk management) was adopted in response to these uncertainties.

Furthermore, there are major uncertainties on whether all related substances with relevant uses have been identified.

Annex G: Stakeholder information

Several consultations have been realised for gathering information on e.g. uses and alternatives.

Table 34: Stakeholder consultations on PFHxA, its salts and related substances.

Consultation	Date	Remark
RMOA-consultation	March - May 2016	mail to importers, manufactures and downstream users of PFHxA, its salts, and related substances as well as concerned industry associations for circulation among their members. Link to consultation was available on DE-CA website and ECHA weekly.
Stakeholder consultation by Ökopol (in cooperation with RISE Research Institute of Sweden) on behalf of German Environment Agency	February - April 2018 (IT survey)	IT survey followed by targeted interviews; see below
public consultation within the context of SVHC-identification	September - October 2018	
Meeting with registrants of either PFHxA, its salts or related substances	9 April 2019 and 27 August 2019	
Meeting /telephone calls with AFFF stakeholders	May - June 2019	e.g. information gathering on alternatives; experience with fires in large tanks
Communication with experts of German Federal Ministry of Defence regarding defence application of AFFF	May – August 2019	
ECHA-Workshop on Per- and Polyfluoroalkyl substances (PFAS) in fire-fighting foams and their alternatives	24 September 2019	

Stakeholder consultation (survey + targeted interview)
The objective of the survey was to increase the information basis on:
1) Manufactured and imported amounts of PFHxA, its salts and related substances;
2) manufactured and imported amounts of their potential alternatives;
3) the type of uses the substances are applied to;
4) the economic effects that are linked to the use of the substances.

The invitation to the survey was sent (Europe-wide) to substance manufactures; formulators of mixtures; end users of substances or mixtures; importers of substances, mixtures or articles as well as article assemblers in the EU; and associations, NGOs or other interested third parties. Furthermore, the survey was promoted on UBA-REACH-website and ECHA Weekly (28 March 2018) with link to the consultation website. Altogether 98 stakeholders (companies as well as associations) have provided information on the survey. Main sectors that contributed information were chemical manufacturers /importers, formulators of chemical mixtures (textile, paper processing, printer inks and colours, surface treatment, firefighting foams), and end users (mainly textile applications, firefighting foams and semiconductor industry).

The submitted information was considered for the preparation of the restriction proposal and is included in the relevant chapters. Further information on the survey itself as well as summaries of the submitted information divided in corresponding role and branches are available in the final report of the UBA-project (Wirth et al., 2019).

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Zhao L., McCausland P.K., Folsom P.W., Wolstenholme B.W., Sun H., Wang N., and Buck R.C. (2013b): 6:2 Fluorotelomer alcohol aerobic biotransformation in activated sludge from two domestic wastewater treatment plants. Chemosphere 92 (4), 464-470. DOI: 10.1016/j.chemosphere.2013.02.032

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Appendix A.1: Additional information on read-across approach

Table 35: Basic substance information and physical chemical properties relevant to justify grouping.

abbreviation	C_4-PFCA	C_6-PFCA	C_8-PFCA	C_9-PFCA	C_{10}-PFCA	C_{11}-PFCA	C_{12}-PFCA	C_{13}-PFCA	C_{14}-PFCA
acronym	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
IUPAC name	butanoic acid, heptafluoro-	hexanoic acid, undecafluoro-	octanoic acid, pentadeca-fluoro-	nonanoic acid, heptadeca-fluoro-	decanoic acid, nonadeca-fluoro-	undecanoic acid, henicosa-fluoro-	dodecanoic acid, tricosafluoro-	tridecanoic acid, pentacosa-fluoro-	tetradecanoic acid, heptacosa-fluoro-
chemical structure	$CF_3(CF_2)_2$-COOH	$CF_3(CF_2)_4$-COOH	$CF_3(CF_2)_6$-COOH	$CF_3(CF_2)_7$-COOH	$CF_3(CF_2)_8$-COOH	$CF_3(CF_2)_9$-COOH	$CF_3(CF_2)_{10}$-COOH	$CF_3(CF_2)_{11}$-COOH	$CF_3(CF_2)_{12}$-COOH
CAS number	375-22-4	307-24-4	335-67-1	375-95-1	335-76-2	2058-94-8	307-55-1	72629-94-8	376-06-7
	physico-chemical data								
molecular weight g/mol	214.04	314.05	414.07	464.08	514.08	564.09	614.10	664.11	714.11
partitioning coefficient log K_{OW}	3.39 ± 0.60 (calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02)	4.06 (calc., COSMOtherm (temp. not specified) (Wang et al., 2011b)	5.30 (calc., COSMOtherm (temp. not specified) (Wang et al., 2011b)	5.9 (calc., COSMOtherm, (Wang et al., 2011b))	6.5 (calc., COSMOtherm, (Wang et al., 2011b))	7.2 (calc., COSMOtherm, (Wang et al., 2011b))	7.8 (calc., COSMOtherm, (Wang et al., 2011b))	8.25 (calc., COSMOtherm, (Wang et al., 2011b))	8.90 (calc., COSMOtherm, (Wang et al., 2011b))
log K_{OA}		6.63 (calc., COSMOtherm (Wang et al., 2011b)	7.23 (calc., COSMOtherm, (Wang et al., 2011b))	7.50 (calc., COSMOtherm, (Wang et al., 2011b))	7.77 (calc., COSMOtherm, (Wang et al., 2011b))	8.08 (calc., COSMOtherm, (Wang et al., 2011b))	8.36 (calc., COSMOtherm, (Wang et al., 2011b))	8.63 (calc., COSMOtherm, (Wang et al., 2011b))	8.87 (calc., COSMOtherm, (Wang et al., 2011b))

abbreviation	C_4-PFCA	C_6-PFCA	C_8-PFCA	C_9-PFCA	C_{10}-PFCA	C_{11}-PFCA	C_{12}-PFCA	C_{13}-PFCA	C_{14}-PFCA
acronym	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
log K_{AW}		-2.66 (calc., (European Chemicals Agency, 2016a))	-1.93 (calc., COSMOtherm, (Wang et al., 2011b))	-1.58 (calc., COSMOtherm, (Wang et al., 2011b))	-1.27 (calc., COSMOtherm, (Wang et al., 2011b))	-0.92 (calc., COSMOtherm, (Wang et al., 2011b))	-0.58 (calc., COSMOtherm, (Wang et al., 2011b))	-0.38 (calc., COSMOtherm, (Wang et al., 2011b))	0.03 (calc., COSMOtherm, (Wang et al., 2011b))
dissociation constant		-0.16 (Zhao et al., 2014)	0.5 (calculated from exp. values, (Vierke, 2014)) 1.3 (López-Fontán et al., 2005)	< 1.6 (calculated from exp. values, (Vierke, 2014)) 0.82 (calc., COSMOtherm, (Wang et al., 2011b))	< 1.6 (calculated from exp. values, (Vierke, 2014)) 2.58 (Moroi et al., 2001)	< 1.6 (calculated from exp. values, (Vierke, 2014))			
partition coefficients log K_d (sediment and overlapping dissolved phase)		1.4 – 3.1 (Li et al., 2011)	0.04 (Ahrens et al., 2010a)*	0.6 (Ahrens et al., 2010a)*	1.8 (Ahrens et al., 2010a)*	3.0 (Ahrens et al., 2010a)*			
log K_{OC} (sediment organic carbon-normalised distribution coefficient)		1.63 – 2.35 (Sepulvado et al., 2011)	2.06 (Higgins and Luthy, 2006) 1.09 (Ahrens et al., 2010a)*	2.39 (Higgins and Luthy, 2006) 2.4 (Ahrens et al., 2010a)*	2.76 (Higgins and Luthy, 2006) 3.6 (Ahrens et al., 2010a)*	3.3 (Higgins and Luthy, 2006) 4.8 (Ahrens et al., 2010a)*			

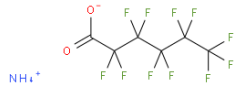
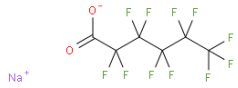
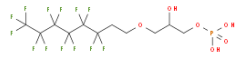
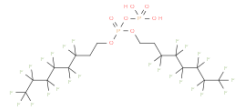
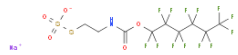
abbreviation	C_4-PFCA	C_6-PFCA	C_8-PFCA	C_9-PFCA	C_{10}-PFCA	C_{11}-PFCA	C_{12}-PFCA	C_{13}-PFCA	C_{14}-PFCA
acronym	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
water solubility		15.7 g/L (25 °C) (Zhao et al., 2014)	9.5 g/L (25° C) 4.14 g/L (22 °C) (European Chemicals Agency, 2013b)		5.14 g/L at 25 °C (European Chemicals Agency, 2016b)	$1.2 \cdot 10^{-4}$ g/L; pH 1 at 25 °C $9.0 \cdot 10^{-4}$ g/L; pH 2 at 25 °C $8.5 \cdot 10^{-3}$ g/L; pH 3 at 25 °C 0.056 g/L; pH 4 at 25 °C 0.14 g/L; pH 5 at 25 °C 0.16 g/L; pH 6-10 at 25 °C (calculated) (European Chemicals Agency, 2012a)	$2.9 \cdot 10^{-5}$ g/L pH 1 at 25 °C $2.2 \cdot 10^{-4}$ g/L pH 2 at 25 °C $2.0 \cdot 10^{-3}$ g/L pH 3 at 25 °C 0.014 g/L pH 4 at 25 °C 0.034 g/L pH 5 at 25 °C 0.039 g/L pH 6 at 25 °C 0.040 g/L pH 7 at 25 °C 0.041 g/L pH 8-10 at 25 °C (calculated) (European Chemicals Agency, 2012d)	$7.3 \cdot 10^{-6}$ g/L; pH 1 at 25 °C $5.5 \cdot 10^{-5}$ g/L; pH 2 at 25 °C $5.1 \cdot 10^{-4}$ g/L; pH 3 at 25 °C $3.5 \cdot 10^{-3}$ g/L; pH 4 at 25 °C $8.6 \cdot 10^{-3}$ g/L; pH 5 at 25 °C 0.0100 g/L; pH 6-10 at 25 °C (calculated) (European Chemicals Agency, 2012c)	$1.9 \cdot 10^{-6}$ g/L; pH 1 at 25 °C $1.4 \cdot 10^{-5}$ g/L; pH 2 at 25 °C $1.3 \cdot 10^{-4}$ g/L; pH 3 at 25 °C $9.3 \cdot 10^{-4}$ g/L; pH 4 at 25 °C $2.2 \cdot 10^{-3}$ g/L; pH 5 at 25 °C $2.6 \cdot 10^{-3}$ g/L; pH 6-10 at 25 °C (calculated) (European Chemicals Agency, 2012b)
vapour pressure		1.98 mm Hg at 25 °C; equals to 263.93 Pa	4.2 Pa (25 °C) extrapolated from		3.1 to 99.97 kPa	0.6 to 99.97 kPa (112 to	1.25 Pa at 25 °C (calculated)	0.48 Pa at 25 °C (calculated)	0.18 Pa at 25 °C (calculated)

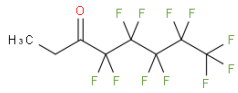
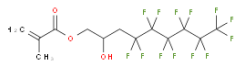
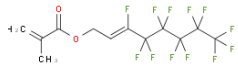
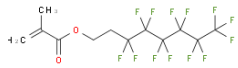
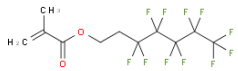
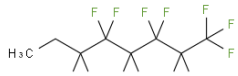
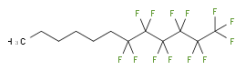
abbreviation	C_4-PFCA	C_6-PFCA	C_8-PFCA	C_9-PFCA	C_{10}-PFCA	C_{11}-PFCA	C_{12}-PFCA	C_{13}-PFCA	C_{14}-PFCA
acronym	PFBA	PFHxA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
		US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.11. Nov, 2012. Available from, as of Jan 11, 2015	measured data 2.3 Pa (20 ° C) extrapolated from measured data 128 Pa (59.3 °C) measured (European Chemicals Agency, 2013b)		(129.6 to 218.9 °C) (calculated) (European Chemicals Agency, 2016b)	237.7 °C) (calculated) (European Chemicals Agency, 2012a)	(European Chemicals Agency, 2012d)	(European Chemicals Agency, 2012c)	(European Chemicals Agency, 2012b)
boiling point		157 °C (Savu, 2000)		218 °C (European Chemicals Agency, 2015b)	218 °C measured (European Chemicals Agency, 2016b)	238.4 °C (calculated) (European Chemicals Agency, 2012a)	249 °C (European Chemicals Agency, 2012d)	260.7 °C (calculated) (European Chemicals Agency, 2012c)	270 °C (European Chemicals Agency, 2012b)

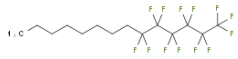
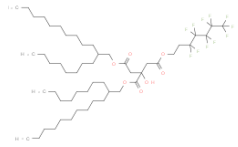
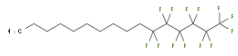
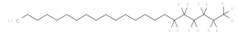
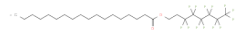
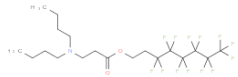
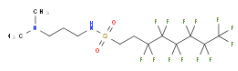
*pH of the water samples analysed 7.1 - 8.3 Temp.: 15.3 – 17.7 °C

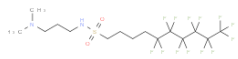
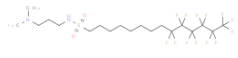
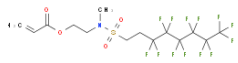
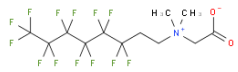
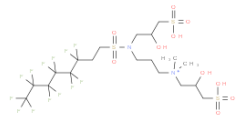
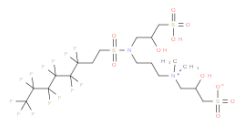
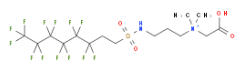
Appendix B.4.1: Precursors of PFHxA predicted via QSAR Toolbox v4.1 (European Chemicals Agency, 2018b)

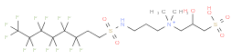
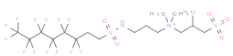
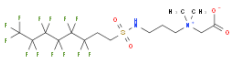
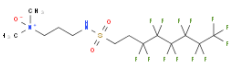
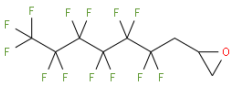
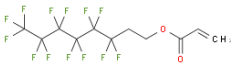
Table 36 Precursors of PFHxA predicted via QSAR Toolbox v4.1 (European Chemicals Agency, 2018b).

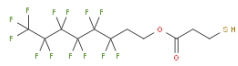
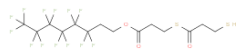
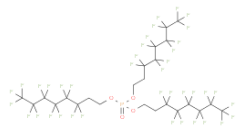
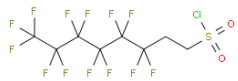
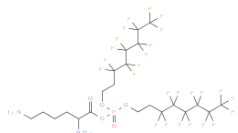
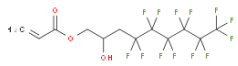
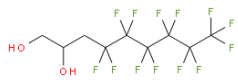
Structure depiction	Structural formula	Degradation pathway	CAS Number
	[NH4+].[O-]C(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by dissociation|PFHxA by hydrolysis (acidic)|PFHxA by hydrolysis (basic)|PFHxA by hydrolysis (neutral)|PFHxA by microbial transformation	21615-47-4 (QSAR toolbox)
	[Na+].[O-]C(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by dissociation|PFHxA by hydrolysis (acidic)|PFHxA by hydrolysis (basic)|PFHxA by hydrolysis (neutral)|PFHxA by microbial transformation	2923-26-4 (QSAR toolbox)
	OC(COCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)COP(O)(O)=O	PFHxA by microbial transformation	
	OP(O)(=O)OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[Na+].[O-]S(=O)(=O)SCCNC(=O)OC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C=C	PFHxA by microbial transformation	84100-13-0 (QSAR toolbox)

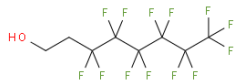
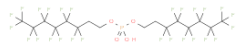
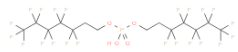
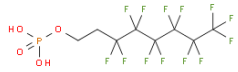
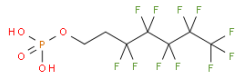
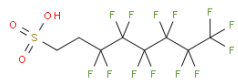
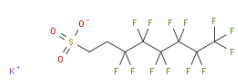
	CCC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CC(=C)C(=O)OCC(O)CC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CC(=C)C(=O)OCC=C(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CC(=C)C(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	2144-53-8 (screening excersise and QSAR toolbox)
	CC(=C)C(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	65530-66-7 (QSAR toolbox)
	CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	80793-17-5 (screening excersise)
	CCCCCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	432-580-1 (EC-number screening exercise)

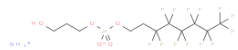
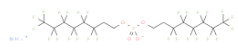
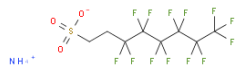
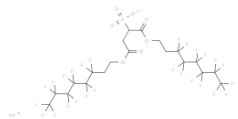
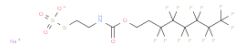
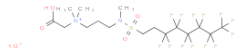
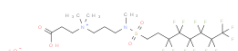
	CCCCCCCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	432-570-5 (EC-number screening exercise)
	CCCCCCCCCCC(CCCCCCCC)COC(=O)CC(O)(CC(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)C(=O)OCC(CCCCCCC)CCCCCCCCC	PFHxA by microbial transformation	214334-16-4 (QSAR Toolbox)
	CCCCCCCCCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	147492-59-9 (QSAR Toolbox)
	CCCCCCCCCCCCCCCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CCCCCCCCCCCCCCCCCC(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CCCCN(CCCC)CCC(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	402-910-7 (EC-Number screening exercise)
	CN(C)CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	34455-22-6 (screening excercise, QSAR Toolbox)

