# ANNEX XV RESTRICTION REPORT

## PROPOSAL FOR A RESTRICTION

**SUBSTANCE NAME(S): $C_9$-$C_{14}$ PFCAs -including their salts and precursors-**

**IUPAC NAME(S): n.a.**

**EC NUMBER(S): n.a.**

**CAS NUMBER(S): n.a.**

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# Abbreviations

| APFN | Ammoniumperfluorononanoate |
|------|----------------------------|
| C9-C14 PFCAs | Perfluorocarboxylic acids containing 9 to 14 carbon atoms in the chain |
| C8-chemistry | Eight carbon atoms in the chain (primarily PFOA and PFOA-related substances) |
| Cn-PFCA | Perfluoro carboxylic acids with n numbers of carbons in the molecular chain |
| C9-PFCA | Perfluorononanoic acid (PFNA) [1] |
| C10-PFCA | Perfluorodecanoic acid (PFDA) [1] |
| C11-PFCA | Perfluoroundecanoic acid (PFUnDA) [1] |
| C12-PFCA | Perfluorododecanoic acid (PFDoDA) [1] |
| C13-PFCA | Perfluorotridecanoic acid (PFTrDA) [1] |
| C14-PFCA | Perfluorotetradecanoic acid (PFTeDA) [1] |
| diPAP | Polyfluoroalkyl phosphoric acid diesters |
| DWR | Durable water repellent |
| FTCA | Fluorotelomer carboxylic acid |
| FTI | Fluorotelomer iodide |
| FT(M)A | Fluorotelomer (meth)acrylates |
| FTO | Fluorotelomer olefin |
| FTOH | Fluorotelomer alcohol |
| FTS | Fluorotelomer sulfonate |
| FTTAoS | Fluorotelomer thioether amido sulfonate |
| FTU | Fluorotelomer urethane |
| FTUCA | Fluorotelomer unsaturated carboxylic acid |
| LOD | Limit of detection |
| Long-chain PFCAs | PFCAs containing 7 or more fully fluorinated carbon atoms |
| monoPAP | Polyfluoroalkyl phosphoric acid monoesters |
| PBT | Persistent Bioakkumulative and Toxic Substances |
| PFPiA | Perfluoroalkyl phosphinic acid |
| PFAA | Perfluoroalkyl acids |

[1] Linear and branched

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| PFAS | Per- and polyfluoroalkyl substances |
|---|---|
| PFCA | Perfluorinated carboxylic acids |
| PFOA | Perfluorooctanoic acid |
| PFOS | Perfluorooctane sulfonic acid |
| PFSA | Perfluorinated sulfonic acids |
| POP | Persistent organic pollutant |
| Related substance (to PFCAs) | Substances that may degrade to PFCAs (e.g. flurotelomerer and side-chain fluorinated polymers)… |
| Short-chain PFCAs | PFCAs containing less than 7 fully fluorinated carbon atoms |
| SVHC | Substances of very high concern |
| vPvB | Very persistentm very bioaccumulative |
| WWTP | Waste water treatment plant |
|  |  |

# Preface

Per- and polyfluoroalkyl substances (PFASs) are emerging pollutants of the 21$^{st}$ century. These man-made chemicals have been produced since the 1950s. Due to their outstanding properties – they provide water, oil, and grease repellency and are very stable – certain PFASs have been used in a variety of consumer products. The chemicals occur in all environmental media as well as in humans. In total, the group of produced and used PFASs consists of more than 3000 compounds. They are characterized by a fully (per-) or partly (poly-) fluorinated carbon chain in connection with different functional groups. PFASs are divided into two main groups depending on the length of the perfluorinated carbon chain: long-chain PFASs and short-chain PFASs.

From the group of long-chain PFASs: Perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are already regulated. PFOS has been identified as a persistent organic pollutant (POP) and was included into Annex B of the Stockholm Convention on Persistent Organic Pollutants. PFOA, its salts and related substances (i.e. substances that can degrade to PFOA) are restricted with certain derogations within the EU with a transitional period until 4 July 2020. Additionally, the inclusion of PFOA into the Stockholm Convention is being discussed and will be decided in 2019.

The Environmental Protection Agency of the United States (US-EPA) launched a voluntary agreement with eight fluoropolymer and -telomere manufacturers on a PFOA-stewardship program in 2006. The first goal of the agreement was a 95 % emission reduction of PFOA, its precursors, and related higher homologue chemicals until 2010 using the emission data of the year 2000 as a baseline. The second goal is the elimination of these chemicals by 2015. Canada prohibited the use of PFOA and long-chain PFCAs in 2016].

This restriction proposal aims at regulating the remaining long-chain perfluorocarboxylic acids (PFCAs) within the EU, substances that were included already in the US-EPA stewardship program and the Canadian ban.

# Summary

The conclusion of the Dossier Submitter's risk assessment is that, despite that no intentional uses were identified so far, a restriction on a Union-wide basis is justified to reduce the release of these substances into the environment and to prevent any future manufacturing, placing on the market and use. This EU-wide measure may be the first step for global action.

On the basis of the analysis of the effectiveness, practicability and monitorability of the Risk Management Options, the following restriction is proposed:

*Proposed restriction*

Title: Restriction on the manufacturing, use, placing on the market and import of C9-C14 PFCAs, their salts and related substances.

| | |
|---|---|
| Perfluoroalkyl carboxylic acids (branched and/or linear) with the formula: CF3-(CF2)$_n$-C, n=7 or 8 or 9 or 10 or 11 or 12 as structural elements including their salts and including all combinations thereof<br><br>Perfluoroalkyl carboxylic acids (branched and/or linear) with the formula: $CF_3$-$(CF_2)_n$-, n=8-13 as a structural element, including their salts<br><br>Any related substance (including its salts and polymers) with the above defined linear and/or branched perfluoroalkyl structural elements that can degrade to C9-C14 PFCA<br><br>The following substances are excluded from this designation:<br>• $CF_3$-$(CF_2)_n$-X, n > 7, where X= F, Cl, Br<br>  including any substance with linear and/or branched perfluoroalkyl elements and all mixtures thereof<br>• $CF_3$-$(CF_2)_n$-SO2X', n > 7 where X'=any group, including salts<br>• $CF_3$-$(CF_2)_n$-C(=O)OH, n > 12 including salts | 1. Shall not be<br>  a) manufactured, or placed on the market as substances on their own;<br>  b) used in the production of, or placed on the market in:<br><br>    i. another substances, as a constituent,<br>    ii. a mixture,<br>    iii. an article or any parts thereof,<br>in a concentration equal to or above 25 ppb for the sum of C9-C14 PFCAs and their salts or 260 ppb for the sum of C9-C14 PFCA related substances<br><br>2. Paragraph 1 shall apply 18 month from entry into force of the restriction<br><br>3. Paragraph 1 shall not apply to<br>  a) the manufacture of a substance where this occurs as an unintended by-product of the manufacture of fluorochemicals with a carbon chain equal to or shorter than 8 atoms;<br>  b) a substance that is to be used, or is used as a transported isolated intermediate, provided that the conditions in Article 18(4) lit. a) to f) of this Regulation are met;<br><br>4. Paragraph 1(b-iii) shall not apply to<br>  a) Articles placed on the market before the restriction becomes effective |

The proposal restricts the manufacturing of C9-C14 PFCAs, their salts and related substances within the EU. Further, the proposal restricts the use, placing on the market and import of C9-C14 PFCAs, their salts and related substances as substances on their own or in a mixture or in an article or parts therein in a concentration equal to or above 25 ppb for the sum of

C9-C14 PFCAs and their salts or 260 ppb for the sum of C9-C14 PFCA related substances. Thus, articles and mixtures manufactured in Europe can comply with the proposed threshold. One stakeholder indicated to use a small amount of C9-C14 PFCAs in imported semiconductors. The use is ongoing until 2019 and due to the shelf live of articles containing semiconductors a longer transitional period until 2023 was requested. However, based on the data provided so far it is not possible to justify this derogation.