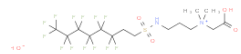
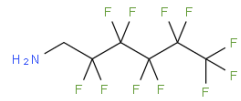
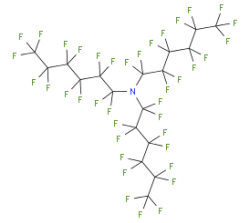
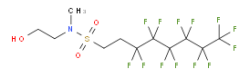
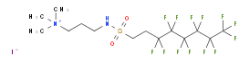
	CN(C)CCCNS(=O)(=O)CCCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CN(C)CCCNS(=O)(=O)CCCCCCCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	CN(CCOC(=O)C=C)S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	49859-70-3 (QSAR Toolbox)
	C[N+](C)(CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CC([O-])=O	PFHxA by microbial transformation	145441-31-2 (QSAR Toolbox)
	C[N+](C)(CCCN(CC(O)CS(O)(=O)=O)S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC(O)CS(O)(=O)=O	PFHxA by microbial transformation	
	C[N+](C)(CCCN(CC(O)CS(O)(=O)=O)S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC(O)CS([O-])(=O)=O	PFHxA by microbial transformation	
	C[N+](C)(CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC(O)=O	PFHxA by microbial transformation	

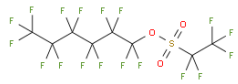
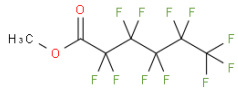
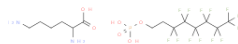
	C[N+](C)(CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC(O)CS(O)(=O)=O	PFHxA by microbial transformation	76201-56-4 (screening excercise)
	C[N+](C)(CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC(O)C[S-](=O)(=O)=O	PFHxA by microbial transformation	76201-56-4 (screening excercise)
	C[N+](C)(CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC([O-])=O	PFHxA by microbial transformation	34455-29-3 (QSAR Toolbox)
	C[N+](C)([O-])CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CC1CO1	PFHxA by microbial transformation	38565-52-5 (QSAR Toolbox)
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCOC(=O)C=C	PFHxA by microbial transformation	17527-29-6 (screening excercise, QSAR Toolbox)
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCOC(=O)CCCCCCCCCCC(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	

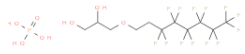
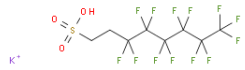
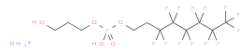
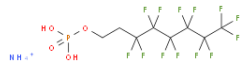
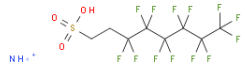
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCOC(=O)CCS	PFHxA by microbial transformation	
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCOC(=O)CCSC(=O)CCS	PFHxA by microbial transformation	
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCOP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)CCS(Cl)(=O)=O	PFHxA by microbial transformation	27619-89-2 (screening excercise, QSAR Toolbox)
	NCCCCC(N)C(=O)OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	OC(COC(=O)C=C)CC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	OCC(O)CC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	

	OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	647-42-7 (screening excercise, QSAR Toolbox); 68391-08-2 (screening excercise)
	OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	65530-62-3 (QSAR Toolbox)
	OP(O)(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	OP(O)(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	65530-61-2 (QSAR Toolbox)
	OS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	27619-97-2 (QSAR Toolbox)
	[K+].[O-]S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	59587-38-1 (QSAR Toolbox)

	[NH4+].OCCCOP([O-])(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[NH4+].[O-]P(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	1764-95-0 (QSAR Toolbox)
	[NH4+].[O-]S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[Na+].[O-]S(=O)(=O)C(CC(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)C(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	54950-05-9 (QSAR Toolbox)
	[Na+].[O-]S(=O)(=O)SCCNC(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	82199-07-3, (QSAR Toolbox)
	[OH-].CN(CCC[N+](C)(C)CC(O)=O)S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	66008-71-7 (QSAR Toolbox)
	[OH-].CN(CCC[N+](C)(C)CCC(O)=O)S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	66008-72-8 (QSAR Toolbox)

	[OH-].C[N+](C)(CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)CC(O)=O	PFHxA by microbial transformation	34455-29-3 (QSAR Toolbox)
	NCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	OCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	375-82-6 (QSAR Toolbox)
	OCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)N(C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	432-08-6 (QSAR Toolbox)
	CN(CCO)S(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	51619-73-9 (QSAR Toolbox)
	[I-].C[N+](C)(C)CCCNS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	94088-80-9 (QSAR Toolbox)

	FC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)OS(=O)(=O)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	COC(=O)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by hydrolysis (acidic)|PFHxA by hydrolysis (basic)|PFHxA by Hydrolysis (neutral)|PFHxA by microbial transformation	
	NCCCCC(N)C(O)=O.OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	NCCCCC(N)C(O)=O.OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	NCCCCC(N)C(O)=O.OP(=O)(OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	NCCCCC(N)C(O)=O.OP(O)(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	

	OP(O)(O)=O.OCC(O)COCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[K+].OS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[NH4+].OCCCOP(O)(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[NH4+].OP(O)(=O)OCCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	
	[NH4+].OS(=O)(=O)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F	PFHxA by microbial transformation	

Appendix B.4.2: Concentrations of PFHxA, its salts and related substances in environmental compartments

Table 37: PFHxA and related substances in wastewater treament plants and landfills (LOQ: Limit of quantification; LOD: Limit of Detection).

Sampling location	PFHxA concen-tration [ng/L]	6:2 FTS concentration [ng/L]	6:2 FTCA concentration [ng/L]	6:2 FTUCA concentration [ng/L]	6:2 diPAP concentration [ng/L]	6:2/8:2 diPAP concentration [ng/L]	Sampling year	Reference
wastewater treatment plant (WWTP)								
9 WWTP effluents along River Elbe, Germany	3.7 – 57.4	< 0.2 - 37.9					2007	(Ahrens et al., 2009b)
4 WWTP (1 industrial and 3 municipal) effluents, China	10.7 – 11.3						2009-2010	(Sun et al., 2011)
sewage sludge of 10 WWTPs (4 domestic, 5 industrial, 1 hospital), South West Nigeria	<0.0105 – 0.2458 ng/g						2012	(Sindiku et al., 2013)
90 European WWTP effluents	5.7 (media) 23800 (max) 72 % > LOQ						2010	(Loos et al., 2013)

Sampling location	PFHxA concen-tration [ng/L]	6:2 FTS concentration [ng/L]	6:2 FTCA concentration [ng/L]	6:2 FTUCA concentration [ng/L]	6:2 diPAP concentration [ng/L]	6:2/8:2 diPAP concentration [ng/L]	Sampling year	Reference
influent from 3 WWTP, Hong Kong	< 0.25				0.92-3.36	3.65 - 5.27	2012	(Loi et al., 2013)
effluent from 3 WWTP, Hong Kong	< 0.25				< 0.25 - 1.44	< 0.25 –-4.59		
sludge from 2 WWTP, Hong Kong	< 0.066 ng/g d.w.				10-13.5 ng/g dw	32.3 - 130 ng/g dw		
waster water, Austria	n.d. - 12 (n = 48, detection rate: 54.2 %, LOD = 0.5)						2014-2016	Provided by the Austrian Environment Agency in the Public Consultation
effluent Norway (urban)	2.2 – 6.6 100 % detection frequency						2017	(Norwegian Institute for Air Research (NILU), 2018b)
influent of two WWTP Australia	13-20 WWTP A 5-17 WWTP B significant positive trend forWWTP B	37 - 138 WWTP A 8.8 - 29 WWTP B samples analysed August 2016-October 2017					March 2014-October 2017	(Nguyen et al., 2019)

Sampling location	PFHxA concen-tration [ng/L]	6:2 FTS concentration [ng/L]	6:2 FTCA concentration [ng/L]	6:2 FTUCA concentration [ng/L]	6:2 diPAP concentration [ng/L]	6:2/8:2 diPAP concentration [ng/L]	Sampling year	Reference
landfill leachates								
one landfill leachate (Canada)	650 – 2500		40 - 280	7 - 64			2010	(Benskin et al., 2012a)
one landfill leachate, Finland	49 -200						2009-2010	(Perkola and Sainio, 2013)
landfill leachates (22 landfill sites in Germany)	<0.37 – 2509						-	(Busch et al., 2010)
effluent /landfill leachate (24 landfill sites in Germany)	< LOD—4256						2009	(Gellrich, 2014)
landfill leachates, (6 landfill sites in the USA)	270 - 790	56 - 280						(Perkola and Sainio, 2013)
landfill leachates laboratory bioreactor	< 2200	< 260					2010	(Perkola and Sainio, 2013)

Table 38: PFHxA in surface water and oceans (LOQ: Limit of quantification; LOD: Limit of Detection).

Sampling location	**PFHxA [ng/L]**	**Sampling year**	**Reference**
Atlantic and Canadian Arctic Oceans (cruises)	Atlantic: < 0.0046 – 0.51 Canadian Arctic: < 0.0024 – 0.0048	2005-2009	(Benskin et al., 2012b)
Northern Europe, Atlantic Ocean and Southern Ocean (cruise)	< 0.003 – 0.117	2008	(Ahrens et al., 2010b)
Greenland Sea, Atlantic and Southern Ocean (cruises)	Greenland Sea: < 0.0059 – 0.038 Atlantic: < 0.0059 – 0.120 Southern Ocean: < 0.0059	2009-2011	(Zhao et al., 2012)
seawater of the Western Merditerranean sea	0.096 (median) 0.02 – 0.189	2014	(Brumovský et al., 2016)
seawater of the German Baltic Sea	0.26 (median) 0.22 – 0.84	2017	(Joerss et al., 2019)
seawater of the German Bight (North Sea)	0.47 – 9.56	2007	(Ahrens et al., 2009a)
Hessian (Germany) surface water (32 samples)	11 (median) 81 % > LOQ	2009	(Gellrich et al., 2012)
10 lakes around Shenyang, China	< 0.63 – 25.0	2009	(Sun et al., 2011)
Guadalquivir and Ebro rivers (Spain)	9.6 – 31.4	2010	(Lorenzo et al., 2015)
40 river samples across the Hyogo prefecture, Japan	< 0.5 – 6.9 65 % > LOD	2010	(Takemine et al., 2014)
38 seawater samples across the Hyogo prefecture, Japan	1.5 – 510 100 % > LOD	2010	(Takemine et al., 2014)
22 surface water samples Ruhr area	< LOQ — 1248	2006	(Skutlarek et al., 2006)
38 surface water samples from River Rhine and selected tributaries	< LOQ — 77.0	2006	(Skutlarek et al., 2006)
12 surface water samples Moehne river and selected tributaries	< LOQ – 3040	2006	(Skutlarek et al., 2006)
River Alna River Drammenselva River Glomma	1.49 - 2.6 0.2 - 0.5 (concentration > LOD reported) 0.2 - 0.5 (concentration > LOD reported)	2016	(Norwegian Institute for Water Research (NIVA), 2017c)
input from storm water. Storm water samples were collected at one occasion at	5.42	2016	(Norwegian Institute for Water Research (NIVA), 2017c)

Sampling location	PFHxA [ng/L]	Sampling year	Reference
four specific sampling points (Bryning, Breivoll/Alnabru terminal, Breivoll downstream terminal and Hasle snow			
input from storm water	3.52	2015	(Norwegian Institute for Water Research (NIVA), 2016b)
Finnish rivers (128 samples from 20 different sites)	< 0.1 – 7.97 (88 % > LOD)	2014-2017	unpublished data, available in database https://wwwp2.ymparisto.fi/scripts/kirjaudu.asp
Finnish lakes (6 samples from different sites)	0.22 - 2.33	2014-2017	unpublished data, available in database https://wwwp2.ymparisto.fi/scripts/kirjaudu.asp (2018)
Deep sea (300 m and 1000 m depth) - Cap de Creus Canyon (north-western Mediterranean Sea)	sedimentary particle analyses: 0.89 to 4.47 ng/g (depth of 300 m) 4.57 to 10.66 ng/g (depth of 1000 m) (88 % > LOD) no PFASs were detected in the supernatant phases	2011/2012	(Sanchez-Vidal et al., 2015)
Ai River around a fluoropolymer plant in Osaka, collected within a 5 km radius of the plant	26.2 – 1 130 ng/L with 35 700 ng/L in 2009 in Ai River; Levels of PFOA decreased greatly over the last few decades, whereas those of PFHxA increased	Surface water 2003-2015	(Shiwaku et al., 2016)

Table 39: PFHxA in groundwater (LOQ: Limit of quantification).

Sampling location	**PFHxA [ng/L]**	**Sampling year**	**Reference**
Hessian (Germany) groundwater (150 samples)	4 (median) 14 % > LOQ	2008	(Gellrich et al., 2012)
groundwater recharge area (several perfluoroalkyl acids (PFAA) sources are present – a former landfill, a military base and a small commercial /industrial area) (Netherlands) Observation wells (OW, n = 2) Pumping wells (PW, n = 5)) – travel distance > 25 years	OW: (downstream of the potential PFAA sources): 0.7 – 570 PW: 0.22 – 0.8	2011	(Eschauzier et al., 2013)
164 individual groundwater samples from 23 European countries	< 0.5 0 % > LOD	2008	(Loos et al., 2010)
groundwater (n = 26) from an unlined firefighter training area at Ellsworth U.S. Air Force Base (AFFF used between 1970 and 1990)	< 100 – 320 000 96 % > LOD	2011	(Houtz et al., 2013)
Ground water (n = 2057) in Germany	< LOQ — 95.0	Not given	(von der Trenck et al., 2018) and Hessian Agency for Nature Conservation (2017) Environment and geology. Wiesbaden, Germany (unpublished data)
2 wells 5 km around a fluoropolymer plant in Osaka, Japan	well water (n = 44) 64.3 - 220 and 110 - 970) continuosly investigated; Levels of PFOA decreased greatly over the last few decades, whereas those of PFHxA increased	2006-2015	(Shiwaku et al., 2016)

Table 40: PFHxA in raw water and drinking water (LOQ: Limit of quantification).

Sampling location	**PFHxA [ng/L]**	**Sampling year**	**Reference**
findings in raw water samples			
raw water from public drinking water system (New Jersey, USA) (12 surface water and 18 groundwater)	<5 – 17 23 % > MRL (minimum reporting level)	2009-2010	(Post et al., 2013)
drinking water production chain, Amsterdam (Netherlands)	intake: 2.3 – 2.4 finished drinking water: 3.8 – 5.3	2010	(Eschauzier et al., 2012)
finding in tap water samples			
26 tap water samples from Germany	< 1 – 6.4 23 % > LOQ	not mentioned	(Gellrich et al., 2013)[26]
3 tap water samples from Norway (households receiving water from different water works)	< 0.11 0.31 0.78	2008-2009	(Haug et al., 2010)
84 tap water samples from Spain and 5 from Germany	Spain: 3.0 (median) 11 (max) 18 % > LOQ Germany: 0.7 (median) 1.8 (max) 80 % > LOQ	2010-2012	(Llorca et al., 2012a)
tap water samples in six European Countries (Sweden, Italy, Belgium, Netherlands, Norway, Germany) (n = 7)	< 0.38 – 5.15 86 % > LOQ	2010	(Ullah et al., 2011)
26 waterworks along the Ruhr River (Germany)	< 10 (median) 40 (max) 49 % > LOD	2008-2009	(Wilhelm et al., 2010)
21 tap water samples from Ruhr area	< LOQ – 56 66.6 % > LOQ	2006	(Skutlarek et al., 2006)
16 tap water samples from Germany (outside Ruhr area)	< LOQ – 9 6.3 % > LOQ	2006	(Skutlarek et al., 2006)
tap water 5 km around a fluoropolymer plant in Osaka	tap water Osaka 6.57-1.18 tap water Kyoto 3.35-4.4	2010-2015	(Shiwaku et al., 2016)

[26] Concentrations of PFHxA were also investigated in 18 spring water samples (Switzerland, Czech Republic and Germany), 14 untreated raw water samples for preparation of mineral water (Germany, Francea and Italy) and 119 bottled or repackaged mineral water samples. No PFHxA was detected above the LOQ (1 ng/L).

Table 41: PFHxA and related substances in soil and sediment (LOQ: Limit of quantification).