C9-C14 PFCAs, their salts and related substances are mainly unintended by-products occurring during the manufacturing of per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms, such as perfluorooctanoic acid (PFOA, C8-PFCA) based substances and perfluorohexanoic acid (C6-PFCA) based substances. The C6-PFCA based substances are alternatives of the C8-based chemistry. During the manufacturing of the C6-PFCA based substances, the fraction mainly containing long-chain PFCAs, the so called C8-fraction can contain up to 30% C9-C14 PFCAs and related substances. In Europe, this C8-fraction is separated and reworked. The remaining C6-fraction is further processed. Mixtures sold to industry contain C9-C14 PFCAs and related substances in trace levels up to 25 ppb and 260 ppb, respectively. It is not the intention of this restriction to prevent the manufacturing of these so called short-chain alternatives. That is why a specific exemption for this manufacturing as well as the use of transported isolated intermediates is included.

## Summary of the justifications

### _Identified hazard and risk_

PFCAs (perfluorocarboxylic acids) are synthetic compounds that contain a common structural feature: a perfluorinated carbon chain combined with a carboxylic group. C9-C14-PFCAs belong to this substance group of long-chain PFCAs with carbon chain lengths of 9-14. They differ only in the number of CF$_2$-groups whereas all other fragments are the same within the group. Because of the highly similar chemical structure and behaviour, it is motivated to consider C9-C14-PFCAs as a group in the scope of this restriction proposal.

The hazard profile of C9-C14 PFCAs is well known:

**CMR, PBT and/or vPvB properties** C9-PFCA and C10-PFCA as well as their sodium and ammonium salts are listed in Annex VI of the CLP Regulation as Carc. 2 and Repr. 1B. In addition, C9-C14 PFCAs are bioaccumulative and extremely persistent. Thus, the substances were added to the REACH Candidate List as substances of very high concern (SVHC) under REACH by unanimous agreement between EU Member States:

- C9- and C10-PFCAs as CMR and PBT (persistent, bioaccumulative and toxic) substances and
- C11-C14 PFCAs as vPvB (very persistent and very bioaccumulative) substances.

C9-C14 PFCAs belong to the most persistent chemical substances known. They do not undergo any further abiotic or biotic degradation under environmentally relevant conditions. In C9-C14 PFCAs the carbon chain is perfluorinated. Any hydrogen atoms are substituted with fluorine atoms. The fluorine atoms shield the carbon backbone from any physical or chemical attack making C9-C14 PFCAs most stable organic compounds.

Due to these properties they are very likely to cause severe and irreversible adverse effects on the environment and human health if their releases are not minimised. According to REACH regulation Article 60 (3) and REACH Annex I para 6.5 the risk to the environment cannot be adequately controlled for PBT/vPvB substances. No safe concentration, thus no threshold (PNEC), can be determined for PBT/vPvB substances.

C9–C14 PFCA related substances share structural elements with C9-C14 PFCAs: the perfluorinated carbon chain. C9-C14 PFCA-related substances additionally contain a non-

fluorinated moiety. C9-C14 PFCA related substances can degrade to the persistent C9-C14 PFCAs in the environment. According to ECHA Guidance R.11, if transformation/degradation products with PBT/vPvB properties are being formed, the substances themselves must be regarded as PBT substances (European Chemicals Agency, 2017a). Therefore, the hazard profiles of C9-C14 PFCAs apply to these substances as well.

## Mobility in the environment and affected compartments

C9-C14 PFCAs have a higher water solubility (compared to other PBT substances) leading to their relatively high mobility in water bodies and between different environmental compartments. Monitoring data show that C9-C14 PFCAs in soil leaches over time and can be a long-term source of contamination to underlying groundwater. This has been shown e.g. at various emission sites of long-chain PFCAs, e.g. airports where the substances were (unintentionally) contained in fire fighting foams. Due to the chemical nature of C9-C14 PFCAs, purification of water contaminated with C9-C14 PFCAs is difficult and costly.

## Long range transport potential and findings in remote areas

C9-C14 PFCAs, their salts and C9-C14 PFCA-related substances do not occur naturally. However, they are found ubiquitously in the environment, also in remote areas. C9-C14 PFCAs are transported over long distances via the atmosphere and aquatic environment via rivers and oceans. C9-C14 PFCA-related substances like 10:2 FTOH have a high vapour pressure and are transported mainly via air. In the atmosphere C9-C14 PFCA-related substances can be degraded to C9-C14 PFCAs. Subsequently, C9-C14 PFCAs are deposited on water and soil. As a consequence, C9-C14 PFCA related substances may be a significant long-term source of C9-C14 PFCAs in remote regions like the Arctic. Here, C9-C14 PFCAs are found in the environment and biota including top predator species like polar bears and seals (Annex B.4.2.5).

## Environmental exposure

C9-C14 PFCAs are ubiquitously present in the environment. Numerous direct and indirect sources of C9-C14 PFCAs, their salts and C9-C14 PFCA related substances contribute(d) to the overall environmental exposure of C9-C14 PFCAs. C9-C14 PFCAs have been detected mainly in the lower pg/L to low ng/L-range in surface waters and in ground water. This can be partly attributed to accidents, inappropriate disposal, previous use of the area (e.g. former fire-training area), or industrial point sources.
In sediments C9-C14 PFCAs were measured in the pg/g (dw)-range in remote areas to and in the low ng/g range in Europe.
In soil measured concentrations vary widely as well (up to 3 ng/g dw) depending among others on factors as sewage sludge application, influence by industrial plants or fire-training activities etc. Temporal trend studies show different pictures: There are some studies showing a decline of the substances in water and biota and others where a decrease of the C9-C14 PFCA levels was not found yet.

C9-C14 PFCAs and related substances have been used (unintentionally) for several decades resulting in an existing stock in the technosphere and the environment. Worldwide total manufacturing volumes of APFN, the ammonium salt of C9-PFCA for the years 1975 to 2004 were estimated to range between 800 – 2300 t. For a more recent period (2011 – 2015) APFN volumes have been estimated to 17- 107 t. Further manufacturing volumes are not available. Additionally, the substances have been manufactured unintentionally during the manufacturing of PFOA (up to 0.21 % C9-C14 PFCAs) and PFOA related substances (20 to 45% C9-C14 PFCA related substances) and were released into the environment. In Europe, the manufacturing of PFOA and PFOA-related substances ceased in 2015, thus releases of C9-C14 PFCAs and related substances from those uses are expected to decline.
According to the consulted stakeholders, today C9-C14 PFCAs, their salts and C9-C14 PFCA-related substances are mainly unintended by-products during the manufacturing of short-chain alternatives such as C6-based chemistries. The fraction mainly containing long-chain PFCAs, the so called C8-fraction which can contain up to 30% C9-C14 PFCAs and related

substances is separated and reworked. The remaining C6-fraction is further processed. Mixtures sold to industry contain C9-C14 PFCAs and related substances in trace levels up to 25 ppb and 260 ppb respectively.