Sampling location	**PFHxA concentration (soil [µg/kg], sediment [pg/kg])**	**6:2 diPAP concentration (soil [µg/kg], sediment [pg/kg])**	**6:2/8:2 diPAP concentration (soil [µg/kg], sediment [pg/kg])**	**Sampling year**	**Reference**
soil [µg/kg]					
soil (0.6 m below surface; n = 16) and aquifer solids (5 - 6 m below surface; n = 10) from an unlined firefighter training area at Ellsworth U.S. Air Force Base (AFFF used between 1970 and 1990)	Soil: < 0.8 – 2 000 88 % > LOQ aquifer solids: 16 – 210 100 % > LOQ			2011	(Houtz et al., 2013)
soil (n = 60) and aquifer solids (n = 16) from a former firefighter training area at Ellsworth Air Force Base (USA)	soil < 0.05 – 2 761 93 % > LOQ Aquifer Solids 0.445 – 297 100 % > LOQ			2011	(McGuire et al., 2014)
soil from a fire fighting training ground at Flesland airport, Norway based on dryweight	0.18 – 18.5			2009	(Klima- og forurensningsdirektoratet (KLIF), 2010)
different sites (n = 10) at Rastatt contaminated with PFHxA	3.1 - 32.3			2015-2017	German Environmental Specimen Bank unpublished data
soil dw 5 stations in Oslo, based on dryweight	0.00043			2016	(Norwegian Institute for Air Research (NILU), 2017a)
sediment [pg/g]					
sediment from 16 locations in Hong Kong, based on dryweight	< 17 – 95	< 17 – 80	< 17	2009	(Loi et al., 2013)

Sampling location	PFHxA concentration (soil [µg/kg], sediment [pg/kg])	6:2 diPAP concentration (soil [µg/kg], sediment [pg/kg])	6:2/8:2 diPAP concentration (soil [µg/kg], sediment [pg/kg])	Sampling year	Reference
surface sediment samples from 26 stations and sediment core samples (n = 31) from 3 stations in Lake Ontario, Canada	surface: < 50 – 56 6 % > LOQ core: < 50 – 409 23 % > LOQ			2006 and 2008	(Yeung et al., 2013)
sediment from Langavatnet near Flesland airport., Norway, based on dryweight	< 600 – 1 600			2009	(Klima- og forurensningsdirektoratet (KLIF), 2010)
cores of sediments from Lake Erie, St Clair and Ontario including pore water	Ponar samples: 0.9 ng/g Ontario (n = 42) 0.3 ng/g St Clair (n = 16) 0.3 ng/g Erie (n = 49) Core samples 1.1 ng/g Ontario (n = 100) 0.4 ng/g St Clair (n = 21) 3.5 ng/g Erie (n = 49)[27]			Lake Ontario in 2013 and Lake Erie and Lake St. Clair in 2014	(Codling et al., 2018)

Appendix B.4.3: Concentrations of PFHxA, its salts and related substances in remote areas

Table 42: Findings of PFHxA and related substances in remote areas (LOQ: Limit Of Quantification).

Environmental Media	Sampling location	PFHxA concentration	6:2FTS [pg/m³]	Sampling year	Reference
ocean	Atlantic and Canadian Arctic Oceans (cruises)	Atlantic: < 0.0046 ng/L – 0.51 ng/L	-	2005-2009	(Benskin et al., 2012b)

[27] In sediment from lake Erie with layers in the core corresponding to 1959 to 2013, concentrations of both PFOS and PFHxA increased from earlier to more recently deposited sediments.

Environmental Media	Sampling location	PFHxA concentration	6:2FTS [pg/m³]	Sampling year	Reference
		Canadian Arctic: < 0.0024 ng/L – 0.0048 ng/L			
snow	European Alps (Colle Gnifetti; 10 m shallow firn core; 1996 - 2008)	0.06 ng/L – 0.34 ng/L 100 % > LOQ	-	2008	(Kirchgeorg et al., 2013)
oceanic plankton seawater	tropical /subtropical Pacific, Atlantic, Indian Oceans	frequency detected: Plankton: 7 % Seawater: 10 %	-	2010	(Casal et al., 2017)
air	Zeppelin (Norwegian Polar research station) monthly mean concentrations	< 0.015 - 0.047 pg/m³ monthly mean concentrations. In 2016, most of the monitored PFASs were below the analytical detection limit in all samples at all sites.	0.154	2016	(Norwegian Institute for Air Research (NILU), 2017b)
		< 0.05 - 0.07 pg/m³. Frequency detected ~20 %	> 0.2	2015	(Norwegian Institute for Air Research (NILU), 2016)
		< 0.05 - < 0.24 pg/m³	< 0.14 - < 0.89	2014	(Norwegian Institute for Air Research (NILU), 2015)
		0.05 - 0.19 pg/m³ PFHxA was observed with high detection frequency	0.22 - 0.53	2013	(Norwegian Institute for Air Research (NILU), 2014; Norwegian Institute for Air Research (NILU), 2015)

Environmental Media	Sampling location	PFHxA concentration	6:2FTS [pg/m³]	Sampling year	Reference
		0.02 – 0.24 pg/m³ (above detection limit in 11 out of 12 samples)	> 0.2	2017	(Norwegian Institute for Air Research (NILU), 2018a)

Appendix B.4.4: Concentrations of PFHxA, its salts and related substances in products and articles and house dust

Table 43: Reported concentrations of PFHxA in cosmetic products.

Data source	**PFHxA**		**µg/kg**		
Brinch et al. (2018)[a]	samples (n)	positive samples	max.	min.	median
all products	18	15	3 340.0	n.d.	4.9
facial scrub	1	1	6.3	5.4	5.9
BB /CC creams	3	3	397.0	12.0	16.5
body lotions	2	2	24.0	4.5	14.2
cream /lotion	2	2	2.6	1.1	2.1
ryeliner	1	0	n.d.	n.d.	n.d.
foundations	4	3	3 340.0	n.d.	178.5
concealer	1	1	1 940.0	1 930.0	1 935.0
highlighter	1	1	18.0	17.0	17.5
hair spray	1	0	n.d.	n.d.	n.d.
powder	1	1	34.0	30.0	32.0
eye shadow	1	1	5.5	5.4	5.5

Schultes et al. (2018)					
all products	31	10	4 640	< 3.35	< 3.35
cremes	7	0			
foundations	9	4	4 640	< 3.35	< 3.35
pencil	1	0			
powders	12	6	447	< 3.35	3.62
shaving Creme	2	0			
Fujii et al. (2013)					
all products	23	18	6 500	< 1.9	350
foundations	9	8	2 100	< 1.9	410
manicure	3	3	140	4.7	24
lip rouge	2	0	< 5.7	< 3.8	
sunscreen (milk)[b]	6	5	6 500	< 4.6	2 800
sunscreen (foundations)	3	2	350	< 2.3	180

[a] two individual products were analyzed per sample

[b] four different lots of a specific sunscreen milk were analyzed

Table 44: Reported Concentrations of PFHxA in House Dust from European Samples.

Reference	Sampling Year	Location	LOD	N	>LOD	Min. [ng/g]	Median [ng/g]	Mean [ng/g]	Max. [ng/g]	Remarks on Sampling and Sieving
Huber et al. (2011)	2007-2008	Norway	0.18-7.89 (MDL)	7	6	<2.2	10.1	11.3	26.7	Living rooms, industrial vacuum cleaner, forensic nozzle, surfaces above floor
				1	1		27.5			Sleeping room, industrial vacuum cleaner, forensic nozzle, surfaces above floor
D'Hollander et al. (2010)	2008	Belgium	0.1 (LOQ)	45			0.3		5.8 (95P)	Nylon socks, only floor, 500 µm
Haug et al. (2011)	2008	Norway	2.1-13 (LOQ)	41	31	4.3	28	33	96	Forensic nozzle, surfaces above floor
Ericson Jogsten et al. (2012)	2009	Catalonia	0,019	10	10	0,40	1.01		2.9	Vaccum cleaner, 150 µm

Eriksson and Karrman (2015)	2013-2014	Greece	1.4 – 7.9	7		<3.21	3.85	6.24	26.2	Vaccum cleaner, 150 µm
	2009	Spain		10		<3.21	3.39	3.16	5.45	
	2013-2014	Sweden		10		<3.21	7.05	9.65	39.6	
Lankova et al. (2015)	2013	Czech Rep.	0.25-1 (LOQ)	18	2	<1			9.73	From 6 households, vacuum cleaner
Karaskova et al. (2016)	2013	Czech Rep.	0.01 ng/ml (LOQ)	16	16	1.4	3.8	12.8	69.1	Polyester sampling sock, 500 µm
Winkens et al. (2018)	2014-2015	Finland	0.82 (MDL)	65	33	<0.82	2.33	5.17	54.5	Childrens bedrooms, Polyester sampling sock, floor after 1 week, 0,5 mm
Bohlin-Nizzetto et al. (2015)	2015	Norway	0.05	36	32	<0.05	9.29		40.2	From 6 households, industrial vacuum cleaner, forensic nozzle, all surfaces
Padilla-Sánchez and Haug (2016)	2015	Norway	Not given	7	3	<LOD	<LOD		10	Vacuum cleaner, 500 µm

N: number of samples; LOD: limit of detection; LOQ: limit of quantification; MDL: method detection limit

Several of the studies gave additional information on precursors of PFHxA in house dust:
According to Eriksson and Karrman (2015), polyfluoroalkyl phosphate esters (PAPs) can be degraded by microbial hydrolysis to fluorotelomer alcohols (FTOH) which can be oxidized to saturated and unsaturated carboxylic acids (FTCA and FTUCA) and form polyfluorinated carboxylic acids (PFCA).
Huber et al. (2011) analyzed indoor air in six of the living rooms where the house dust samples were taken. They found 6:2 FTOH concentrations between 16.0 and 332 pg/m³ and a strong positive correlation between 6:2 FTOH concentrations in indoor air and PFHxA concentrations in dust.
In the house dust samples taken by Eriksson and Karrman (2015), mono-and diPAPs accounted for a vast majority of the analyzed perfluorinated compounds. 6:2 diPAP contributed 27 % to the total amount of diPAP homologues in the whole study, 6:2/8:2 diPAP 17 % and 6:2/10:2 diPAP 13 %. The median values for 6:2 diPAP were 5.26 ng/g in Greece, 2.08 ng/g in Spain and 15.4 ng/g in Sweden.
Also in the study by Winkens et al. (2018), the house dust samples were dominated by PAPs and FTOHs. Medians were 16.6 ng/g for monoPAP, 53.9 ng/g for 6:2 diPAP and 27.6 ng/g for 6:2 FTOH.

Table 45: Ocurrence of PFHxA in food.

Data Source	Countries	Foods with detects	Range of reported Detects [µg/kg]	N (no bracket: Samples, []: Groups)	N > LOD	LOD [µg/kg]	Remarks
Fromme et al. (2007)	Germany	whole diet	0.1 - 3.18	214	19	0.2	
Ericson Jogsten et al. (2009)	Spain	meat, vegetables	0.012 - 0.118	40	5	0.001	
Clarke et al. (2010)	UK	fish	2 - 7	252	3	1	
Haug et al. (2010)	Norway	vegetables, potato, dairy products, cereals, egg, fish	0.00098 - 0.014	16	7	0.0001 -0.66	
ANSES (2011)	France	fish	0.002	591 [25]	1	0.0029 -0.194	1 out of 25 groups had > 1 detect
Domingo et al. (2012)	Spain	fish and seafood, dairy products	0.031 - 0.007	40 [12]	2		2 out of 12 groups had > 1 detect
Vestergren et al. (2012a)	Sweden	oils, cereals, egg, vegetables, fruit, potatoes, sugar and sweets, softdrinks	0.0014 - 0.011	36	22	-	
Vestergren et al. (2012b)	Sweden	whole diet, vegetables, meat	0.0099 - 0.131	[5]	3	0.0024	3 out of 5 groups had > 1 detect
Gebbink et al. (2015)	Sweden	sugar and sweets	0.0156 - 0.107	14 / 22*	6	-	*14 Samples, of which 8 were measured unprepared and prepared

Herzke et al. (2013b)	Belgium, Czech Republic, Italy, Norway	vegetables	0.00289 - 0.099	62	19	0.002-0.05	
Yamada et al. (2014)	France	fish	0.03 - 4.01	481 [46]	36	0.007-0.95	36 out of 46 groups (all fish) had > 1 detect

Appendix B.4.5: Concentrations of PFHxA, its salts and related substances in biota and humans

Table 46: Concentration of PFHxA in different organisms (LOQ Limit of quantification; MDL method detection limit; MQL method quantification limits; MLOD method limits of detection; n.d. not detected).

Organisms	PFHxA concentration [ng/g] ww	Sampling location	Reference /Sampling year
zooplankton herring sprat guillemot egg	< 0.04 (MQL), < 0.2 (MQL) < 0.5 (MQL) 0.0026	Baltic Sea	(Gebbink et al., 2016) 2013-2014
albatross liver albatross muscle albatross adipose	0.09 n. d. – 0.06 n. d. – 0.05	Midway Atoll (North Pacific Ocean	(Chu et al., 2015) 2011
fish muscle fish liver prawn	68 % recovery 44 % recovery 38 % recovery All samples < LOQ	Australia, contaminated estuaries	(Taylor and Johnson, 2016) 2015
crucian carp blood crucian carp liver mandarin fish blood mandarin fish liver	n. d. – 0.36 n. d. n. d. n. d.	Korea	(Lam et al., 2016) 2010 - 2012
amphipod damselfly shrimp sunfish bullhead turtle plasma	2.22 < MDL (0.25) < MDL (0.25) < MDL (0.25) < MDL (0.25) < MDL (0.1)	Hamilton, Canada; downstream of an airport	(de Solla et al., 2012) 2007 - 2010
wild boar (liver)	0.49	Ingolstadt, Germany	(Klein et al., 2016) 2011 - 2012
fish skin fish liver fish muscle roe fish algae guano algae penguin dung penguin tissue	< MLOD – 12.3 207 – 232 < MLOD - 72 1.44 – 2.31 3.4 – 240 < MLOD – 1190 < MLOQ 17.3 – 237 0.26 – 0.61	Tierra del Fuego Tierra del Fuego Tierra del Fuego Tierra del Fuego Tierra del Fuego Tierra del Fuego Antarctica Antarctica Antarctica	(Llorca et al., 2012b)
beaver, liver cod, blood velvet scoter eider duck long-tailed duck long-tailed duck red-throated diver razorbill	0.08 0.17 pg/mL < 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Poland	(Falandysz et al., 2007) 2003
roe deer	Recovery 5.5 % < 0.02 (LOQ) – 0.7	Germany	(Falk et al., 2012) (2010)

Organisms	**PFHxA concentration [ng/g] ww**	**Sampling location**	**Reference /Sampling year**
zooplankton Arctic cod ringed seal bearded seal	n.d. (LOD 0.3) n.d. (LOD 0.3) n.d. (LOD 0.3) n.d. (LOD 0.3)	Canadian Western Arctic	(Powley et al., 2008) 2004
PFHxA detected in 3 of 16 monitored organisms: white shrimp whitebait gobies	 2.11 0.815 3.29	Taihu Lake China	(Fang et al., 2014) 2012
fish homogenates	4.67	Ohio, Missouri, and Upper Mississippi Rivers	(Ye et al., 2008)
fish plasma (European chub)	0.2 (not found in Liver, Gills, Gonads, Muscle)	Orge River (nearby Paris)	(Labadie and Chevreuil, 2011) 2010
soft tissue of seafood samples, PFHxA detected in 1 of 16 monitored organisms: swimming crab	 0.29	fish market China	(Gulkowska et al., 2006) 2004
common eider European shag kittiwake glaucous gull polar bear mink	0.0 – 0.06 100 % detection frequency < 0.10 – 0.03 40 % detection frequency < 0.10 – 0.09 40 % detection frequency < 0.10 – 0.03 40 % detection frequency 0.06 – 0.05 40 % detection frequency < 0.10 0 % detection frequency	Norwegian Arctic	(Norwegian Institute for Air Research (NILU), 2018b)
common gull	< 0.10 – 0.04 20 %	Norway (urban)	(Norwegian Institute for Air Research (NILU), 2018b)

Organisms	**PFHxA concentration [ng/g] ww**	**Sampling location**	**Reference /Sampling year**
Cod liver	< LOD	Coastal waters Norway	(Guelfo et al., 2018; Norwegian Institute for Water Research (NIVA), 2013; Norwegian Institute for Water Research (NIVA), 2014; Norwegian Institute for Water Research (NIVA), 2015; Norwegian Institute for Water Research (NIVA), 2016a; Norwegian Institute for Water Research (NIVA), 2017a)
ice amphipod polar cod black guillemot glaucous gull	n.d. (LOD 0.41) 6:2 FTS: n.d. – 1.68 (LOD) 0.64 – 5.38 n.d. – 0.39 (LOD 0.22) n.d. – 1.55 (LOD 0.22)	Barants Sea	(Haukas et al., 2007) 2004
polychaeta blue mussel krill prawns herring cod gull blood gull egg	All < LOD	Urban Fjord, Norway	(Norwegian Institute for Water Research (NIVA), 2017b)

Organisms	**PFHxA concentration [ng/g] ww**	**Sampling location**	**Reference /Sampling year**
earthworm eggs of fieldfare eggs of tawny owl red fox liver sparrowhawk egg brown rat liver	3.28 < LOD 0.01 < LOD < LOD < LOD	Oslo	(Norwegian Institute for Air Research (NILU), 2017a)

Appendix B 5: Human health hazard assessment

B.5.1 Toxicokinetics (absorption, distribution, metabolism and elimination)

Regarding the evaluation of the bioaccumulation potential, elimination half-lives have been proven to be of importance for long-chain PFASs. Elevated levels of PFOA in human blood and a half-life in humans of 2-4 years lead to the conclusion that PFOA is bioaccumulative (ECHA, 2013b).