The intentionally used short-chain substances provide special properties, such as high friction resistance, dielectric properties, resistance to heat and chemical agents, low surface energy, as well as water, grease, oil, and dirt repellency. These substances are therefore used for various articles, mixtures and applications such as textiles, paper, and fire-fighting foam today. The substances are released into the environment during different life cycle steps and via various exposure pathways (such as manufacturing of the substances, processing, use and at the waste stage).

Thus, releases will continue because the substances are unintentional by products during the manufacturing of short-chain alternatives, such as the C6-based chemistries and some remaining uses of C8-based chemistries (derogated uses, such as firefighting foams).

**Human exposure**: In contrast to PBT substances that have been identified based on environmental toxicity C9- and C10- PFCAs were been identified as PBT substances because they are toxic to reproduction in humans. The toxicological properties of C9- and C10-PFCAs also include effects on other human health endpoints. Hence, in contrast to a PBT substance where toxicity relates to environmental toxicity emissions of C9- and C10-PFCA can cause damage to human health. This is of particular concern, because the general population is widely exposed to C9-C10 PFCAs via the environment with long elimination half-lives of up to 12 years from the human serum.
Human exposure occurs via the environment, e.g. consumption of food and drinking water, and via inhalation of contaminated air or indoor dust.

Human biomonitoring data, including remote locations such as Greenland, show that C9-C14 PFCA are widely detected in body fluids such as serum and breast milk in human populations at pg/ml to ng/ml levels. Temporal trend studies show increasing levels from 1980s until approximately 2010 where the levels seem to level out or decrease.

*Hence, there is a high potential that ongoing releases of these substances into the environment will result in long-term human and environmental exposure to C9-C14 PFCAs.*

### *Justification that action is required on a Union-wide basis*

The risks associated with articles and mixtures (particularly imported) containing intentionally and unintentionally used C9-C14 PFCAs, their salts and related substances need to be addressed on a Union-wide basis because of two main facts:

- Exposure takes place in all Member States, and
- The free movement of goods within the Union

The restriction on PFOA, PFOA-related substances and its salts will become binding in 2020 with certain derogations. This so called C8-chemistry represents the preferred choice of chain length for almost all fluorinated applications due to its superior properties with regard to quality and cost. A large part of the industry has already substituted C8-based chemicals towards C6-technology or fluorine free alternatives. It is believed that the vast majority of the remaining companies using C8-chemistry will gradually substitute to C6 or fluorine free alternatives. However, it is possible that companies will consider the use of C9-C14 PFCAs, their salts and related substances as substitutes for PFOA, its salts and related substances in the future, especially after the relevant restriction on PFOA becomes binding in 2020. Thus, an EU-wide measure is necessary to prevent possible future manufacturing and use resulting in increasing releases into the environment.

Moreover, during the manufacturing of C6-PFCA based substances in the EU the C8-fraction is separated and reworked, resulting in lower concentrations of C8-C14 PFCAs and related

substances in the end product. It is not known if this technology is applied outside the EU as well. Thus imported articles and mixtures may contain higher amounts of unintentionally manufactured c9-C14 PFCAs, their salts and related susbtances.

Additionally, the proposed restriction is in-line with the US-EPA stewardship program and the restriction of long-chain per- and polyfluorinated substances in Canada. Moreover, a restriction within the EU could offer a good basis for considering needs for global action.

### Effectiveness

Since we have not identified any user of C9-C14 PFCAs withinin the EU, and only one user in imports (semiconductors), there are also few costs and benefits to compare. We argue that enforcement costs are lower than on average since these costs can be shared with the enforcement costs connected with the implementation of the PFOA restriction. The average enforcement cost of EUR 55 600 per year for Member States is here seen as a high estimation of these costs. Cost might also occur if C9-C14 PFCAs are included in imported articles to a large extent. We have not been able to verify the extent of use of C9-C14 in imports, and therefore see this as a potential uncertainty. The benefits from the risk reducing capacity of this proposed restriction are not quantifiable, but we argue that they exceed the moderate enforcement costs described above, making the restriction proportionate, with an either unchanged or slightly improved benefit-cost ratio.

Thus, it is concluded that the proposed restriction is capable of ensuring the reduction of further releases of intentionally used C9-C14 PFCAs, their salts and related substances into the environment.

However, releases into the environment will continue at a relatively low level, since the substances occur as by-products in short-chain fluorinated alternatives. And since these substances are also released from landfills, and other parts of the technosphere (this is however not in the scope of this restriction).

### Practicality

The proposed restriction is practical because it is implementable, enforceable and manageable.

#### Implementability

The proposed restriction is considered to represent an implementable option for the actors involved within the timeframe of 18 months. This restriction should be enforced together with the restriction of PFOA. It appears that the necessary technology, techniques and alternatives are available and economically feasible. The RMO is in line with the US-EPA Stewardship Program. Thus, many industry actors are already preparing for using different substances and technologies from 2015 on.

#### Enforceability

Enforcement authorities can set up efficient supervision mechanisms to monitor industry`s compliance with the proposed restriction. Although there are no standard analytical methods to measure the content of C9-C14 PFCAs, their salts and related substances in articles and mixtures yet available, those methods are being developed already for the restriction of PFOA and related substances. The same methods can be applied for testing C9-C14 PFCAs and related substances.

#### Manageability

The costs for industry and enforcement agencies were assessed to be negligible. A transitional period of (even less than) 18 months seems to be manageable. However one user of C9-C14

PFCAs was reported in the stakeholder consultation, (at a late stage), with regard to imported semiconductors. This company have asked for a time derogation. At the moment not enough information is present in order to assess if a request for a time derogation should be accepted (or rejected).

*Monitorability*

For imported articles, compliance control can be accomplished by border authorities and notifications of any violation of the restriction can be reported in the RAPEX system (Rapid Exchange of Information System).

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.

# Report

# 1. The problem identified

# 1.1. Hazard, exposure and risk

### 1.1.1. Identity of the substances and physical and chemical properties

Perfluoroalkyl carboxylic acids (branched and/or linear) with the formula:

CF3-(CF2)$_n$-C, n=7 or 8 or 9 or 10 or 11 or 12 as structural elements including their salts and including all combinations thereof

Perfluoroalkyl carboxylic acids (branched and/or linear) with the formula:

CF$_3$-(CF$_2$)$_n$-, n=8-13 as a structural element, including their salts

Any related substance (including its salts and polymers) with the above defined linear and/or branched perfluoroalkyl structural elements that can degrade to C9-C14 PFCA

The following substances are excluded from this designation:

- CF$_3$-(CF$_2$)$_n$-X, n > 7, where X= F, Cl, Br
  including any substance with linear and/or branched perfluoroalkyl elements and all mixtures thereof

- CF$_3$-(CF$_2$)$_n$-SO2X', n > 7
  where X'=any group, including salts

- CF$_3$-(CF$_2$)$_n$-C(=O)OH, n > 12 including salts

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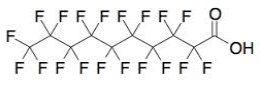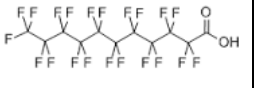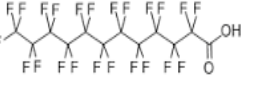
### 1.1.1.1. Name and other identifiers of the substances

1.1.1.1.1. C9-C14 PFCAs

*Table 1- 1: Substance identities of C9-C14 PFCAs*

| Abbreviation | C$_9$-PFCA | C$_{10}$-PFCA | C$_{11}$-PFCA | C$_{12}$-PFCA | C$_{13}$-PFCA | C$_{14}$-PFCA |
|---|---|---|---|---|---|---|
| Acronym | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| EC number | 206-801-3 | 206-400-3 | 218-165-4 | 206-203-2 | 276-745-2 | 206-803-4 |
| EC name | Perfluorononan-1-oic acid | Nonadecafluorodecanoic acid | Henicosafluoroundecanoic acid | Tricosafluorododecanoic acid | Pentacosafluorotridecanoic acid | Heptacosafluorotetradecanoic acid |
| CAS number: | 375-95-1 | 335-76-2 | 2058-94-8 | 307-55-1 | 72629-94-8 | 376-06-7 |
| CAS name: | Nonanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro- | Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro- | Undecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-henicosafluoro- | Dodecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-tricosafluoro- | Tridecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,11,11,12,12,13,13,13-pentacosafluoro- | Tetradecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,11,11,12,12,13,13,14,14,14-heptacosafluoro- |
| IUPAC name: | heptadecafluorononanoic acid | nonadecafluorodecanoic acid | henicosafluoroundecanoic acid | tricosafluorododecanoic acid | pentacosafluorotridecanoic acid | heptacosafluorotetradecanoic acid |
| Index number in Annex VI of the CLP Regulation: | 607-718-00-9 | 607-720-00-X (10th ATP) | - | - | - | - |

| Molecular formula: | C$_9$HF$_{17}$O$_2$ | C$_{10}$HF$_{19}$O$_2$ | C$_{11}$HF$_{21}$O$_2$ | C$_{12}$HF$_{23}$O$_2$ | C$_{13}$HF$_{25}$O$_2$ | C$_{14}$HF$_{27}$O$_2$ |
|---|---|---|---|---|---|---|
| Molecular weight or molecular weight range: | 464.08 g/mol | 514.08 g/mol | 564.09 g/mol | 614.10 g/mol | 664.11 g/mol | 714.11 g/mol |
| Synonyms: | Perfluorononanoic acid, PFNA, Perfluorononan-1-oic acid, C9-PFCA | Perfluorodecanoic acid, PFDA, C10-PFCA | Perfluoroundecanoic acid, PFUnDA, C11-PFCA | Perfluorododecanoic acid, PFDoDA, C12-PFCA | Perfluorotridecanoic acid, PFTrDA, C13-PFCA | Perfluoromyristic acid; Perfluorotetradecanecarboxylic acid; Perfluorotetradecanoic acid; PFTDA, C14-PFCA |
| Length of carbon chain | 9 | 10 | 11 | 12 | 13 | 14 |
| Structural formula: |  |  |  |  |  | $F_3C-(CF_2)_{12}-CO_2H$ |
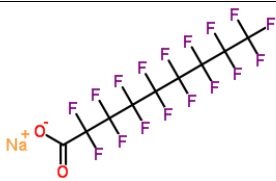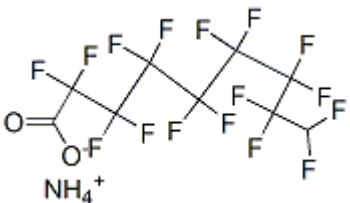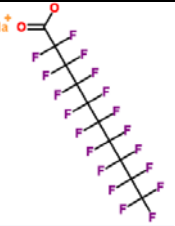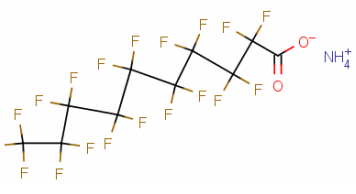
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## 1.1.1.1.2. C9-C14 salts

In the table below examples of C9-C14 PFCA salts are listed. The substances were screened from the OECD-List (2007).

*Table 1- 2: Examples of C9-C14-PFCA salts*

| Substance name | CAS-No. | Molecular formula | Structural formula |
|---|---|---|---|
| Perfluorononan-1-oic acid, sodium salt | 21049-39-8 | $C_9F_{17}O_2 \cdot Na$ |  |
| Perfluorononan-1-oic acid, ammonium salt | 4149-60-4 | $C_9F_{17}O_2 \cdot NH_4$ |  |
| Sodium nonadecafluorodecanoate | 3830-45-3 | $C_{10}F_{19}NaO_2$ |  |
| Ammonium nonadecafluorodecanoate | 3108-42-7 | $C_{10}H_4F_{19}NO_2$ |  |

## 1.1.1.1.3. C9-C14 PFCA related substances

Any substance (including its salts and polymers) that can degrade to C9-C14 PFCAs, having linear or branched perfluoroalkyl derivatives with the formula: CF3-(CF2)n-C, n= 7 or 8 or 9 or 10 or 11 or 12 as a structural element, including their salts, and including all combinations thereof,

and any other substance having linear or branched perfluoroalkyl derivatives with the formula: CF3-(CF2)n=8-13- as a structural element, including its salts,
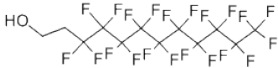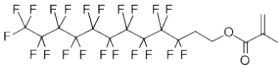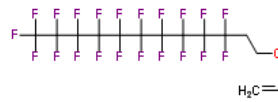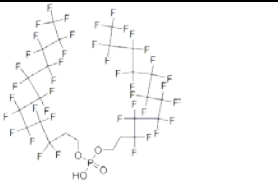
except those derivatives with the formula:

- CF3-(CF2)n-X, n > 7, where X= F, Cl, Br including any substance with linear and/or branched perfluoroalkyl elements and all mixtures thereof,

- CF3-(CF2)n-SO2X', n>7, where X' = any group, including salts,

- CF3-(CF2)n-C(=O)OH, where n > 12

Some examples for C10-PFCA related substances are given here. More examples are shown in Appendix B.1.

*Table 1- 3: Examples for C10-PFCA-realted substances. More examples can be found in Appendix B.1.*

| Synonyms | CAS-Name | CAS | Chemical Structure |
|---|---|---|---|
| **Fluorotelomer alcohols** | | | |
| 10:2 Fluorotelomer alcohol (10:2 FTOH) | 1-Dodecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,11,11,12,12,12- heneicosafluoro- (TSCA, DSL, AICS) | 865-86-1 |  |
| **Polyfluorinated acrylates and methacrylates** | | | |
| 10:2 Methacrylate | 2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,11,11,12,12,12- heneicosafluorododecyl ester (TSCA, DSL, ENCS, AICS) | 2144-54-9 |  |
| 10:2 Acrylate | 2-Propenoicacid,3,3,4,4,5,5,6, 6,7,7,8,8,9,9,10,10,11,11,1 2,12,12- heneicosafluorododecylester | 17741-60-5 |  |
| **Polyfluorinated phosphates** | | | |
| 10:2 DiPap | bis[3,3,4,4,5,5,6,6,7,7,8,8,9 ,9,10,10,11,11,12,12,12- henicosafluorododecyl] hydrogen phosphate | 1895-26-7 |  |

### 1.1.1.2. Dissociation of C9-14-PFCAs and their salts in aqueous media

Under environmental conditions in aqueous media the free perfluorinated carboxylic acids (PFCAs) stay in equilibrium with their conjugate bases, the perfluorinated carboxylates. The fraction of each species depends on the acid dissociation constant (pKa) and the pH of the environmental compartment. Salts of PFCAs, which are sometimes used in laboratory experiments, will be in equilibrium with the corresponding acid in aqueous phases as well. Currently used techniques for analysis and quantification of PFCAs in i.e. environmental samples are not able to distinguish between both of the species. Therefore, reported concentrations always include the acids as well as the bases. If reported concentrations are used for the determination of bioaccumulation factors or for experiments determining the persistency, aqueous phase concentrations include both species. Experimental determination of pKa is difficult for PFCAs, i.e. because of the surface active properties. Calculated values should be taken with care, because for most of the models it is unclear whether PFCAs are within their applicability domain. For assessing the intrinsic properties of the PFCAs within this dossier the exact knowledge of the fraction of each species is not required, because both of the species will be available independently from the starting conditions.