The free undecafluorohexanoic acid (PFHxA) is in equilibrium with undecafluorohexanoate (PFHx), the conjugate base; however, due to its low pK_a (< 1), PFHxA primarily exists in the environment as an anion. However, some laboratories report results for the acidic form of PFHxA and the standards used by some laboratories to perform toxicity testing include various PFHxA salts, such as ammonium perfluorohexanoate (CAS-No 21615-47-4) and sodium perfluorohexanoate (CAS-No 2923-26-4). This is important, as the acid has been shown to be more irritating than associated salts. However, regardless of the administered compound, once absorbed into the bloodstream, the PFHx-anion will form. Additionally, when the salt or acid exists in liquids, it will dissociate and the salt or acid will break off, resulting in the anion (Luz et al., 2019).

Absorption

Oral absorption.

PFHxA and APFHx were rapidly absorbed after oral (gavage) administration. In rats of both sexes maximum levels of PFHxA in serum were reached one hour after repeated oral administration (Chengelis et al., 2009b). Following repeated oral dosing, approximately 90 % of the administered daily dose of PFHxA was recovered in the urine of male rats during 24 h post dosing. Urinary elimination in female rats was variable, with about 70 – 100 % of the administered daily dose of PFHxA recovered in the urine 24 h post-dosing (Chengelis et al., 2009b).

From the study performed by (Iwai, 2011) it can be concluded that up to 90 % of the administered dose is systemically absorbed and excreted within 24 h after single and repeated (14d) oral administration of 50 mg/kg APFHx to male and female rats and mice.

The rapid absorption can also be demonstrated by the rapid achievement of the maximum serum concentration after oral administration of radiolabeled ^{14}C-PFHx in male and female CD-1 mice and Sprague Dawley rats. Within 15 - 30 minutes after administration of 2 or 100 mg/kg of the substance, maximum serum concentrations were achieved (Gannon et al., 2011b). Based on the fact that PFHxA is mainly excreted via urine at the longest 24 h after dosing, it can be assumed that the uptake of the substance via the gastrointestinal tract of rat and mice is rapid and complete.

No data are available for oral absorption in humans. The fact that PFHxA can be detected in human blood, serum, plasma or urine samples is a proof that the systematic absorption occurs. The detection of the substance in human bio material does not allow any statement about the route of administration. Although the oral route (e.g. via drinking water or food) is more likely than the others.

Dermal absorption.

No data are available for dermal absorption in experimental animals or humans. According to the physicochemical properties of PFHxA and the rule of achieved (Gannon et al., 2011b), the dermal absorption was assumed as 100 %.

De Heer et al. defined criteria to discriminate between chemicals with high and low dermal absorption assuming that there is an optimum in log P_{OW} and a maximum in molecular weight for facilitating percutaneous absorption. If the molecular weight is higher than 500 Da and the log P_{OW} is smaller than -1 or higher than 4, the dermal absorption would be estimated with 10 %. If the molecular weight and the log P_{OW} are different, 100 % dermal absorption would be assumed (de Heer et al., 1999). The assumption of 100 % dermal absorption is a conservative approach, because PFHxA contains an acid group which might counteract the dermal absorption.

Inhalation absorption.

No data are available for inhalation absorption in experimental animals or humans. However, the study of (Nilsson et al., 2010b) suggests a significant inhalation exposure of ski waxers. Nilsson et al. (2013b) measured concentrations from 27 to 14 900 ng/m³ of PFHxA in the air of the breathing zone of some ski wax technicians. PFHxA exposure via inhalation was supposed to contribute to the increased blood level measured during the World Cup season. The lower blood concentrations of PFHxA in pre- and postseason are accompanied by no or decreased inhalation exposure. Further information on inhalation exposure, especially on further source, are given in chapter E.2.9.

Distribution

After oral administration, PFHxA was mainly detected in plasma, kidney, liver and bladder of rats and mice (Gannon et al., 2016).

In another study, 50 mg/kg bw/d APFHx were orally administered to male and female Sprague Dawley-rats and CD-1 mice for 14 days. 7 days after the final dose, the substance remained quantifiable in blood and liver of both species and sexes. In all other examined organs the contents of PFHxA were very low or below the limit of detection (Iwai, 2011).

Numata et al. (2014) and coworkers report that accumulation of PFHxA in fattening pigs mainly occurs in plasma, fat and muscle tissue (i.e. meat) liver and kidney.

Guruge et al. (2016) showed that PFHxA was rapidly absorbed by micromini pigs after administration of a single capsulated dose of 3 mg/kg and the maximum blood levels were achieved 12 h after administration.

PFHxA has been shown to occur in several human tissues (Pérez et al., 2013). PFHxA was found in lung, brain, liver, kidney and bone. PFHxA represented the highest median PFAS-concentrations in brain and liver (brain: mean 180 ng/g and median 141 ng/g; liver: mean 115 ng/g and median 68.3 ng/g wet weight). The concentrations of 21 PFASs were analysed from 99 samples of autopsy tissues (brain, liver, lung, bone, and kidney) from 20 subjects which have been living in Catalonia, Spain. PFHxA showed the highest concentrations in the brain and liver. In brain, mean concentration of PFHxA was higher than all other PFAS and was detected in all the samples at concentrations ranging from 10.1 to 486 ng/g. In liver,

PFHxA was detected in the samples at concentrations up to 353 ng/g. In general terms, the highest concentrations of PFAS were found in lung tissues (PFHxA mean: 50.1 ng/g and median 207 ng/g, ranging up to 559 ng/g). Mean concentrations of PFHxA in the bone and kidney were 36 and 6 ng/g. Results from this study support the conclusion that the substance is distributed to multiple organs.

PFHxA strongly binds to serum albumin. (Bischel et al., 2011) investigated with equilibrium dialysis the binding of PFCAs to bovine serum albumin (BSA). More than 99 % of PFHxA was bound to BSA and the protein water distribution coefficient (log K_{PW}) was 4.05 (Bischel et al., 2011)). An increase in K_{PW} with increasing carbon chain length was observed for PFCAs with four to six fluorinated carbons. For PFCAs with greater than six fluorinated carbons, K_{PW} values generally decreased. The authors suggest that increased rigidity associated with long-chain PFCAs may contribute to the observed nonlinear relationship of K_{PW} with the fluorocarbon tail length. The comparison with PFOA shows that the fraction bound to BSA is equally high with > 99 % and that the K_{PW} of PFHxA is higher than for PFOA (log K_{PW} was 4.14). However, there are huge differences in the elimination half-lives of PFOA (years) and PFHxA (days) in humans.

The general population is exposed to PFHxA and its precursors via different routes and different sources. Oral administration occurs via drinking water and food intake. Dermal and inhalation exposure also contribute to the general uptake of PFHxA. The exposure estimation via biomonitoring data reflects all sources of exposure. A summary of measured levels of PFHxA in human blood samples is given in Table 47-Table 49. It seems that the type of medium in which PFHxA is determined has an influence on the detectability of PFHxA. Poothong et al. (2017) showed that the best medium to determine the content of PFHxA is whole blood.

Table 47: Concentrations of PFHxA in human **whole blood** [ng/mL] (LOD: limit of detection; FOD: frequency of detection; n.r.: not reported).

Country / Study	**Sample Size**	**LOD**	**FOD**	**Max**	**Min**	**Mean**	**Median**	**95th per-centile**	**Reference**
Sweden/ Stockholm	66	< 0.1 – 0.5 ng/mL	8 %	1.6	< 0.1	n.r.	n.r.	n.r.	(Kärrman et al., 2006)
Norway / A-Team Study	**58**	**0.09**	**100 %**	**1.65**	**0.14**	**0.68**	**0.62**	**n.r.**	(Poothong et al., 2017)
Poland/ Gdansk or nearby	15 dockers	not given	20 %	0.02	< 0.002	0.004	< 0.002	n.r.	(Falandysz et al., 2006)
Poland/ Gdansk or nearby	15 farmers	not given	n.r.	0.06	0.005	0.03	0.02	n.r.	(Falandysz et al., 2006)
Poland/ Gdansk or nearby	15 fish-dish fanciers	not given	n.r.	0.24	0.01	0.06	0.03	n.r.	(Falandysz et al., 2006)
Poland/ Gdansk or nearby	15 reference group	not given	n.r.	0.07	0.004	0.03	0.03	n.r.	(Falandysz et al., 2006)

Table 48: Concentrations of PFHxA in human **serum** [ng/mL] (LOD: limit of detection; FOD: frequency of detection; n.r.: not reported).

Country / Study	**Sample Size**	**LOD**	**FOD**	**Max**	**Min**	**Mean**	**Median**	**95th per-centile**	**Reference**
U.S. / C8 Health Study	67 000	< 0.5	53 %	n.r.	n.r.	1.4	1.0	n.r.	(Frisbee et al., 2009)
New Zealand/ POP Study	747	< 0.5	0 %	< LOD	< LOD	< LOD	< LOD	< LOD	(New Zealand Ministry of Health, 2013)
U.S. / American Red Cross (year 2000-2001)	**645**	**< 0.02 – 0.1**	**3.4** %	**6**	**< LOQ**	**< LOQ**	**n.r.**	**0.05**	(Olsen et al., 2017)
South Korea	1 874	< 0.11	0 %	< LOD	< LOD	< LOD	< LOD	< LOD	(Lee et al., 2017)
Canada/ Health Measures Study	1 524	< 0.1	2 %	< LOD	< LOD	< LOD	< LOD	< LOD	(Environment Canada Health Canada, 2013)
Japan/ Exposure to Chemical Compounds	326	< 0.1	0 %	< LOD	< LOD	< LOD	< LOD	< LOD	(Ministry of the Environment Japan, 2016)
China/ General Population Study of Three Provinces	202	< 0.01	53 %	1.1	< LOD	0.07	0.01	n.r.	(Li et al., 2017b)
Norway/ A-Team Study	61	0.045	0 %	< LOD	< LOD	< LOD	< LOD	n.r.	(Poothong et al., 2017)
Germany/ HBM Studie Altötting	**906**	**< 0.25**	**1.98** %	**1.88**	**< LOD**	**n.r.**	**n.r.**	**< 0.25**	(LGL, 2018)
Italy/ Veneto Region	257 ex-posed	not given	20 %	0.68	< LOQ	n.r.	< LOQ	0.27	(Ingelido et al., 2018)
Italy/ Veneto Region	250 un-ex-posed	not given	18 %	0.26	< LOQ	n.r.	< LOQ	0.09	(Ingelido et al., 2018)

Table 49: Concentrations of PFHxA in human **plasma** [ng/mL] (LOD: limit of detection; FOD: frequency of detection; n.r.: not reported).

Country / Study	**Sample Size**	**LOD**	**FOD**	**Max**	**Min**	**Mean**	**Median**	**95th per-centile**	**Reference**
U.S. / American Red Cross (year 2006)	600	< 0.02 – 0.1	2.8 %	**1.5**	< LOQ	**< LOQ**	n.r.	< LOQ	(Olsen et al., 2017)
U.S. / American Red Cross (year 2010)	600	< 0.02 – 0.1	18 %	0.4	< LOQ	< LOQ	n.r.	0.13	(Olsen et al., 2017)
U.S. / American Red Cross (year 2015)	616	< 0.02 – 0.1	3.3 %	0.27	< LOQ	< LOQ	n.r.	< LOQ	(Olsen et al., 2017)
Canada/ Health Measures Study	1 524	< 0.1	2 %	n.r.	< LOD	< LOD	< LOD	< LOD	(Environment Canada Health Canada, 2013)
Norway/ A-Team Study	59	0.045	0 %	< LOD	< LOD	< LOD	< LOD	n.r.	(Poothong et al., 2017)
Canada/ onreserve and crown land population aged 20 years old and older,	473	< 100 ng/L	0 %	< LOD	< LOD	< LOD	< LOD	< LOD	(AFN, 2013)

PFHxA was also found in breast milk as shown in Table 50.

Table 50: Concentrations of PFHxA in human breast milk (LOD: limit of detection; FOD: frequency of detection).

Country / Study	**Sample year**	**Sample Size**	**PFHxA concentration [ng/mL]**	**LOD [ng/ml]**	**FOD**	**Reference**
South Korea/PFAS in human breast milk	2013	264	median: 0.047	n.r.	70.8 %	(Kang et al., 2016)
Spain/ PFAS in breast milk	2012	10	mean: 0.006 median: 0.06	0.0003	10 %	(Lorenzo et al., 2016)
France/ PFAS in human breast milk	2013	48	< LOD - 0.053	0.05	2 %	(Antignac et al., 2013)

Metabolism

No metabolism of APFHx was observed when incubating isolated primary hepatocytes from rats with a concentration of 50 µM for 120 minutes (Gannon et al., 2011b). The authors neither observed any changes in the concentration of APFHx nor found any metabolites in the cell culture medium. After oral administration of APFHx to CD-1 mice and Sprague Dawley rats, (Gannon et al., 2011b) did not detect any metabolites of the substance in the urine,

faeces or plasma samples of the animals. Therefore, it can be concluded that APFHx is a highly stable substance that is not metabolised to a detectable extent.

Elimination

Several studies proved that renal excretion via urine is the main route of elimination of PFHxA or APFHx (Chengelis et al., 2009b; Fujii et al., 2015; Gannon et al., 2011b; Guruge et al., 2016).

Gannon et al. (2011b) reported that in mice >99 % of the oral dose of ^{14}C-PFHxA was eliminated within 24 hours and 48 hours by males and females, respectively. In rats, 100 % of an orally administered dose was excreted in the urine after 24 hours in both males and females. The excretion via faeces was negligible.

Chengelis et al. (2009c) reported that 80 % of the i.v. administered dose was excreted in urine within 24 hours in rats. Following repeated oral exposure, 70 - 100 or 90 % of PFHxA was excreted within 24 hours in males and females, respectively.

From the study performed by (Iwai, 2011) it can be concluded that up to 90 % of the administered dose is systemically absorbed and excreted within 24 hr after single and repeated (14d) oral administration of 50 mg/kg APFHx to male and female rats and mice whereas 9.6 to 12.9 % of the dose is excreted via faeces.

Fujii et al. (2015) reported for mice the recovery of 68.8 – 100 % of the administered dose (0.313 µmol/kg). The majority was found in the urine (47 – 100 %). Only 4.7 - 15.6 % were detected in the faeces.

The amount of PFHxA eliminated in the faeces in both mice and rats was negligible. After a single oral dose, 7 - 15.5 % of 14C-PFHx was eliminated in faeces by mice and rats, and 10 -13 % of APFHx was eliminated after repeated exposure (Gannon et al., 2011b; Iwai, 2011).

PFHxA was also detected in human urine. The summary of PFHxA concentrations found in human urine samples is given in Table 51.

Table 51: Concentrations of PFHxA in human urine (LOD: limit of detection; FOD: frequency of detection).

Country / Study	Sample year	Sample Size	PFHxA concentration [ng/mL]	LOD/ LOQ [ng/mL]	FOD	Reference
Austria/ human urine from male and female adults aged 25-46 years	2016	11	median: 0.0015 mean: 0.0016 creatinine-adjusted concentrations	0.0002/ 0.0005	100 %	(Hartmann et al., 2017)
South Korea/ children aged 5-13 years	2012	120	< LOD-2.34 (mean: 1.38) (LOD: 0.163)	n.r.	11 %	(Kim et al., 2014)
South Korea/ adults	2012	n.r.	< LOD-5.63 µg/L (mean: 1.38 µg/L) (LOD: 0.163 µg/L)	n.r.	5 %	(Kim et al., 2014)

Beside elimination via urine, the serum or plasma elimination kinetics in mammals were also analysed in different species. The serum elimination occurs in a biphasic pattern. High amounts of PFHxA were rapidly eliminated in the first or alpha phase.

For mammals, there are several studies available reporting on elimination half-lives of PFHxA. The summary of reported half-lives is given in Table 52.

Table 52: Serum or plasma elimination half-lives of PFHxA in humans and laboratory animals.

Organism	**Half-life PFHxA (M = male, F = female)**	**Comments**	**Reference**
Rat	M: 1.0 h, F: 0.42 h in serum	mean β-phase of two compartment model with first-order elimination, single IV dose of 10 mg/kg	Chengelis et al. (2009b)
	M: 2.2 h, F: 2.7 h in Serum	mean β-phase of two compartment model with first-order elimination, repeated oral dose of 50 mg/kg, day 25	Chengelis et al. (2009b)
	M: 2.7 h, F: 2.4 h in serum	mean β-phase of two compartment model with first-order elimination, repeated oral dose of 150 mg/kg, day 25	Chengelis et al. (2009b)
	M: 2.8 h, F: 2.3 h in serum	mean β-phase of two compartment model with first-order elimination, repeated oral dose of 300 mg/kg, day 25	Chengelis et al. (2009b)
	M: 1.7 h, F: 0.5 h in serum	mean β-phase of one compartment model with first-order elimination, single oral dose of 2 mg/kg	Gannon et al. (2011b)
	M: 1.5 h, F: 0.7 h in serum	mean β-phase of one compartment model with first-order elimination, single oral dose of 100 mg/kg	Gannon et al. (2011b)
Mice	0.89 - 1.24 h in serum	mean β-phase elimination	Russell et al. (2013)
Pig	M, F: 4.1 d in plasma	mean β-phase of two compartment model with first-order elimination, 21 d exposure to 48 µg/kg	Numata et al. (2014)

Organism	Half-life PFHxA (M = male, F = female)	Comments	Reference
		dw in diet	
Monkey	M: 5.3 h, F: 2.4 h (mean) in serum	mean β-phase of two compartment model with first-order elimination, single IV dose of 10 mg/kg	Chengelis et al. (2009b)
Human	Male: 7.2 d in blood	serum elimination half-life of one compartment model	Hethey et al., unpublished
	Male: 5.1 d in serum	serum elimination half-life for β phase elimination	Buck and Gannon (2017) cited by Luz et al. (2019)

Available studies suggest a gender specific difference in PFHxA serum clearance in rats, as female rats eliminated PFHxA about two to three times faster (0.42 h compared to 1.0 h). This would be in line with (Gannon et al., 2011b) observing also serum elimination half-lives of PFHxA in rats and mice in the range of hours, with two- to three-fold faster elimination half-lives in female rats compared to male rats. However, there was no appreciable gender-specific difference in the extent or rate of urinary elimination. The gender-specific difference in serum clearance in Sprague-Dawley rats remains to be established, especially in view of the conclusions drawn by (Russell et al., 2013) who stated that "the half-lives of PFHxA in mice, rats, monkeys and humans were proportional to body weight with no differences observed between genders, indicating similar volumes of distribution and similar elimination mechanisms among mammalian species."

Nilsson et al. (2010b) monitored blood samples of ski wax technicians using fluorinated ski wax containing PFHxA during ski season. Using these data, (Russell et al., 2013) estimated the mean serum elimination half-life at 32 d. However, a calculation of exact elimination half-lives from the monitoring data in this study is very uncertain. In the original study it is stated that "it is not possible to calculate an exact terminal half-life". The half-life of PFHxA in humans could therefore only be estimated as less than four weeks (32 days as geometric mean; (Russell et al., 2013).

In a recent reevaluation of the data from the ski technicians, a serum elimination half-life of 5.1 d was proposed, Buck and Gannon (2017) cited by Luz et al. (2019).

Reevaluation of the Nilsson-data by the German CA

Due to the discrepancy of half-lives calculated from data of the ski technicians the German CA reevaluated the data published by Nilsson et al. (2010b) and Nilsson et al. (2013b).

A toxicokinetic model was developed, calibrated and validated to predict internal dose (= blood concentrations), given some external dose (= exposure) for PFHxA in humans.

Ultimately, this model allows to correlate external exposure (e.g. a dose eqivalentl to the derived no-effect level (DNEL)) with the corresponding internal dose.

The approach focused on reports documenting the occupational exposure of ski technicians to fluorinated ski wax (Nilsson et al., 2010a; Nilsson et al., 2013a; Nilsson et al., 2010b). A non-linear mixed effects modelling approach was used and accounted – in contrast to previous studies (Russell et al., 2015) – for the information about observations below the limit of quantification and /or limit of detection. As the reports extended to other substances beyond PFHxA, also including the kinetically much better characterized PFOA, the validity of the approach was checked against the results of additional external kinetic studies.

Preparation of data and definition of exposure function

Three types of data were integrated: (1) Inhalation exposure, (2) Ski World Cup dates and (3) Blood kinetics over five years. With respect to (1), reported air concentrations in the breathing zone of individual ski technicians (Nilsson et al., 2010b) informed the definition of a Bayesian prior on the amounts of substance per ski season (AMT) to which the technicians were exposed. Combination of (1) with publically available data on (2), reported working time of the technicians and the alveolar inhalation rate for light work (Birnbaum et al., 1994) resulted in the definition of a time dependent *exposure function*. This exposure function had the form of a step function switching between constant exposure (during skiing seasons) and no exposure (rest of the year).

Development and calibration of the toxicokinetic models

Single compartment models were parameterized via first order elimination rate constant (k) and volume of distribution (V) for PFOA and PFHxA, respectively. Assuming total bioavailability for both substances, the exposure function directly dosed into the central compartment. Unknown parameters (AMT for each of 5 seasons, k and V) were estimated with the stochastic expectation maximisation algorithm implemented in Monolix (Lavielle, 2014).

The calibrated models for were positively assessed with respect to acceptable precision of the estimated parameters (relative standard errors < 150 %) and practical parameter identifiability indicated by low sensitivity of the parameter estimates on variation on the initial values for the optimisation problem.

Results for PFOA

Distinctive differences between reported 2007 and 2008 measurements of the air concentration of PFOA propagated to the corresponding AMT estimates. Consistently, the estimated AMT of the individual technicians to PFOA dropped over time (seasons 2006, 2007 and 2008 compared to 2009 and 2010 season at least one order of magnitude). The blood half-life based on the population estimate was 2.8 (2.2 – 3.6) years, with the 95 % confidence interval in brackets. This compares reasonably well to 3.5[28] (3.1 – 4.4) years reported in

[28] Geometric mean

previous kinetic studies (Olsen et al., 2007). The population estimate for V was 818 L, which is in line with reports of PFOA mainly distributing in body compartments different from.

Results for PFHxA

Compared to PFOA, no distinctive drop in AMT was estimated with on-going seasons. The half-life in blood was estimated to be 7.2 (4.2 – 27.5)[29] days, with a volume of distribution of 361 L. The inter-individual variability for the kinetic parameters V and k was low compared to observed variability in the exposure parameters AMT for 2008, 2009 and 2010 based on the measured air concentrations.

Prediction of internal dose

The model was used to calculate internal PFHxA exposure from external exposure values, e.g. for deriving an internal blood PFHxA concentration at derived external DNELs (see section B5.11). In order to do so, the following assumptions were made: body weight of 75 kg, light work alveolar ventilation rate of 20 L/min (Birnbaum et al., 1994) and total bioavailability of PFHxA.

Since precursor substances may be metabolized to PFOA and PFHxA during the course of the study, the corresponding half-life estimated based on decay in blood concentrations is an *apparent* half-life. This apparent half-life represents an overprediction of the underlying exposure-independent half-life. However, as inhalation exposure for the PFOA and PFHxA precursors were reportedly low (Nilsson et al., 2010a), the apparent half-life was expected to be a good approximation for realistic simulation scenarios.

Inference of the parameter correlation via stochastic approximation of the fisher information matrix revealed some negative correlation between k and V (correlation coefficient -0.52 for PFHxA). Accordingly, the individual estimates should be used with caution. Furthermore and per definition of a concentration, AMT and V show strong positive correlations (up to correlation coefficient 0.72 for PFOA). Thus, for a more precise estimation of V, more precise information on the exposure would be needed.

Unfortunately, the authors did not report the exact sampling time-points, but rather the month. While the analysis under the assumption of sampling at the start of each month already gave meaningful results on the time-scale of this 5 year study, even more precise estimates will be expected with full information on sampling time-points. A query to the authors is still pending.

Summary of elimination

In general, the reported half-lives for PFHxA in mammals are considerably lower when compared to PFOA. For PFOA, half-lives in mice, rat, pig and monkey are up to one order of magnitude higher compared to PFHxA, ranging from 0.08 days in female rat, 236 days in pig and several years in humans.

[29] PFHxA values were modeled as described in text. The values correspond roughly to the median and the 95 % confidence interval

On basis of the considerably lower half-life reported for PFHxA of 5.1 or 7.2 days in comparison to the half-lives of PFOA, it is concluded that PFHxA is less bioaccumulative.

B.5.2 Repeated dose toxicity

A **subacute toxicity study** was performed with rats (Harlan Sprague Dawley) using ten animals /sex /dose. Animals received PFHxA via gavage (0 /62.6 /125 /250 /500 and 1 000 mg/kg bw/d) over a study period of 28 days (NTP, 2018). The doses were split and administered twice per day. The mentioned doses are the total daily doses. The study was GLP compliant.

No mortality was observed. In the highest dose group, the mean body weight of males was significantly lower in comparison to the control group (13 %). In the females, the mean body weight was unaffected by PFHxA treatment.

Furthermore, a significant decrease of haematocrit, haemoglobin and red blood cell count was observed in all dose groups of males and from 250 mg/kg bw/d upwards in females. The decrease is below 10 % up to 250 mg/kg bw/d in males and females. In addition, the decrease of red blood cells was accompanied by an increase of reticulocytes from 500 mg/ kg bw/d in both sexes. The increase of reticulocytes in the 500 and 1 000 mg/kg bw/d groups were 152 % and 456 % in males and 189 % and 323 % in females, respectively. Additionally, the mean cell haemoglobin and the mean cell haemoglobin concentration were elevated in both sexes. At the highest dose group of both sexes, the increases of mean cell haemoglobin exceed the 10 % value. In the highest dose group of both sexes, the amount of platelets was increased. In males, the level of basophils was halved from 250 mg/kg bw/d upwards. In highest dose group of females, the amount of neutrophils was significantly higher in comparison to the control group.

Furthermore, there were elevations in the alanine aminotransferase (ALT) and aspartate aminotransferase (ASAT) in both sexes from 500 mg/kg bw/d upwards. In both sexes, the increase of ALT in the 500 and 1 000 mg/kg bw/d dose groups was 126 % and 164 % in males and 135 % and 144 % in females, respectively. In males, ASAT was increased by 116 % and 136 % at 500 and 1 000 mg/kg bw/d. In females, ASAT was increased by 111 % and 118 % in the mentioned dose groups. Alkaline phosphatase (ALP) was only elevated in the 500 and 1 000 mg/kg bw/d male group and exceeds 150 % in the highest dose group. A decrease was observed for the amount of globulin and total protein in males from 125 mg/kg bw/d upwards and in females at 1 000 mg/kg bw/d, respectively. Furthermore, in males from 250 mg/kg bw/d upwards and in females at 1 000 mg/kg bw/d, the albumin/ globulin ratio was significantly higher in comparison to the corresponding control groups. Beyond the mentioned treatment-related effects of PFHxA, the levels of some clinical biochemical parameters were decreased in the 1 000 mg/kg bw/d group of males (creatinine, albumin, sorbitol dehydrogenase). The levels of cholesterol were reduced in both sexes, in males from 62.6 mg/kg bw/d upwards and in females at 1 000 mg/kg bw/d, respectively. Additionally, the levels of total and indirect bilirubin were reduced in both sexes at 500 and 1 000 mg/kg bw/d in males and at 1 000 mg/kg bw/d in females. Furthermore, the mount of bile salt and acids was increased at the highest dose in both sexes.

A statistically elevated relative kidney weight was observed in males from 500 mg/kg bw/d upwards (11.8 and 18.8 %, respectively) and in the females of the highest dose group (11.5 %). Additionally, the relative liver weights were increased in males from 250 mg/kg bw/d upwards (14.3, 31.6, 63.6 %, respectively) and in females from 500 mg/kg bw/d upwards (15.2 and 47.5 %). The absolute liver weights were also elevated from 500 mg/kg bw/d upwards in both sexes. In males, there were increases of 27 and 42 % observed and in the females for 14.1 and 44.2 %, respectively. In the 1 000 mg/kg bw/d males, the weights of several organs were reduced (absolute heart weight and absolute thymus weight). Beyond that, the weights of several organs were increased in comparison to the control (relative lung weight, relative spleen weight, relative testis weight). In the highest dose group of females, the absolute kidney weights and the relative spleen weights were increased.

The aforementioned increase of liver weight was accompanied by histological changes. Cytoplasmic alterations and a hypertrophy of hepatocytes were observed in males of the 500 and 1 000 mg/kg bw/d dose group and in females of the 1 000 mg/kg bw/d dose group, respectively. As result of the mentioned effects on red blood cells, increased extramedullary haematopoiesis in the spleen was observed in both sexes from 500 mg/kg bw/d upwards. Besides, the olfactory epithelium was also affected by PFHxA treatment. In both sexes, degeneration (male rats 0/10, 0/10, 1/10, 6/10, 6/10 and 6/10; female rats 0/10, 1/10, 3/10, 9/10, 9/10 and 6/10) and hyperplasia of the olfactory epithelium (male rats 0/10, 0/10, 0/10, 6/10, 5/10 and 6/10; female rats 0/10, 0/10, 3/10, 4/10, 7/10 and 3/10) were observed. Furthermore, inflammation of the olfactory epithelium was observed (male rats 0/10, 0/10, 0/10, 0/10, 3/10 and 6/10; female rats 0/10, 0/10, 0/10, 1/10, 5/10 and 8/10).

Treatment-related changes associated with PFHxA treatment were also observed on the amount of thyroid hormones, namely T3 and T4, respectively. In males, total T3, total T4 and free T4 were significantly decreased in all dose groups. Even in the lowest dose group (62.6 mg/kg bw/d) the decrease of total T3, total T4 and free T4 was approximately 20 % lower in comparison to the control group. At the highest dose groups, free and total T4 were 73 % and 59 % lower than the control values. TSH levels were unaffected by PFHxA treatment. In accordance with the unaffected TSH level, the thyroid gland weight is unaffected. In females, the levels of thyroid hormones were unaffected by PFHxA treatment.

For comparison, PFOA is known to reduce the level of thyroid hormones, namely T3 and T4, in male monkeys and rats (Butenhoff et al., 2002; Martin et al., 2007). The mentioned substance also does not affect the TSH level. Therefore, it is assumed that the described influence on thyroid hormones is a common property of perfluorinated chemicals.

Significant reductions in T3 /T4 levels alone were considered as adverse effects even if no associated increase in TSH was observed (ECHA / EFSA, 2018; Ghassabian et al., 2014). The lack of increases in TSH expected as feedback response is considered as not contradictory as difficulties in the measurement in rats may occur (Kortenkamp et al., 2017). No further information is available on the underlying mode of action. T4 reduction of PFHxA was consistently observed in studies on PFOA.

Dose-related increased incidences of degenerated olfactory epithelium were observed in all dose groups. However, no information on the severity is available and the incidences at the low dose levels of 62.5 and 125 mg/kg bw/d were low (1/10). Thus the effects at these dose levels were considered as not robust enough to derive a N/LOAEL. Treatment-related

increased incidences were observed at doses from 250 mg/kg bw/d with incidences of 3/10 and 6/10 animals affected either for degeneration or hyperplasia (most likely of regenerative nature) of the olfactory epithelium.

Adverse effects were identified in the liver. Coincidentally, increased relative liver weights, increased incidence of cytoplasmic alterations and liver cell hypertrophy and increased activities of liver enzymes ASAT and ALP were observed with liver weight increase starting at 250 mg/kg bw/d as the most sensitive effect. At this dose, decreases in red blood cell parameters indicated adverse anemic effects.

Based on the significantly decreased levels of thyroid hormones (total T3, total T4 and free T4), a LOAEL of 62.6 mg/kg bw/d was derived.

A **subchronic toxicity study** was performed with male and female rats (Crl:CD(SD), at least 10 animals/sex/dose). Animals received PFHxA dissolved in deionised water via gavage (0, 10, 50, 200 mg PFHxA/kg bw/d) over a study period of three months (Chengelis et al., 2009c). The publication made no statement on guideline conformity.

No mortality was observed. There were no treatment-related clinical observations. Mean body weight of males was significantly lower in the 50 and 200 mg/kg bw/d group. Similar trends were obtained in 50 and 200 mg/kg bw/d group females, but these were not statistically significant. Slightly but significantly decreased red blood cell counts, hemoglobin and hematocrit (< 10 %) were noted in males and females of the 200 mg/kg bw/d group. These changes were reversible following the 28-day recovery period. Additionally, the mean reticulocytes in the 200 mg/kg bw/d group males were significantly increased. Furthermore, there were elevations in alanine transaminase (ALT), aspartate transaminase (AST) and alkaline phosphatase (ALP) in the 50 and 200 mg/kg bw/d male groups (although not statistically significant at 50 mg/kg bw/d) and statistically significant decreases in cholesterol in the 50 and 200 mg/kg bw/d males. Decreases also occurred in globulin in males and females in the 200 mg/kg bw/d group with lower total protein and higher albumin/globulin ratio in males only.

Statistically significantly increased relative kidney weights were observed in males at 10 ($p < 0.05$), 50 ($p < 0.05$) and 200 ($p < 0.01$) mg/kg bw/d and females in the 50 ($p < 0.01$) and 200 (without statistical significance) mg/kg bw/d group. Relative liver weight increased in males in the 200 mg/kg bw/d group. Liver samples of males of the 200 mg/kg bw/d group showed an increased peroxisomal beta oxidation activity using palmitoyl-CoA (coenzyme A) as substrate (only the 200 mg group was compared to controls).

Treatment-related histological changes associated with PFHxA administration were limited to the liver in high-dose males only. Minimal centrilobular hepatocellular hypertrophy was observed in seven of ten animals. One animal had moderate hepatocellular necrosis that was characterised by multifocal foci of coagulative necrosis with variable number of inflammatory cells within or around the necrosis.

Based on this subchronic study a LOAEL of 50 mg/kg bw/d could be derived based on lower body weight throughout the dosing period gain in male rats (NOAEL 10 mg/kg bw/d).

In a **combined subacute /reproductive /subchronic study** in rats (Crl:CD(SD)) the subchronic part of the study was in conformity to OECD TG 408. Animals (at least 10/sex/dose) were treated orally (0, 20, 100, 500 mg/kg bw/d) via gavage with sodium perfluorohexanoate (NaPFHxA, CAS-No. 2923-26-4) as the sodium salt of PFHxA for 90 days (Loveless et al., 2009a).

No clinical signs of toxicity or mortality related to the NaPFHxA administration were observed in the rats during the course of the study. Statistically significant decreases in mean body weight were observed in male rats in the 500 mg/kg bw/d group. Liver weights were increased in male rats dosed with 100 and 500 mg/kg bw/d. Mild to minimal degeneration /atrophy of olfactory epithelium was present in male and female rats at 100 and 500 mg/kg bw/d. In males 4/10 animals at 100 mg/kg bw/d and 7/10 animals at 500 mg/kg bw/d showed lesions. In females this was the case for 5/10 animals at 100 mg/kg bw/d and for 4/10 animals at 500 mg/kg bw/d.