Furthermore, due to the uncertainties of pKa values it is not wise to calculate partition coefficients under environmental pH conditions. We would like to mention that tThere is an

ongoing scientific discussion showing that the partitioning of PFCAs in the environment can be described by the properties of the neutral PFCAs only (Webster and Ellis, 2011).

### 1.1.1.3. Physicochemical properties and partition coefficients of C9-14-PFCAs and some salts

The experimental determination of i.e. partition coefficients is difficult for example because of the surface active properties of the ionic PFCAs. The presence of ionic PFCAs depends on the dissociation of PFCAs in aqueous media (see B.1.3.1 for details). Nevertheless, there are models available, i.e. COSMOtherm calculating partitioning coefficients of neutral PFCAs. COSMOtherm is a quantum chemistry-based method that requires no specific calibration. This calibration would be difficult because of missing measured data of PFCAs. Therefore, COSMOtherm is expected to be able to estimate properties for PFASs. Studies have shown that properties estimated with COSMOtherm show good agreement with the experimental data for a number of per- and polyfluorinated chemicals, i.e. C8-PFCA (Wang et al. 2011; Arp et al. 2006). Again, whether neutral PFCAs are present in aqueous media depends in the dissociation of the acids. Air-water as well as octanol-water partition coefficients are of course different for PFCAs with 8 to 14 carbon atoms but they show a clear increasing, trend with chain length (see Table 1- 4 (Wang et al., 2011b)). This can be explained by the increasing molecular volume with each additional CF2-unit. The trend of the fate of PFCAs with chain length is supported by information on sorption of PFCAs on sediment. Sorption increases with increasing chain length (Higgins and Luthy, 2006) also under environmental conditions (Ahrens et al., 2010b).

*Table 1- 4: Physical chemical properties of C9-C14 PFCAs*

| Abbreviation | C$_9$-PFCA | C$_{10}$-PFCA | C$_{11}$-PFCA | C$_{12}$-PFCA | C$_{13}$-PFCA | C$_{14}$-PFCA |
|---|---|---|---|---|---|---|
| Acronym | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| CAS No | 375-95-1 | 335-76-2 | 2058-94-8 | 307-55-1 | 72629-94-8 | 376-06-7 |
| Chemical Structure | $CF_3(CF_2)_7$-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 |
| Molecular Weight g/mol | 464.08 | 514.08 | 564.0909 | 614.0984 | 664.1059 | 714.11 |
| Partitioning Coefficient log K$_{OW}$ | 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$_{OA}$ | 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)) |
| log K$_{AW}$ | -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 | <1.6 (Vierke et al., 2013b) 0.82 (calc., COSMOtherm, | <1.6 (Vierke et al., 2013b) 2.58 (Moroi et al., 2001) | <1.6 (Vierke et al., 2013b) | | | |

| Abbreviation | C$_9$-PFCA | C$_{10}$-PFCA | C$_{11}$-PFCA | C$_{12}$-PFCA | C$_{13}$-PFCA | C$_{14}$-PFCA |
|---|---|---|---|---|---|---|
| Acronym | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| | (Wang et al., 2011b)) | | | | | |
| Partition coefficients log K$_d$ (sediment and overlapping dissolved phase) | 0.6 (Ahrens et al., 2010b) * | 1.8 (Ahrens et al., 2010b) * | 3.0 (Ahrens et al., 2010b) * | | | |
| Log Koc (sediment organic carbon-normalised distribution coefficient) | 2.39 (Higgins and Luthy, 2006)# <br><br> 2.4 (Ahrens et al., 2010b)* | 2.76 (Higgins and Luthy, 2006)# <br><br> 3.6 (Ahrens et al., 2010b)* | 3.3 (Higgins and Luthy, 2006)# <br><br> 4.8 (Ahrens et al., 2010b) * | | | |
| Water solubility | | 5.14 g/L at 25°C (Kauck and Diesslin, 1951) | 1.2E-4 g/L; pH 1 at 25°C <br><br> 9.0E-4 g/L; pH 2 at 25°C <br><br> 8.5E-3 g/L; pH 3 at 25°C <br><br> 0.056 g/L; pH 4 at 25°C <br><br> 0.14 g/L; pH 5 at 25°C <br><br> 0.16 g/L; pH 6-10 at 25°C <br><br> (calculated) <br><br> (European Chemicals Agency, 2012b) | 2.9E-5 g/L pH 1 at 25°C <br><br> 2.2E-4 g/L pH 2 at 25°C <br><br> 2.0E-3 g/L pH 3 at 25°C <br><br> 0.014 g/L pH 4 at 25°C <br><br> 0.034 g/L pH 5 at 25°C <br><br> 0.039 g/L pH 6 at 25°C <br><br> 0.040 g/L pH 7 at 25°C <br><br> 0.041 g/L pH 8-10 at 25°C <br><br> (calculated) <br><br> (European Chemicals Agency, 2012e) | 7.3E-6 g/L; pH 1 at 25 °C <br><br> 5.5E-5 g/L; pH 2 at 25 °C <br><br> 5.1E-4 g/L; pH 3 at 25 °C <br><br> 3.5E-3 g/L; pH 4 at 25 °C <br><br> 8.6E-3 g/L; pH 5 at 25 °C <br><br> 0.0100 g/L; pH 6-10 at 25 °C <br><br> (calculated) <br><br> (European Chemicals Agency, 2012d) | 1.9E-6 g/L; pH 1 at 25 °C <br><br> 1.4E-5 g/L; pH 2 at 25°C <br><br> 1.3E-4 g/L; pH 3 at 25°C <br><br> 9.3E-4 g/L; pH 4 at 25°C <br><br> 2.2E-3 g/L; pH 5 at 25°C <br><br> 2.6E-3 g/L; pH 6-10 at 25°C <br><br> (calculated) <br><br> (European Chemicals Agency, 2012c) |
| Vapour pressure | | 3.1 to 99.97 kPa (129.6 to 218.9 ℃) <br><br> (calculated) <br><br> (Kaiser et al., 2005) | 0.6 to 99.97 kPa (112 to 237.7°C) <br><br> (calculated) <br><br> (European Chemicals | 1.25 Pa at 25°C (calculated) <br><br> (European Chemicals Agency, 2012e) | 0.48 Pa at 25°C (calculated) <br><br> (European Chemicals Agency, 2012d) | 0.18 Pa at 25 °C (calculated) <br><br> (European Chemicals |

| Abbreviation | C$_9$-PFCA | C$_{10}$-PFCA | C$_{11}$-PFCA | C$_{12}$-PFCA | C$_{13}$-PFCA | C$_{14}$-PFCA |
|---|---|---|---|---|---|---|
| Acronym | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| | | | Agency, 2012b) | | | Agency, 2012c) |
| Boiling point | 218°C (Yaws, 2008) | 218°C measured (Kauck and Diesslin, 1951) | 238.4 °C (Kaiser et al., 2005) (calculated) | 249 °C SRC PhysProp Database | 260.7°C Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) | 270 °C (BIG Database) |

## 1.1.2. Justification for grouping

C9-C14-PFCAs belong to the same substance category of long-chain 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 with sufficient reliability that the behaviour of the PFCAs follows a regular pattern: with increasing chain length water solubility decreases and the sorption potential increases (Please see Table 1- 4 and Annex B.1.4).

Because of the highly similar chemical structure and behaviour in the environment it is motivated to consider C9-C14-PFCAs as a group in the scope of this restriction proposal. A grouping of substances is needed to eliminate the risks resulting from the exposure of humans and the environment to C9-C14 PFCAs. PFOA, which also belongs to the group of long-chain PFCAs will be restricted from 2020 on. Thus, with this restriction the whole group of long-chain PFCAs will be regulated within the EU.

The following substances belong to the same substance category of long-chain perfluorinated carboxylic acids (PFCAs). Please see Annex B.1.4 for further information.

*Table 1- 5: Long-chain PFCAs*

| EC number | CAS number | Substance name | Length of the carbon chain |
|---|---|---|---|
| 206-397-9 | 335-67-1 | Pentadecafluorooctanoic acid (PFOA, C8-PFCA) | 8 |
| 206-801-3 | 375-95-1 | Perfluorononanoic acid (PFNA, C9-PFCA) | 9 |
| 206-400-3 | 335-76-2 | Nonadecafluorodecanoic acid (PFDA, C10-PFCA) | 10 |
| 218-165-4 | 2058-94-8 | Henicosafluoroundecanoic acid (PFUnDA, C11-PFCA) | 11 |
| 206-203-2 | 307-55-1 | Tricosafluorododecanoic acid (PFDoDA, C12-PFCA) | 12 |

| 276-745-2 | 72629-94-8 | Pentacosafluorotridecanoic acid (PFTrDA, C13-PFCA) | 13 |
|-----------|------------|---------------------------------------------------|----|
| 206-803-4 | 376-06-7 | Heptacosafluorotetradecanoic acid (PFTDA, C14-PFCA) | 14 |

It is known that some C9-C14 PFCA-related substances can be degraded to the corresponding perfluorinated acids under environmentally relevant conditions (D'eon and Mabury, 2011a; Wang et al., 2005a) (for more details see Annex B.4.1.2). Therefore, these C9-C14 PFCA-related substances also contribute to the exposure of humans and the environment of C9-C14 PFCAs and are thus also included in the scope of this restriction proposal. Besides such C9-C14 PFCA-related substances, for which their degradation to the corresponding perfluorinated acids has already been shown in different studies, other substances (for examples see Appendix B.1.) show high similarities in their molecular structures compared to C9-C14 PFCAs and related substances for which degradation to C9-C14 PFCAs was shown. This high similarity and the nature of the chemical binding of the perfluorinated alkyl moiety to other parts of the molecules lead to the hypothesis that degradation is very likely, but has simply not yet been investigated in detail. Besides the substances registered under REACH further C9-C14 PFCA related substances are known which could be used within the EU and may also be imported into the EU via imported articles and mixtures (Ministry of Environmental Protection of the People`s Republic of China, 2013). A grouping approach via chemical sum formula is therefore the most appropriate way to cover all relevant substances.

### 1.1.3. Classification and labelling

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

C9-PFCA and C10-PFCA as well as their sodium and ammonium salts are listed in Annex VI of CLP Regulation (C9-PFCA: 9$^{th}$ ATP; C10-PFCA: 10$^{th}$ ATP)

*Table 1- 6: Harmonized classification of C9-PFCA and its sodium and ammonium salts (Index No 607-718-009) and C10-PFCA and its sodium and ammonium salts (Index No 607-720-00-X)*

| Substance | CAS No | Classification | | Labelling | |
|-----------|--------|----------------|---|-----------|---|
| | | Hazard Class and Category Code(s) | Hazard statement Code(s) | Hazard Statement Code(s) | Pictogram, Signal Word Code(s) |
| perfluorononan-1-oic acid [1] and its sodium [2] and ammonium [3] salts | 375-95-1 [1] <br> 21049-39-8 [2] <br> 4149-60-4 [3] | Carc. 2 Repr. 1B Lact. Acute Tox. 4 Acute Tox. 4 STOT RE 1 Eye Dam. 1 | H351 H360Df H362 H332 H302 H372 (liver, thymus, spleen) H318 | H351 H360Df H362 H332 H302 H372 (liver, thymus, spleen) H318 | GSH08 GSH07 GHS05 Dgr |
| nonadecafluorodecanoic acid; [1] ammonium nonadecafluorodecanoate; [2] | 335-76-2 [1] <br> 3108-42-7 [2] <br> 3830-45-3 [3] | Carc. 2 Repr. 1B Lact. | H351 H360Df H362 | H351 H360Df H362 | GHS08 Dgr |

| | | | | |
|---|---|---|---|---|
| sodium nonadecafluorodecanoate [3] | | | | |

### 1.1.3.2. Self classification(s)

The following industry self-classification(s) and labelling for C9-C14 PFCAs were publicly available in ECHAs C&L Inventory on July 2017.

*Table 1- 7: Notified classification and labelling according to the C&L Inventory*

| Substance | CAS No | Hazard Class and Category Code(s) | Hazard statement Code(s) | Number of Notfiers |
|---|---|---|---|---|
| C9-PFCA | 375-95-1 | Skin Irrit. 2 | H315 | 27 |
| | | Eye Irrit. 2 | H319 | 27 |
| | | STOT SE 3 | H335 | 27 |
| | | Skin Corr. 1C | H314 | 4 |
| | | Eye Dam. 1 | H318 | 1 |
| C10-PFCA | 335-76-2 | Acute Tox. 3 | H301 | 31 |
| | | Skin Irrit. 2 | H315 | 26 |
| | | Eye Irrit. 2 | H319 | 26 |
| | | STOT SE 3 | H335 | 26 |
| | | Skin Corr. 1B | H314 | 4 |
| | | Acute Tox. 3 | H311 | 2 |
| | | Acute Tox. 3 | H331 | 2 |
| | | Eye Dam. 1 | H318 | 1 |
| C11-PFCA | 2058-94-8 | Skin Irrit. 2 | H315 | 26 |
| | | Eye Irrit. 2 | H319 | 26 |
| | | Acute Tox. 4 | H302 | 24 |
| | | Acute Tox. 4 | H312 | 24 |
| | | Acute Tox. 4 | H332 | 24 |
| | | Not classified | | 3 |
| | | STOT SE 3 | H335 | 1 |
| C12-PFCA | 307-55-1 | Skin Irrit. 2 | H315 | 24 |
| | | Eye Irrit. 2 | H319 | 24 |
| | | STOT SE 3 | H335 | 24 |
| | | Skin Corr. 1B | H314 | 3 |
| | | Met. Corr. 1 | H290 | 1 |
| | | Eye Dam. 1 | H318 | 1 |
| | | Aquatic Acute 1 | H400 | 1 |
| | | Aquatic Chronic 1 | H410 | 1 |
| | | Acute Tox. 4 | H302 | 1 |
| | | Acute Tox. 4 | H312 | 1 |
| | | Acute Tox. 4 | H332 | 1 |
| C13-PFCA | 72629-94-8 | No entry | | |
| C14-PFCA | 376-06-7 | Not classified | | 3 |
| | | Skin Corr. 1B | H314 | 3 |

### 1.1.4. Hazard assessment

C9-C14-PFCAs were added to the REACH Candidate List as substances of very high concern (see Table 1- 8). C9- and C10-PFCAs as toxic for reproduction (Repr 1B) and persistent and bioaccumulative, whereas C11- C14 PFCAs as very persistent and very bioaccumulative

ANNEX XV RESTRICTION REPORT – C$_9$-C$_{14}$ PFCAs -including their salts and precursors-

substances. Detailed information on the PBT/vPvB assessment are provided in chapter B.8. of the Annex.