Other adverse changes observed included hepatic peroxisomal β-oxidation and hepatic changes, generally at lowest observed adverse effect levels (LOAELs) of 100 mg/kg bw/d in males and 500 mg/kg bw/d in females.

Minimal hypertrophy of thyroid follicular epithelium was present in male and female rats in the 500 mg/kg bw/d group. The effects were reversible after 90 days of recovery but not following 30 days of recovery.

Based on nasal lesions in this study, the NOAEL was derived with 20 mg/kg bw/d.

In a **combined chronic toxicity/carcinogenicity study** in rats (Crl:CD(SD), male/female rats (at least 60 animals/sex/dose) were orally exposed via gavage (0, 2.5, 15, and 100 mg PFHxA/kg bw/d (males) and 5, 30, and 200 mg PFHxA/kg bw/d (females)) over a study period of 104 weeks (Klaunig et al., 2015a). Purity of the substance was 98.1 %. At the scheduled necropsy after 104 weeks of treatment, no statistically significant difference was seen in survival rates in male rats in any of the three groups compared to controls. Only in high-dose female rats a significant dose-related decrease in survival rates was seen.

No effect of PFHxA treatment on body weights or food consumption was seen in male and female rats.

Histopathological investigations of kidneys of females of the 200 mg/kg bw/d treatment group showed papillary necrosis (17/70 - 24 %) (0/60 in controls – 0 %) and tubular degeneration (7/70 – 10 %) (1/60 in controls – 1.7 %). Liver effects such as hepatocellular necrosis were seen in females at 30 mg/kg bw/d (3/60 – 5 %) and at 200 mg/kg bw/d (12/70 – 17 %). In male rats the liver showed 25 % congestion in the control group (15/60 animals) and 33 % in the treated group at 100 mg/kg bw/d (23/70). Congestions in the lung were observed in males (control 5/60 - 8.3 %, low-dose 9/60, medium-dose 9/60 - 15 % and high-dose 19/70 - 27 %). In females of the 200 mg/kg bw/d group 21/70 (30 %) alveolar macrophages in the lung were shown compared to 3/60 (5.0 %) in the control group. In females of the high-dose group erosions in the glandular stomach (16/70 - 23 % compared to 5/60 - 8.3 % in controls) were observed (Klaunig et al., 2015a).

In this 104 week study the NOAEL of 30 mg/kg bw/d was identified based on the papillary kidney necrosis in females at 200 mg/kg bw/d (LOAEL).

Summary and discussion of repeated dose toxicity

One oral subacute toxicity study, two oral subchronic toxicity studies and one oral chronic toxicity study of PFHxA in rats are available. All studies show treatment-related effects. The subacute study showed an influence of PFHxA on clinical chemistry such as altered level of AST, ASAT and ALP in both sexes. Additionally, altered organ weights were observed in males and females. The relative liver and kidney weights were decreased in both sexes. Furthermore, PFHxA had an effect on haematological parameters: haematocrit, reduced levels of red blood cells and haemoglobin exceeded the 10 % level at doses of at 250 mg/kg bw/d. Degeneration and hyperplasia of the olfactory epithelium was observed in both sexes in a dose-dependent manner, relevant increase in incidences were noted at 250 mg/kg bw/d and above. The most sensitive effect was a significant reduction of total T3, total T4 and free T4 at all dose groups of males justifying a LOAEL of 62.6 mg/kg bw/d.

The first subchronic study with PFHxA showed significantly lower mean body weights of males at 50 and 200 mg/kg bw/d group and similar trends in female rats at 50 and 200 mg/kg bw/d. Slight effects (< 10 % ranges) on haematological parameters were seen in 200 mg/kg bw/d-rats of both sexes. Furthermore, the liver enzymes ALT, AST and ALP were increased in 200 mg/kg bw/d in male rats, this was accompanied with minimal centrilobular hepatocellular hypertrophy in seven of ten animals. Kidney effects such as increased relative kidney weight at 50 mg/kg bw/d were not accompanied by other histopathological findings. Based on this subchronic study a LOAEL of 50 mg/kg bw/d could be derived based on lower body weight gain in male rats (NOAEL 10 mg/kg bw/d).

The second subchronic study was performed with sodium PFHxA and showed lower body weights in high-dose males in comparison to control values. Furthermore, liver weights (without any other abnormality) were increased in male rats at 100 and 500 mg/kg bw/d. The relevant adverse effect is the mild to minimal degeneration/atrophy of the olfactory epithelium in male and female rats at 100 and 500 mg/kg bw/d. The NOAEL was derived with 20 mg/kg bw/d.

After chronic gavage administration of PFHxA to Sprague Dawley rats a dose-dependent decrease in survival rate was observed in female animals only. In histopathological investigations the kidney and liver of female rats of the 200 mg/kg bw/d group showed degenerative/necrotic lesions. Thus, kidneys and livers represented the main targets for non neoplastic effects after chronic administration of PFHxA. Up to oral doses of 100 (males) and 200 (females) mg/kg bw/d over 104 weeks, no carcinogenic effects were observed. Thyroid hormone levels, shown to be sensitive effects in subacute studies, were not investigated in this chronic study. Histological examination of the thyroid was not performed. According the protocol cited by the authors (Fiette and Slaoui, 2011) the thyroid gland with the parathyroids should be weighed, but the results were not given in the publication.

B.5.3 Mutagenicity

A bacterial reverse mutation test was performed with NaPFHxA in either the presence or absence of S9 (Aroclor-induced rat liver S9) metabolic activation in the following tester strains: TA98, TA100, TA1535, TA1537 and WP2*uvr*A. A positive control and a vehicle control was investigated for each strain, the test was performed according to OECD TG 471. No toxicity, NaPFHxA precipitation or positive mutagenic responses were observed at any dose level or with any tester strain (Loveless et al., 2009a).

The ability of NaPFHxA to induce structural and numerical chromosome aberrations *in vitro* was evaluated using human peripheral blood lymphocytes from a healthy volunteer donor in the absence and presence of an exogenous metabolic activation system (arochlor-induced rat liver S9) according to OECD TG 473. Mitomycin C and cyclophosphamide were used as positive controls. Based on the results from preliminary experiments, the chromosome aberration assay was performed with cytogenetic evaluations conducted at 2 000, 3 000, and 3 860 µg/mL (10 mM) for the 4-h non-activated test condition and at 250, 500, and 1 000 µg/mL (2.59 mM) for the 4-h activated and 22-h non-activated test condition (Loveless et al., 2009a).

A reduction in the mitotic index of > 50 % in the NaPFHxA treated cells was observed. The percentage of cells with structural or numerical aberrations in the NaPFHxA-treated groups was not significantly increased above that of the vehicle control at any concentration. NaPFHxA was not found to induce structural or numerical chromosomal aberrations in human peripheral blood lymphocytes in either the non-activated or S9-activated test system (Loveless et al., 2009a).

DNA damage was measured using the comet assay in HepG2 cells. Positive and negative controls were investigated. Cells were exposed to concentrations of 100 or 400 µM PFHxA. PFHxA did not generate DNA damage (Eriksen et al., 2010).

A bacterial reverse mutation test was performed with PFHxA in either the presence or absence of S9 (phenobarbitone- and ß-naphtoflavone-induced rat liver S9) metabolic activation in the following tester strains: TA98, TA100, TA1535, TA1537 and TA1538. The test was performed according to OECD TG 471. PFHxA did not show any mutagenic responses (Buhrke et al., 2013).

The in vitro mammalian cell micronucleus test was performed with V79-cells according to OECD TG 487. Cells were incubated with PFHxA with and without metabolic activation (phenobarbitone- and ß-naphtoflavone-induced rat liver S9). Positive and negative controls were included. PFHxA did not show any clastogenic potential (Buhrke et al., 2013).

A bacterial reverse mutation test was performed with PFHxA in presence or absence of 10 % S9 metabolic activation in S. typhimurium TA98 and TA100 and E. coli WP2 uvrA pKM101. PFHxA did not show any mutagenic responses (NTP, 2018).

Furthermore, the mutagenic properties of PFHxA were analysed in an *in vivo* micronucleus assay in peripheral blood. The results were equivocal in male and negative in female rats (NTP, 2018).

Summary and discussion of mutagenicity

The dossier submitter concludes on PFHxA that the studies presented give no evidence for mutagenic properties of PFHxA.

B.5.4 Carcinogenicity

In a combined chronic toxicity /carcinogenicity study in rats (Crl:CD(SD), male /female at least 60 animals/sex/dose) were orally exposed via gavage to 0, 2.5, 15, and 100 mg PFHxA/kg bw/d (males) and 5, 30, and 200 mg PFHxA/kg bw/d (females) over a study period of 104 weeks (Klaunig et al., 2015a). The publication made no statement on guideline conformity.

At the scheduled necropsy after 104 weeks of treatment, no statistically significant difference was seen in survival rates in male rats in any of the three groups compared to controls. The survival rate of males, excluding the incidental deaths, at the end of week 104 in the control, 2.5, 15, and 100 mg/kg bw/d group was 31 %, 43 %, 43 % and 47 %. In contrast, in treated female rats, a significant dose-related decrease in survival rates was seen. In addition, there was a statistically significant decrease in pairwise comparisons between the control group and high-dose group. The survival rate of females, excluding the incidental deaths, at the end of week 104 in the control, 5, 30, and 200 mg/kg bw/d group was 36 %, 43 %, 33 % and 22 %.

No increase in neoplasms related to treatment of PFHxA at any of the three dosage levels examined after treatment for 104 weeks was seen in either male of female rats (Klaunig et al., 2015a).

Summary and discussion of carcinogenicity

Based on the information available there is no indication for carcinogenic properties of PFHxA. However, this conclusion is based on the publication of study results available in public literature. The original study report was not available for evaluation.

B.5.5 Toxicity for reproduction

Effects on fertility

A one-generation reproductive toxicity study was performed with NaPFHx (CAS-No. 2923-26-4) in Crl:CD(SD) rats (Loveless et al., 2009a). According to the authors, the study was in alignment with OECD TG 415. Nano pure water was used as vehicle and the substance was administered by oral gavage at dose levels of 0, 20, 100 and 500 mg/kg bw/d using a dose volume of 5.0 mL/kg. P1 female rats were dosed for about 70 days prior to cohabitation, through gestation and lactation for a total of about 126 days. P1 male rats were dosed for about 110 days. F1 rats were not dosed. Clinical observations, bodyweights, and food consumption were determined weekly throughout the study. Estrous cycle, sperm parameters, survival, and reproductive performance parameters were assessed. Litter examinations (number of live and dead, individual pup weights, clinical observations) were determined on day four pp, and weekly during lactation. F1 offsprings were given a gross

pathological examination at weaning. A subset of F1 generation rats was maintained for six weeks after weaning to assess developmental landmarks. The subset was given a gross pathological examination and selected reproductive organs were weighed.

No mortalities were observed in parental animals. Compared to controls, overall body weight gain was reduced by 12 and 29 % at 100 and 500 mg/kg bw/d, respectively. No substance-related effects were observed on mating, fertility, gestation length, number of implantation sites, estrous cyclicity, sperm parameters, litter size, sex ratio, pup clinical observations, pup survival, or F1 adult developmental landmarks at any dose tested. Substance-related effects on mean pup weights (17 - 18 % lower than control group) were observed during lactation at the highest dose tested. Overall bodyweight gain from test day 0 to 39 for F1 adults (postweaning) was comparable across dose levels for both sexes and no substance-related organ weight changes were observed at any dose in F1 adult males or females. No treatment-related gross pathology findings were observed at any dose in animals designated for the reproductive evaluation.

Developmental toxicity

An OECD TG 414 study investigated developmental toxicity of NaPFHx in Crl:CD(SD) rats (Loveless et al., 2009a). Nano pure water was used as vehicle and the substance was administered by oral gavage at dose levels of 0, 20, 100 and 500 mg/kg bw/d using a dose volume of 5.0 mL/kg. 22 animals per group were dosed once daily on days 6 – 20 of gestation. In-life observations were recorded and rats sacrificed on gestation day (GD) 21. All dams underwent a gross pathological examination and the fetuses were removed from the uteri by Cesarean section. Fetuses were weighed and sexed and examined for morphological alterations. All fetuses were examined for external and skeletal alterations, and approximately 50 % of the fetuses were examined for soft tissue and visceral head examinations.

There were no NaPFHxA-related deaths or gross postmortem findings in dams at any dose. Maternal toxicity occurred at 500 mg/kg bw/d and consisted of reductions in bodyweight parameters of total weight gain from GD 6 to 21 and overall net gain (corrected body weight gain minus products of conception on day 21), which were 19 % and 26 % lower compared to the control group, respectively at a 5 % reduction in food consumption. Developmental toxicity was limited to an approximately 10 % lower fetal weight at 500 mg/kg bw/d in comparison to controls.

Based on reduced body weight in maternal and offspring animals, a maternal and developmental NOAEL of 100 mg/kg bw/d was derived.

In a study according to ICH Harmonised Tripartite Guideline S5(R2), stages C through F, **Iwai and Hoberman (2014)** investigated the developmental toxicity of ammonium perfluorohexanoic acid in female mice (Crl:CD I(ICR). The guideline stages C to F integrate the following sequences of one life cycle:

C. Implantation to closure of the hard palate (adult female reproductive functions, embryonic development, major organ formation).
D. Closure of the hard palate to the end of pregnancy (adult female reproductive functions, fetal development and growth, organ development and growth).
E. Birth to weaning (adult female reproductive functions, neonate adaptation to extrauterine life, preweaning development and growth).

F. Weaning to sexual maturity (postweaning development and growth, adaptation to independent life, attainment of full sexual function).

Post-weaning observations on female and male pups were finalised on PPD 20 and 26, respectively. Thus, duration of the testing took approximately 104 days. The test substance had a purity of 93.4 %. In phase I of the study doses of 0, 100, 350 and 500 mg/kg bw/d were applied; the full study report has been published in Hoberman (2011a). In phase II of the study the doses were 0, 7, 35 and 175 mg/kg bw/d; the full study report has been published in (Hoberman, 2011b). Twenty time mated animals were used per group. The substance was dissolved in deionised water and applied orally via gavage (5 mL/kg bw). The animals were treated once daily from gestation day (GD) 6 to 18. Both parts of the study have been performed in compliance with GLP.

Parental animals were observed for viability and clinical findings and body weights were recorded throughout dosage and post-dosage periods. Animals were evaluated for adverse clinical signs observed during parturition, duration of gestation, litter sizes (all pups delivered) and pup viability at birth, fertility index, gestation index, number of offspring per litter (live and dead pups), number of implantation sites, general condition of dam and litter during the postpartum period, viability indices, and lactation index (percentage of pups born that survive 20 days). Maternal behaviour was evaluated on postnatal days (PND) 0, 4, 7, 14, and 20.

The pups in each litter were counted once daily; clinical observations, body weights, viability and eye opening were recorded during pre- and /or postweaning periods. Female mice were evaluated for vaginal patency (from PND 20) and male mice were evaluated preputial separation (from PND 26). On PND 20, all pups not selected for continued evaluation were killed by carbon dioxide asphyxiation and examined for gross lesions. Five pups per sex per group were killed on PND 41 for determination of body burden. In the following two tables results of both study phases are summarised.

Deaths of parental animals during lactation occurred in phase I only (3 controls, 6 at 100 mg/kg bw/d, one at 350 mg/kg bw/d and 500 mg/kg bw/d group (see Table 54).

At PND 0 there was no difference in body weights of control dams and any treatment group. Taken together with fact that the only clinical observations related to PFHxA were slight excess salivation in three of 20 mice at 350 mg/kg bw/d and slight to moderate excess salivation in six of 20 mice at 500 mg/kg bw/d, no maternal toxicity was observed during gestation and at PND 0 in any treatment group. Body weight gains from PNDs 0 – 20 were 97.7 %, 110.3 %, and 64.4 % of the control group values; however, these differences were not statistically significant (see Table 54).

Table 53: Developmental toxicity of PFHxA in mice according to (Hoberman, 2011b) (GD = day of gestation, PND = postnatal day).

	control	**7 mg/kg bw/d**	**35 mg/kg bw/d**	**175 mg/kg bw/d**
no of dams	20	20	20	20
pregnant dams	20	17	20	20
mortality	0	0	0	0
BW gain (GD 6-18) in g	25.1 ± 3.8	26.0 ± 4.6	23.7 ± 5.6	22.8 ± 4.8
BW gain (PND 0-20) in g	9.5 ± 3.3	9.4 ± 4.0	8.5 ± 2.8	10.9 ± 3.6
BW PND 0 in g	33.6 ± 2.2	34.3 ± 1.8	34.5 ± 2.1	33.2 ± 2.4
litters delivered	20	17	19	20
pups delivered	249	213	232	241
dams with stillborn pups	0	0	0	1
dams with no liveborn pups	0	0	0	0
dams with all pups dying days 0-3	0	1	0	0
stillborn N	0	0	0	**3 (1.2 %)****
stillborn in 23 control groups [a]	0 – 2.3 %			
no. of pups dead on day 0 N	0	0	0	**4 (1.7 %)****
pups dead on days 1-4 N	3 (1.2 %)	6 (2.8 %)	2 (0.9 %)	3 (1.3 %)
day 4 viability index	98.8 %	97.2 %	99.1 %	97.0 %
day 7 viability index	98.4 %	97.2 %	99.1 %	95.8 %
mortality in dams during lactation	0	0	0	0
pup weight day 0 in g [b]	1.6 ± 0.1	1.6 ± 0.1	1.6 ± 0.1	**1.4 ± 0.2 ***

Treatment occurred on days 6 through 18 of gestation

[a] Data from (Iwai et al., 2019)

[b] Data were statistically reevaluated based on individual animal data. The influence of litter size was considered in the evaluation.