Due to these properties they may cause severe and irreversible adverse effects on the environment and human health.

*Table 1- 8: C9-C14 PFCAs (and salts) were added to the Candidate List based on PBT and vPvB-properties*

| Substance | CAS-No | Intrinsic properties referred to in Article 57 and date oc inclusion in Candidate List | Reference |
|---|---|---|---|
| C9-PFCA and its sodium and ammonium salts | 375-95-1, 21049-39-8, 4149-60-4 | Toxic for reproduction (Article 57c) PBT (Article 57d) Included on Candidate List 17 December 2015 | (European Chemicals Agency, 2015b) |
| C10-PFCA and its sodium and ammonium salts | 335-76-2, 3830-45-3, 3108-42-7 | Toxic for reproduction (Article 57c) PBT (Article 57d) Included in Candidate List 12 January 2017 | (European Chemicals Agency, 2017b) |
| C11-PFCA | 2058-94-8 | vPvB (Article 57e) Included in Candidate List 19 December 2012 | (European Chemicals Agency, 2012a) |
| C12-PFCA | 307-55-1 | vPvB (Article 57e) Included in Candidate List 19 December 2012 | (European Chemicals Agency, 2012a) |
| C13-PFCA | 72629-94-8 | vPvB (Article 57e) Included in Candidate List 19 December 2012 | (European Chemicals Agency, 2012a) |
| C14-PFCA | 376-06-7 | vPvB (Article 57e) Included in Candidate List 19 December 2012 | (European Chemicals Agency, 2012a) |

C9-C14 PFCA related substances can degrade to C9-C14 PFCAs in the environment (see chapter B.4.1.2). Therefore, the hazard profiles of C9-C14 PFCAs apply to these substances as well. According to REACH, if transformation/degradation products with PBT/vPvB properties are being generated, the substances themselves must be regarded as PBT substances (European Chemicals Agency, 2017a).

## 1.1.5. Exposure assessment

### 1.1.5.1. Environmental exposure assessment

1.1.5.1.1. Releases of C9-C14 PFCAs their salts and related substances within the EU

C9-C14 PFCAs, their salts and related substances are manufactured unintentionally during the manufacturing of C8 PFCA salts (such as the ammonium salt of PFOA (APFO)), C8-PFCA related substances and C6 PFCA related substances (see Table below).

*Table 1- 9*: *Estimated (unintentional) concentrations of C9-C14 PFCAs, their salts and related substances during manufacturing of other substances.*

| Process | Content of C9-C14 PFCAs and their salts | Content of C9-C14 PFCA related substances | Remarks | Reference |
|---|---|---|---|---|
| Manufacturing C8 and C8 related substances | | | | |
| Manufacturing of APFO (C8-PFCA salts) | 0.21 % | | Ceased within the EU | (Prevedouros et al., 2006) |
| Manufacturing of PFOA related substances (C8-PFCA related substances) | | 20-45 % | Ceased within the EU in 2015 | Stakeholder information |
| Manufacturing of C6 related substances | | | | |
| In the C8 fraction | | up to 30 % | This fraction is separated and reworked | Stakeholder information |
| In the C6-fraction | | Low ppm range | Transported isolated intermediates | Stakeholder information |
| | Up to 25 ppb | Up to 260 ppb | Mixtures sold to industry | Stakeholder information |

As described in Annex A.2 in more detail, C9-C14-PFCAs, their salts and related substances were historically (unintentionally) used within the EU in many applications. The substances could be detected in various consumer articles and mixtures such as textiles, carpets, upholstery, paper, leather, toner, cleaning agents and carpet care solutions, sealants, floor waxes, paints and impregnating agents.

As reported by European industries C9-C14 PFCAs, their salts and related substances are not intentionally manufactured in the EU anymore (see Annex A1 for details). Moreover, the consulted stakeholders reported that in the past there was no intentional use of these substances within the EU. However, there are indications that C9-C14 PFCAs, their salts and related substances are used outside the EU and are imported in articles and mixtures. Thus,

the substances might still be present in articles and mixtures imported into the EU (see Annex A.2 for examples).

The substances are, according to industry still manufactured as unintended side fraction during the manufacturing of per- and polyfluorinated chemicals containing a carbon chain of less than nine carbon atoms, e.g. based on a C6- perfluorinated carbon chain. Thus, releases of C9-C14 PFCAs are still ongoing. Because of the wide range of uses of those chemicals (see Annex A.2 for details) and manifold sources releases cannot be quantified for single uses. Thus, in the following chapters releases of C9-C14 PFCAs, their salts and related substances are described only for three scenarios:

- Releases from manufacturing fluoropolymers and use of fluoropolymers (see chapter A.2.2 in the annex for details on manufacturing of fluoropolymers)
- Releases from impurities in articles/mixtures intentionally containing PFCAs with a carbon chain of less than nine carbon atoms (example use of fire-fighting foams and textiles in Annex B.9.1.2.2 ans B.9.1.2.3)
- Releases to waste water, sludge, landfill and deposits

The substances are released into the environment during every life cycle step and via various exposure pathways. Consequently, it can be distinguished between direct and indirect sources of C9-C14 PFCAs: Environmental release from the manufacture and use of PFOA-related substances can either be direct, i.e. C9-C14-PFCAs contained as impurities, or indirect due to degradation of C9-C14 PFCA-related substances. This definition is used to better describe the releases of the substances and is in-line with the previous restriction on PFOA, its salts and related substances and the UNEP/OECD global group (OECD 2013).

**Direct sources** include releases from:

- the intentional manufacture and use of C9-C14 PFCAs, their salts and related substances (propably not relevant for the EU, but
- the manufacture and use of FCAs and related substances containing a carbon chain of less than 9 carbon atoms (C9-C14 PFCAs contained as impurities)
- the life-cycle of articles and mixtures that contain these substances as constituents, impurities or residues.

For example, articles treated with fluoropolymers- such as polyvinylidene fluoride (PVDF) may contain C9-PFCA as residue when the substance has been used as processing aid.

**Indirect sources** refer to the formation of C9-C14 PFCAs from C9-C14 PFCA-related substances

Generally, depending on physicochemical properties, manufacturing procedures, use and disposal patterns, C9-C14 PFCAs and their potential precursors may enter the environment via various exposure routes. Since the substances can be transported via air and water globally, the following indirect sources are also relevant for the EU.