* Significantly different from the vehicle control group ($p \leq 0.05$)

** Significantly different from the vehicle control group ($p \leq 0.01$)

Table 54: Developmental toxicity of PFHxA in mice according to Hoberman (2011a) (GD = day of gestation, PND = postnatal day).

	control	**100 mg/kg bw/d**	**350 mg/kg bw/d**	**500 mg/kg bw/d**
no of dams	20	20	20	20
pregnant dams	19	19	20	18
mortality	0	0	1	1
BW gain (GD 6-18) in g	26.7 ± 7.8	29.6 ± 3.6	26.2 ± 6.5	26.6 ± 7.6
BW gain (PND 0-20) in g	8.7 ± 2.7	8.5 ± 1.9	9.6 ± 4.8	5.6 ± 4.2
BW PND 0 in g	34.0 ± 1.8	34.9 ± 2.1	34.5 ± 3.0	35.3 ± 3.0
litters delivered	19	19	19	17
pups delivered	221	250	245	177
dams with stillborn pups	2	0	5	**7****
dams with no liveborn pups	0	0	0	1
dams with all pups dying days 0-3	1	0	2	**5****
stillborn N	4 (1.8 %)	0	5 (2.0 %)	**16 (9.0 %)****
Stilborn in 23 control groups [a]	0 – 2.3 %			
pups dead on day 0 N	0	0	3 (1.3 %)	**21 (14.0 %)****
pups dead on days 1-4 N, (%)	2 (0.9 %)	3 (1.2 %)	**25 (10.9 %)****	**20 (15.5 %)****
day 4 viability index	99.1 %	98.8 %	87.9 %	**72.7** %**
day 7 viability index	98.6 %	98.4 %	**86.6** %*	**72.7** %**
mortality in dams during lactation N	3	6	0	2
pup weight day 0 in g[b]	1.6 ± 0.2	1.5 ± 0.1	**1.4 ± 0.2****	**1.4 ± 0.2****

Treatment occurred on days 6 through 18 of gestation
[a] Data from (Iwai et al., 2019)
[b] Data were statistically reevaluated based on individual animal data by the dossier submitter. The influence of litter size was considered in the evaluation.
* Significantly different from the vehicle control group ($p \leq 0.05$)
** Significantly different from the vehicle control group ($p \leq 0.01$)

As shown in Table 54, pregnancy occurred in 19, 19, 20, and 18 of the 20 mated female mice in the 0 (vehicle), 100, 350, and 500 mg/kg bw/d dosage groups, respectively. The number of stillborn pups was significantly ($p \leq 0.01$) increased at 500 mg/kg bw/d (16/177). The number of pups dying on the day of delivery (PND 0) was (non-significantly) increased at 350 mg/kg bw/d (3/232) and significantly increased ($p \leq 0.01$) at 500 mg/kg bw/d (21/150). The

number of pups dying on PNDs 1 to 4 in the two highest dose groups was significantly increased ($p \leq 0.01$) compared to controls. Furthermore, viability indices were significantly reduced at the highest dose, PND 7 viability index also at 350 mg/kg bw/d. Statistically significantly reduced pup body weights were observed at doses ≥ 350 mg/kg bw/d tested ($p \leq 0.01$) compared to the control group (see Table 54). Compared to controls, percentage of pups per litter with open eyes was significantly reduced at 350 and 500 mg/kg bw/d on PND 14.

In phase II body weights and body weight gains of dams during the gestation and lactation periods were unaffected by dosages of the test substance as high as 175 mg/kg/d. Pregnancy occurred in all the 20 mated female mice in all dose groups including vehicle. The number of stillborn pups (3/241) and pups dying on day 0 postpartum (4/238) were significantly increased ($p \leq 0.01$). Furthermore, the average pup weight per litter was significantly reduced on day 0 postpartum at 175 mg/kg bw/d dosage group (1.4 ± 0.2) compared to controls (1.6 ± 0.1) (see Table 53). Comparing the results of both study phases for the pup weight at PND 0, a dose-related effect was observed (see Table 53 and Table 54).

The study authors considered 175 mg/kg bw/d as a maternally toxic dose without giving a justification to support this statement. In fact, the original publication does not indicate any sign of maternal toxicity at 175 mg/kg bw/d and so does not the study report of (Hoberman, 2011a).

Based on the outcome of this study a NOAEL of 100 mg/kg bw/d can be derived for developmental toxicity. The DS interpreted the outcome of the phase II study as to the significantly increased number of pups dying on PND 0 as a borderline effect. The incidence of 4/238 pups dying on PND 0 appears to just gain the significance level and was not robust enough to conclude on developmental toxicity. The observed decrease in pup survival at PND 0 was minimal (non-significant) at 350 mg/kg bw/d in the phase I study, but a clear and significant ($p \leq 0.01$) decrease in pup survival was seen at the 500 mg/kg bw/d dose. Comparing death rates in pups on PND 1-4 no significant increase was seen at 175 mg/kg bw/d (phase II), while the incidence was significantly elevated at 350 mg/kg bw/d (phase I).

Summary and discussion of reproductive toxicity

In an one generation reproductive toxicity study with NaPFHxA in rats no substance-related effects were observed on mating, fertility, gestation length, number of implantation sites, estrous cyclicity, sperm parameters, litter size, sex ratio, pup clinical observations, pup survival, or F1 adult developmental landmarks at any dose tested. Substance-related effects were observed during lactation at 500 mg/kg bw/d on mean pup weights (17-18 % decrease compared to controls).

In a guideline study on prenatal developmental toxicity of NaPFHxA in rats, there were no substance-related deaths or gross post-mortem findings in dams at any dose. Maternal and developmental toxicity occurred at 500 mg/kg bw/d and consisted of reductions in bodyweight.

In a non-guideline study on prenatal developmental toxicity of ammonium perfluorohexanoate in mice adverse effects on offspring occurred at 175 mg/kg bw/d and higher whereas no maternal toxicity was observed up to 500 mg/kg bw/d. The number of stillborn pups and pups dying on day 0 and from day 1-4 postpartum were significantly increased on day 0 postpartum

at 500 mg/kg bw/d. The significant increase of stillborn pups furthermore indicated an effect from exposure of the fetuses during maternal treatment due to placental transfer of the compound. Additionally, the pup weight was reduced dose-dependently from 1.6 g to 1.4 g; the first effect was noted at 175 mg/kg bw/d.

A developmental NOAEL of 100 mg/kg bw/d was derived.

In comparison to the developmental LOAEL of PFHxA of 175 mg/kg bw/d, the restriction dossier of PFOA reported LOAEL values of 1.0 (maternal) and 3.0 (foetal) mg/kg bw/d (ECHA, 2015a) for developmental toxicity. In conclusion, there are indications that PFHxA has a considerably lower potency when compared to PFOA under the experimental conditions of the tests conducted so and thus presumably a lower potential to affect fertility and development.

B.5.6 Derivation of DNEL(s)/DMEL(s)

Uncertainties

The key study for the derivation of DNELs was the NTP study (NTP, 2018). This study was a subacute toxicity study. The relevant effects were decreased levels of free and total T4 and total T3. It was not possible to derive a NOAEL. Therefore, the LOAEL value was used for DNEL derivation. The uncertainties due to both aspects (short study duration and LOAEL as point of departure) were reflected using additional assessment factors of 6 and 3. It should be noted that the assessment factor of 6 for the extrapolation from subacute to chronic reflects not only the short period of exposure in the subacute study but also the smaller numbers of animals per group in a subacute toxicity study compared to the number of animals per group in a chronic toxicity study. The resulting additional assessment factor of 18 adequately addresses the uncertainty following the use of this subacute toxicity study.

The NOAEL of 10 mg/kg bw/d (Chengelis et al., 2009c) is the lowest value; however, it was not used as PoD (point of departure) for DNEL-derivation. The body weights at 50 and 200 mg/kg bw/d in males were significantly lower in comparison to the control group, but at the highest dose the difference between treated and control animals is below 10 %. Therefore, the observed effect is assessed as insufficient to be used as PoD for DNEL-derivation.

Instead, the LOAEL of 62.6 mg/kg bw/d was chosen as PoD for DNEL-derivation. The reduction of thyroid hormones, namely free and total T4 and total T3, is assessed to be the most sensitive endpoint regarding PFHxA treatment.

All relevant NOAEL and LOAEL values were summarised in Table 14.

Table 55: Assessment factors (AF) and DNEL-derivation (long-term, systemic, oral, general population) based on reduced level of thyroid hormones in rats (NTP, 2018).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subacute to chronic	6	*
dose response	LOAEL as starting point	3	*
overall AF for general population		**1 800**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, oral

LOAEL for reduced level of thyroid hormones: 62.6 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{62.6\ \frac{mg}{kg}bw/d}{1800}$ = **0.03 mg/kg bw/d**

In order to derive an inhalation DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into NOAEC is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA, absorption via inhalation was assumed to be 100 %. The standard respiratory volume (sRV) of rat is 0.2 L/min corresponding to 0.8 L/min/kg bw. For general population, the exposure is set to 24 h, therefore the sRV is estimated to be 1.15 m³/kg bw.

NOAEC was calculated according to the following equations:

$$NOAEC = NOAEL\ oral \cdot \frac{1}{SV\ rat} .* \frac{Abs\ oral\ rat}{Abs\ inh\ human}$$

$$NOAEC = \frac{62.6\ \frac{mg}{kg}bw}{d} \cdot \frac{1}{1.15} \cdot 0.9$$

NOAEC=49 mg/m³

Table 56: Assessment factors (AF) and DNEL-derivation (long-term, systemic, inhalation, general population) based on reduced level of thyroid hormones in rats(NTP, 2018).

		Assessement factors	**Comments**
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subacute to chronic	6	*
dose response	LOAEL as starting point	3	*
overall AF for general population		**450**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, inhalation

NOAEC for reduced level of thyroid hormones: 48.99 mg/m³

$DNEL_{general\ population}$: $\frac{49\ mg/m^3}{450}$ = **0.11 mg/m³**

In order to derive a dermal DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into a dermal NOAEL is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated as 90 %. According the physicochemical properties of PFHxA and the rule of de Heer, the dermal absorption was assumed as 100 %. De Heer et al. defined criteria to discriminate between chemicals with high and low dermal absorption assuming that there is an optimum in log P_{OW} and a maximum in molecular weight for facilitating percutaneous absorption. If the molecular weight is higher than 500 Da and the log P_{OW} is smaller than -1 or higher than 4, the dermal absorption would be estimated with 10 %. If the molecular weight and the log P_{OW} are different, 100 % dermal absorption would be assumed (de Heer, 1999). The assumption of 100 % dermal absorption is a conservative approach, because PFHxA contains an acid group which may counteract the dermal absorption.

$NOAEL_{dermal}$ was calculated according to the following equations:

$$NOAEL_{dermal} = NOAEL\ oral \cdot \frac{Abs\ oral\ rat}{Abs\ dermal\ human}$$

$$NOAEL_{dermal} = \frac{62.6 \frac{mg}{kg} bw}{d} \cdot 0.9$$

$NOAEL_{dermal}$ = 56.34 mg/kg bw/d

Table 57: Assessment factors (AF) and DNEL –derivation (long-term, systemic, dermal, general population) based on reduced level of thyroid hormones in rats(NTP, 2018).

		Assessment factors	**Comments**
interspecies difference	Rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subacute to chronic	6	*
dose response	LOAEL as starting point	3	*
overall AF for general population		**1 800**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, dermal

NOAEL for reduced level of thyroid hormones: 56.34 mg/kg bw/d

DNEL $_{\text{general population}}$: $\frac{56.34 \frac{\text{mg}}{\text{kg}} \text{bw/d}}{1800}$ = **0.031 mg/kg bw/d**

Table 58: Assessment factors (AF) and calculation of DNEL (long-term, systemic, oral, general population) based on lower body weight in comparison to the control group (Chengelis et al., 2009c).

		Assessment factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subchronic to chronic	3	*
overall AF for general population		**300**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, oral

NOAEL for lower body weight in comparison to the control group: 10 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{10\frac{mg}{kg}bw/d}{300}$ = **0.03 mg/kg bw/d**

In order to derive the inhalation DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into a NOAEC is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated to be 90 %. According to the physicochemical properties of PFHxA, the absorption via inhalation was assumed to be 100 %. The sRV of rat is 0.2 L/min corresponding to 0.8 L/min/kg bw. For general population, the exposure is set to 24 h, therefore the sRV is estimated to be 1.15 m³/kg bw.

NOAEC was calculated according to the following equations:

$$NOAEC = NOAEL\ oral \cdot \frac{1}{SV\ rat} \cdot \frac{Abs\ oral\ rat}{Abs\ inh\ human}$$

$$NOAEC = \frac{10\frac{mg}{kg}bw}{d} \cdot \frac{1}{1.15\frac{m^3}{kg}bw} \cdot 0.9$$

NOAEC = 7.83 mg/m³

Table 59: Assessment factors (AF) and DNEL-derivation (long-term, systemic, inhalation, general population) based on lower body weight in comparison to the control group (Chengelis et al., 2009c).

		Assessment Factors	**Comments**
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subchronic to chronic	3	*
overall AF for general population		**75**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, inhalation

NOAEC for lower body weight in comparison to the control group: 7.83 mg/m³

$DNEL_{general\ population}$: $\frac{7.83\ mg/m^3}{75}$ = **0.10 mg/m³**

In order to derive a dermal DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into dermal NOAEL is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA and the rule of de Heer et al., the dermal absorption was 100 %.

$NOAEL_{dermal}$ was calculated according to the following equations:

$$NOAEL_{dermal} = NOAEL\ oral \cdot \frac{Abs\ oral\ rat}{Abs\ inh\ human}$$

$$NOAEL_{dermal} = \frac{10\frac{mg}{kg}bw}{d} \cdot 0.9$$

$$NOAEL_{dermal} = 9\frac{mg}{kg}bw/d$$

Table 60: Assessment factors (AF) and DNEL-derivation (long-term, systemic, dermal, general population) based on lower body weight in comparison to the control group (Chengelis et al., 2009c).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subchronic to chronic	3	*
overall AF for general population		**300**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, dermal

$NOAEL_{dermal}$ for lower body weight in comparison to the control group: 9 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{9\frac{mg}{kg}bw/d}{300}$ = **0.03 mg/kg bw/d**

Table 61: Assessment factors (AF) and DNEL-derivation (long-term, systemic, oral, general population) based on nasal lesions (Loveless et al., 2009b).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subchronic to chronic	3	*
overall AF for general population		**300**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, oral

NOAEL for nasal lesions: 20 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{20\frac{mg}{kg}bw/d}{300}$ = **0.067 mg/kg bw/d**

In order to derive the inhalation DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into a NOAEC is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated to be 90 %. According to the physicochemical properties of PFHxA, the inhalation absorption was 100 %. The sRV of rat is 0.2 L/min corresponding with 0.8 L/min/kg bw. For general population, the exposure is set to 24 h, therefore the sRV is estimated with 1.15 m³/kg bw.

NOAEC was calculated according to the following equations:

$$NOAEC = NOAEL\ oral * \frac{1}{SV\ rat} \cdot \frac{Abs\ oral\ rat}{Abs\ inh\ human}$$

$$\text{NOAEC} = \frac{20\,\frac{\text{mg}}{\text{kg}}\,\text{bw}}{\text{d}} \cdot \frac{1}{1.15\,\frac{\text{m}^3}{\text{kg}}\,\text{bw}} \cdot 0.9$$

NOAEC=15.65 mg/m³

Table 62: Assessment factors (AF) and DNEL-derivation (long-term, systemic, inhalation, general population) based on nasal lesions (Loveless et al., 2009b).

		Assessment Factors	**Comments**
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subchronic to chronic	3	*
overall AF for general population		**75**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, inhalation

NOAEC for nasal lesions: 15.65 mg/m³

$\text{DNEL}_{\text{general population}}$: $\frac{15.65\frac{\text{mg}}{\text{m}^3}}{75}$ = **0.21 mg/m³**

In order to derive the dermal DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into dermal NOAEL is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA and the rule of de Heer et al., the dermal absorption was 100 %.

$\text{NOAEL}_{\text{dermal}}$ was calculated according to the following equations:

$$\text{NOAEL}_{\text{dermal}} = \text{NOAEL}_{\text{oral}} \cdot \frac{\text{Abs oral rat}}{\text{Abs dermal human}}$$

$$\text{NOAEL}_{\text{dermal}} = \frac{20\,\frac{\text{mg}}{\text{kg}}\,\text{bw}}{\text{d}} \cdot 0.9$$

$$\text{NOAEL}_{\text{dermal}} = 18\,\frac{\text{mg}}{\text{kg}}\,\text{bw/d}$$

Table 63: Assessment factors (AF) and DNEL-derivation (long-term, systemic, dermal, general population) based on nasal lesions (Loveless et al., 2009b).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
duration	subchronic to chronic	3	*
overall AF for general population		**300**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, dermal

NOAEL for nasal lesions: 18 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{18 \frac{mg}{kg} bw/d}{300}$ = **0.06 mg/kg bw/d**

Table 64: Assessment factors (AF) and DNEL-derivation (long-term, systemic, oral, general population) based on kidney necrosis (Klaunig et al., 2015b).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**100**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, oral

NOAEL for kidney necrosis: 30 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{30\frac{mg}{kg}bw/d}{100}$ = **0.3 mg/kg bw/d**

In order to derive the DNEL or long-term systemic effects on general population after inhalation, the conversion of the oral NOAEL into NOAEC is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA, the inhalation absorption was 100 %. The sRV of rat is 0.2 L/min corresponding with 0.8 L/min/kg bw. For general population, the exposure is set to 24 h, therefore the sRV is estimated with 1.15 m³/kg bw.

NOAEC was calculated according to the following equations:

$$NOAEC = NOAEL_{oral} \cdot \frac{1}{SV\ rat} \cdot \frac{Abs\ oral\ rat}{Abs\ inh\ human}$$

$$NOAEC = \frac{30\frac{mg}{kg}bw}{d} \cdot \frac{1}{1.15\frac{m^3}{kg}bw} \cdot 0.9$$

NOAEC=23.48 mg/m³

Table 65: Assessment factors (AF) and DNEL-derivation (long-term, systemic, inhalation, general population) on kidney necrosis (Klaunig et al., 2015b).

		Assessment Factors	**Comments**
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**25**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL –derivation for general population, long-term, systemic effects, inhalation

NOAEC for kidney necrosis: 23.48 mg/m³

$DNEL_{general\ population}$: $\frac{23.48\ \frac{mg}{m^3}}{25}$ = **0.94 mg/m³**

In order to derive the dermal DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into dermal NOAEL is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA and the rule of de Heer et al., the dermal absorption was 100 %.

$NOAEL_{dermal}$ was calculated according to the following equations:

$$NOAEL_{dermal} = NOAEL_{oral} \cdot \frac{\text{Abs oral rat}}{\text{Abs dermal human}}$$

$$NOAEL_{dermal} = \frac{30\ \frac{mg}{kg}\ bw}{d} \cdot 0.9$$

$$NOAEL_{dermal} = 27\ \frac{mg}{kg}\ bw/d$$

Table 66: Assessment factors (AF) and DNEL-derivation (long-term, systemic, dermal, general population) based on kidney necrosis (Klaunig et al., 2015b).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**100**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL –derivation for general population, long-term, systemic effects, dermal

$NOAEL_{dermal}$ for kidney necrosis: 27 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{27\ \frac{mg}{kg}bw/d}{100}$ = **0.27 mg/kg bw/d**

Table 67: Assessment factors (AF) and DNEL-derivation (long-term, systemic, oral, general population) based on lower fetal body weight gain in comparison to the control group (Loveless et al., 2009b).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**100**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL –derivation for general population, long-term, systemic effects, oral

NOAEL for lower fetal body weight gain in comparison to the control group: 100 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{100\frac{mg}{kg}bw/d}{100}$ = **1 mg/kg bw/d**

In order to derive the inhalation DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into NOAEC is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA, the inhalation absorption was 100 %. The sRV of rat is 0.2 L/min corresponding with 0.8 L/min/kg bw. For general population, the exposure is set to 24 h, therefore the sRV is estimated with 1.15 m³/kg bw.

NOAEC was calculated according to the following equations:

$$NOAEC = NOAEL_{oral} \cdot \frac{1}{SV\ rat} \cdot \frac{Abs\ oral\ rat}{Abs\ inh\ human}$$

$$NOAEC = \frac{100\,\frac{mg}{kg}\,bw}{d} \cdot \frac{1}{\frac{1.15\ m^3}{kg}\,bw} \cdot 0.9$$

$NOAEC = 78.26\ mg/m^3$

Table 68: Assessment factors (AF) and DNEL-derivation (long-term, systemic, inhalation, general population) based on lower fetal body weight gain in comparison to the control group (Loveless et al., 2009b).

		Assessment Factors	**Comments**
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**25**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL-derivation for general population, long-term, systemic effects, inhalation

NOAEC for lower fetal body weight gain in comparison to the control group: 78.26 mg/m³

DNEL $_{general\ population}$: $\frac{78.26\ \frac{mg}{m^3}}{25}$ = **3.13 mg/m³**

In order to derive the dermal DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into dermal NOAEL is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA and the rule of de Heer et al., the dermal absorption was 100 %.

$NOAEL_{dermal}$ was calculated according to the following equations:

$$NOAEL_{dermal} = NOAEL_{oral} \cdot \frac{\text{Abs oral rat}}{\text{Abs dermal human}}$$

$$NOAEL_{dermal} = \frac{100\,\frac{mg}{kg}\,bw}{d} \cdot 0.9$$

$$NOAEL_{dermal} = 90\,\frac{mg}{kg}\,bw/d$$

Table 69: Assessment factors (AF) and DNEL-derivation (long-term, systemic, dermal, general population) on lower fetal body weight gain in comparison to the control group (Loveless et al., 2009b).

		Assessment Factors	**Comments**
interspecies difference	rat	4	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**100**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL–derivation for general population, long-term, systemic effects, dermal

$NOAEL_{dermal}$ for lower fetal body weight gain in comparison to the control group:
90 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{90\ \frac{mg}{kg}bw/d}{100}$ = **0.9 mg/kg bw/d**

Table 70: Assessment factors (AF) and calculation of DNEL (long-term, systemic, oral, general population) on lower absolute fetal body weight in comparison to the control group (Hoberman, 2011b).

		AF	**Comments**
interspecies difference	mouse	7	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**175**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL –derivation for general population, long-term, systemic effects, oral

NOAEL for lower absolute fetal body weight in comparison to the control group: 100 mg/kg bw/d

$DNEL_{general\ population}: \frac{100\frac{mg}{kg}bw/d}{175}$ = **0.57 mg/kg bw/d**

In order to derive the inhalation DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into NOAEC is necessary. Based on toxicokinetic data, the oral absorption of mouse was estimated with 90 %. According to the physicochemical properties of PFHxA, the inhalation absorption was 100 %. The sRV of mouse is 0.02 L/min/mouse corresponding with 0.52 L/min/kg bw. For general population, the exposure is set to 24 h, therefore the sRV is estimated with 0.749 m³/kg bw (US EPA, 1988).

NOAEC was calculated according to the following equations:

$$NOAEC = NOAEL_{oral} \cdot \frac{1}{SV\ mouse} \cdot \frac{Abs\ oral\ mouse}{Abs\ inh\ human}$$

$$NOAEC = \frac{100\frac{mg}{kg}bw}{d} \cdot \frac{1}{0.749\frac{m^3}{kg}bw} \cdot 0.9$$

$NOAEC = 120\ mg/m^3$

Table 71: Assessment factors (AF) and DNEL-derivation (long-term, systemic, inhalation, general population) on lower absolute fetal body weight in comparison to the control group (Hoberman, 2011b).

		Assessment Factors	**Comments**
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**25**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL –derivation for general population, long-term, systemic effects, inhalation

NOAEC for lower absolute fetal body weight in comparison to the control group: 0.120 mg/m³

$DNEL_{general\ population}$: $\frac{120\frac{mg}{m^3}}{25}$ = **4.80 mg/m³**

To be able to derive the dermal DNEL for long-term systemic effects in the general population, the conversion of the oral NOAEL into dermal NOAEL is necessary. Based on toxicokinetic data, the oral absorption of rats was estimated with 90 %. According to the physicochemical properties of PFHxA and the rule of de Heer et al., the dermal absorption was 100 %.

$NOAEL_{dermal}$ was calculated according to the following equations:

$$NOAEL_{dermal} = NOAEL_{oral} \cdot \frac{\text{Abs oral mouse}}{\text{Abs dermal human}}$$

$$NOAEL_{dermal} = \frac{100\,\frac{mg}{kg}\,bw}{d} \cdot 0.9$$

$NOAEL_{dermal}$ = 90 mg/kg bw/d

Table 72: Assessment factors (AF) and DNEL-derivation (long-term, systemic, dermal, general population) on lower absolute fetal body weight in comparison to the control group (Hoberman, 2011b).

		Assessment Factors	Comments
interspecies difference	mouse	7	*
remaining differences on toxicodynamics		2.5	*
intraspecies difference	general population	10	*
overall AF for general population		**175**	

* Default values for systemic effects obtained from ECHA guidance on chemical safety assessment, Chapter R.8, table R.8-3 and table R.8-6

DNEL –derivation for general population, long-term, systemic effects, dermal

$NOAEL_{dermal}$ for lower absolute fetal body weight in comparison to the control group: 90 mg/kg bw/d

$DNEL_{general\ population}$: $\frac{90\frac{mg}{kg}bw/d}{175}$ = **0.51 mg/kg bw/d**

All DNEL values for general population were summarised in Table 15.

The external total DNEL was calculated with 3.17 mg/d (based on effects on thyroid hormones T3 and T4).

The total DNEL was estimated as follows:

$$DNEL_{total} = 2 \cdot 0.03 \left[\frac{\frac{mg}{kg}bw}{d}\right] \cdot 1e^{3} \left[\frac{ng}{mg}\right] \cdot 75 \text{ [kg bw]} + 0.11 \left[\frac{mg}{m^3}\right] \cdot 1e^{3} \left[\frac{ng}{mg}\right] \cdot 20 \left[\frac{L}{min}\right] \cdot 1440 \left[\frac{min}{d}\right]$$

The overall external DNEL of 3.17 mg/d DNEL corresponds to a blood level of 91.7 ng/mL.

The steady state blood concentration (C_{ss}) was calculated as followed:

$$C_{SS} = \frac{AMT}{V \cdot k \cdot \tau}$$

$$C_{SS} = \frac{3172200 \text{ [ng]}}{3.61 \cdot e^{0.5}\text{[mL]} \cdot 0.0958 \left[\frac{1}{d}\right] \cdot 1 \text{ [d]}}$$

The PK modell proposed a volume of distribution at 361 L.

Appendix E.1: Available methods for extracting and analysing PFHxA, its salts and related substances

Table 73: Overview of methods for extracting and analysing PFHxA, its salts and related substances as well in environmental comprtments as in products and articles.

Source	Substances to be determinated	Matrix to be investigated	LOD		LOQ		Scope	Method applicable to:	Extraction method	Extraction Solvents	Derivati-sation (substance or method)	derivat actually is measured	Detection method	Remarks	uncertainties
			ppb	ng/L (kg)	ppb	ng/L (kg)									
**Water quality — Determination of perfluoro-octanesulfonate (PFOS) and perfluorooctanoate (PFOA) — Method for unfiltered samples using solid phase extraction and liquid chromatography/ mass spectrometry, ISO 25101:2009E*	**linear isomer of PFOS-anion**	**drinking water, ground water, surface water**	0.002	2			deter-mination of linear isomers of PFOS and PFOA	non-linear isomers of PFOS-and PFOA anions, other per-fluorinated acids **including PFHxA** (linear- and nonlinear isomers)	solid-phase extraction followed by solvent elution	ammonia / methanol solution			liquid chromato-graphy with tandem mass-spectrometric detection	focus on PFAs	only perfluo-rinated acids are captured, no primary detection of related substances with perfluorinated side chains
	linear isomers of PFOA-anion		0.01	10											
**German standard methods for the examination of water, waste water and sludge - Jointly determinable substances (group F) - Part 42: Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42), DIN 38407-42:2011*	**perfluorinated carboxylic and sulfonic anions (linear and branched isomers)**	**drinking water, ground water, surface water**	0.001	1			deter-mination of linear and branched isomers of per-fluorinated alkylic and sulfonic acids in water		solid-phase extraction of sampled water without adding further chemicals followed by solvent elution	ammonia / methanol solution			liquid chromato-graphy with tandem mass-spectrometric detection	amendmet of ISO 25101 to detect further perfluorinated substances and branched isomers	

**Determination of perfluoroalkyl compounds in water, sediment, and biota, ICES, Ahrens et al. 2010*	**anions from perfluorinated acids 3 - 18 C-atoms (including C6), anions from sulfonic acids anions from 4 - 10 C-atoms (including C6), several perfluorinated telomer substances (including C6)**	**water, sediment, and biota**			de-pending on the matrix and the ana-lytical methods		monitoring of aquatic and marine environ-ment		solid-phase extraction followed by solvent elution, several alternatives are provided for different com-partments respectively	several alternatives provided			liquid chromato-graphy coupled with a tandem mass spectrometer and interfaced with an electrospray ionization source in negative-ion mode (LC/(−)ESI-MS/MS	several methods provided, the most efficient method should be selected depending on the compartment to be investigated and the LOQ is sufficient	the suitable method has to be chosen for the results which are expected
SOP for Extraction of Residuals from Fluoropolymer Products, Chemours,	**residuals from fluoropolymer products**	**fluoro-polymer cubes and granular, fine powder and micropowder fluoro-polymers**					extraction and quanti-fication of residual com-pounds in <u>two polymer matrices</u>	perfluor-inated acids (linear- and nonlinear isomers), **including PFHxA** - see ISO 25101!	method described in ISO 25101	0.4 % potassium hydroxide / methanol solution, Vertrel XF®			method described in ISO 25101		which residues are meant? The perfluorinated acids itself or substances related to the acids of different chain length, like perfluorinated telomer substances?
Method for the Quantitative Determination of PFOA in Fluorotelomer- Based Intermediates and Products, Chemours,	**C8-fluorotelomer-based intermediates and products**	**perfluor-inated inter-mediates in different production steps**			50	50 000	quanti-tative deter-mination of potential PFOA precursor sub-stances in fluorotelo-mer-based inter-mediates and products	fluorotelo-mer-based inter-mediates and products with different chain length, **including perfluor-inated C6-telomer substances**		acetonitrile, Vertrel XF®			gas chromato-graphic separation followed by detection via a dual mass spectrometer operating in the TRM mode (GC/MS/MS)		very high LOQ, reliable results in final products not proven, yet; extraction method is not further described

Method for the Quantitative Determination of PFOA in Fluorotelomer-Based Intermediates and Products, Chemours,	**PFOA-anion**	**finished products and inter-mediates**	0.5	500	12.5	12 500	deter-mining con-centration of residual PFOA in finished products and inter-mediates	Perfluor-inated acids of different chain length, **including PFHxA**			methanolic sulfuric acid	methyl ester of the perfluor-inated acids	gas chromato-graphic separation followed by detection via a dual mass spectrometer (GC/MS/MS)		method was developed to determine perfluorinated acids
Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams, Dauchy et al. 2017	**anions from perfluorinated acids 3 - 18 C-atoms (including C6), anions from sulfonic acids anions from 4 - 10 C-atoms (including C6), several perfluorinated telomer substances (including C6)**	**fire fighting foams**			0.004 - 0.025 (water samples)	4 - 25 (water samples)	quanti-tatively deter-mining of specific PFAS sub-stances in fire fighting foams and in environ-mental com-partments	potentially to all perfluor-inated (side chain) substances	solid-phase extraction followed by subsequent solvent elution based on (Boiteux et al., 2017); oxidative conversion method according to (Houtz and Sedlak, 2012)	methanol, methanol-ammonium hydroxide, NH_4OH-isopropanol/ dichloro-methane	derivatisation with hydroxyl radicals, generated by thermolysis of persulfate under alkaline pH conditions (oxidative conversion method)	related PFCAs of the perfluori-nated chain length	high performance liquid chromato-graphy coupled to a mass spectrometer interfaced with an electrospray ionization source in a negative-ion mode, liquid chromatograph coupled with a quadrupole ion trap mass spectrometer according (Boiteux et al., 2017)		artefacts like from polymer degradation by the oxidative conversion method are likely

Chemical Analysis of Selected Fire-fighting Foams on the Swedish Market 2014, Kemi 2015	**perfluorinated alkyl acids and sulfonates (PFCAs, PFSAs), fluorotelomer-sulfonates (FTS), sulfonamides including perfluoro-octane sulfonamides (PFOSA, N-ethylFOSA, NmethylFOSA) and perfluoro-octane-sulfonamido-ethanols (FOSEs), unsaturated and saturated telomer acids (FTUCAs and FTCAs)**	**fire fighting foam concentrares**			0.002 (sedi-ment samples)	2 (sedi-ment samples)	detection of perfluori-nated sub-stances in fire-fighting foams	all liquid or soluble matrices	dilution in a polar solvent and filtration via GHP filters	methanol and MilliQ water	no derivatisation		liquid chromato-graphy coupled with a mass spectrometer; gas chromato-graphy coupled with a mass spectrometer		only capturing of easy extractable perfluorinated substances
Oxidative conversion as a mean of detecting precursors to perfluoroalkyl acids in urban runoff, Houtz, E. F., & Sedlak, D. L. 2012	**substances with C8 perfluorinated side chains, including sulfonamides**	**water**			0.025	25	quanti-fication of PFCA precursors in sum	other substances with perfluori-nated side chains of different chain length, including C6	solid-phase extraction followed by solvent elution	0.1 % NH_4OH in methanol	thermolysis of persulfate ($S_2O_8^{2-}$) to generate OH-radikals, oxidation of precursors to respective perfluorinated acid with these OH-radikals	Perfluori-nated carboxylic and sulfonic acid	analysis before and after oxidation step with liqud chro-matography coupled with mass spectrometry	TOP-assay, detection of sumarised precursors related to respective perfluorinated carboxylic and sulfonic acids	special precursor substances are unknown
Further methods are available – see confidential annex															

** Methods accepted and recommended by international organisations*