(i) through fugitive releases or through waste streams (exhaust gases, wastewater, sludge, solid wastes) from manufacturing sites (including manufacturing of C6 based chemistries)

(ii) through volatilization along the supply chain from manufacturers to downstream industrial users or end consumers;

(iii) through fugitive releases or through waste streams (exhaust gases, wastewater, sludge, solid wastes) from downstream industrial user sites (e.g., fluoropolymer manufacturing sites, paper and textile factories), where articles containing perfluorinated alkyl acids and their potential precursors are applied, further processed or incorporated into industrial/consumer articles;

(iv) through volatilization, wash off or direct use in the environment during use phase of articles containing PFCAs and their potential precursors;

(v) through inappropriate treatments of wastes containing C9-C14 PFCAs, their salts and related substances, including use of sewage sludge as fertiliser, untreated outgassing from landfills or insufficient wastewater treatments, etc. (OECD, 2013)

## 1.1.5.1.2. Releases from manufacturing and use of fluoropolymers

Fluoropolymers can be manufactured either in the emulsified or in the dry form. For the emuslified form an emulsifier is needed. Based on information from the literature one of the most important polymer manufactured with salts of C9-C14 PFCAs is polyvinylidene fluoride (PVDF). APFN, the ammonium salt of C9-PFCA has been used as an emulsifier for manufacturing polyvinylidenefluoride (PVDF) (Annex A.2.2).

During the stakeholder consultation (see Annex G) industry stated not to use C9-C14 PFCAs for fluoropolymer manufacturing within the EU. However, imported articles and mixtures may contain fluoropolymers manufactured with salts of C9-C14 PFCAs outside the EU. Thus, imported articles and mixtures may contain impurities of C9-C14 PFCA salts.

Worldwide, 41.000 t of polyvinylidene fluoride (PVDF) have been used in 2015 (Krämer and Schlipf, 2016). It is estimated that Europe consumed about 20 % of worldwide produced fluoropolymers. Thus, about 8,200 t of PVDF were estimated to be used in Europe in 2015. The fluoroplastics marked is rapidly growing. An annual growth of 3 to 5 % is predicted until 2022 in Europe (Krämer and Schlipf, 2016). So, an annual consumption of PVDF in Europe of about 11,500 t could be deduced for the year 2022. The share of the PVDF manufactured with C9-C14 PFCA salts is not known, neither the share of imported PVDF into the EU. Moreover the content of C9-C14 PFCA salts in the final polymer and the articles and mixtures placed on the market is not known either. Thus, emissions into the environmenment cannot be calculated. However, it can be considered that C9-C14 PFCAs may be present in traces in the imported final articles and mixtures (containing i.e. PVDF manufactured outside the EU with C9-C14 PFCAs) and may be released into the environment during use and disposal. Since the market for fluoropolymers is growing worldwide (see chapter B.9.1.2.3 in the Annex for details) the release from C9-C14 PFCAs, their salts and related substances may increase within the EU from articles and mixtures containing fluoropolymers.

As summarized in Table 1-10 it is further assumed that C9-C14 PFCAs also occur as unintended by-products in fluoropolymers manufactured intentionally with PFOA. During 2015 and 2020 0.01 t/a of C9-C14 PFCAs and their salts are assumed to be released into the EU environment from the manufacturing and use of fluoropolymers such as polytretrafluoroehtylene (PTFE).

## 1.1.5.1.3. Releases resulting from impurities in articles and mixtures containing PFCAs with a carbon chain of less than nine carbon atoms

Long-chain PFCAs are present as impurities not only in fluoropolymers. They also occur unintentionally in articles and mixtures containing PFCAs with a carbon chain of less than nine carbon atoms. According to van der Putte up to 0.2 % C9-PFCA is unintentionally manufactured during the manufacturing of the ammonium salt of C8-PFCA (APFN) (van der Putte et al., 2010). C10-C14 PFCAs their salts and related substances may be unintentionally present up to 0.01 % in articles and mixtures containing APFO. Thus, the substances may be present in all articles and mixtures where PFOA and its salts have been used.

For manufacturing C8-based fluorochemicals (PFOA-related substances) 20-45% longer chain homologues have been occurring in the reaction mixtures according to information from stakeholders. Applying release factors of 0.05 %, approximately 1.65 to 3.71 t/a of C9-C14

PFCA related substances were released post 2015 within the EU from manufacturing estimated 165 t of PFOA-related substances (see Table 1-10). However, manufacturing of PFOA-related substances ceased in December 2015 within the EU and releases of C9-C14 PFCA related substances post 2015 are zero. However, we assume that stocks are still available for certain applications. Especially, considering the longer transitional periods and derogations for some uses e.g. medical products and fire-fighting foams. Thus, releases of unintentionally occurring C9-C14 PFCAs, is ongoing within the EU. Additionally articles and mixtures treated with C8-PFCA and related substances have life-times from days to decades (e.g. wrapping paper vs. furniture). Thus, emissions into the environment will continue although the main uses for C8-based fluorochemicals may discontinue in the near future.

In the background document for the restriction of PFOA (European Chemicals Agency, 2015a) it was estimated that approximately 1,600 t/a of PFOA-related substances were imported and used in the EU post 2015 (Table 1-10). The total volume of PFOA-related substances in imported articles and mixtures is unknown. Based on that assumption and on the content of C9-C14 PFCA related substances given by stakeholders (20-45%), and applying different release factors (see Table 1-10) approximatley 12.6 t C9-C14 PFCA related substances were released post 2015 as unintended impurities from the use of PFOA related substances in textiles, fire-fighting foams, paper, paints and inks, photographic applications and semiconductors. According the the restriction of PFOA and PFOA-related substances from 2020 on the release of C9-C14 PFCA related substances will be reduced to 1.43t/a after 2020 (see Table 1-10).

With industry shifting to short C6-based fluorochemicals, the amount of C9-C14 PFCAs as unintentional by-products is lower (see chapter A.1.1 in the Annex for further details). Mixtures sold to industry contain C9-C14 PFCAs and related substances in trace levels up to 25 ppb and 260 ppb, respectively. However, the manufactured volume of C6 based fluorochemicals used within the EU and imported into the EU is not known. Therefore, release rates of C9-C14 PFCAs, their salts and related substances from manufacturing and using those short chain alternatives cannot be quantified.

During the manufacturing of C6 related substances, up to 30% C9-C14 PFCAs, their salts and related substances are intentionally manufactured. In the EU this fraction is seperated and reworked. However it is not sure if this technology is used outside the EU as well. Thus, imported mixtures of C6-based fluorochemicals may contain higher levels of C9-C14 PFCAs, their salts and related substances.

No information is available on the uses of C9-C14 PFCAs outside Europe. Wang et al., 2014 estimated a decreasing trend in countries outside the EU, but a phase out is not foreseen in the near future (see chapter B.9.1.2.1 for details).

In conclusion emissions of C9-C14 PFCAs, their salts and related substances from articles and mixtures containing intentionally used C6- and C8-based fluorochemicals are possible. A continued exposure from those uses with a decreasing trend is expected during the next years within the EU.

## 1.1.5.1.4. Releases of C9-C14 PFCAs from waste water treatment plants

C9-C14 PFCAs, their salts and related substances occur as impurity in a huge amount of consumer articles and mixtures such as textiles, cosmetics and cleaning agents, that contain other per- and polyfluorinated substances. Articles and mixtures purchased some years ago may contain perfluorinated substances higher levels of C9-C14 PFCAs and related substances than those available today. The reason is that C8-based fluorochemicals were used which contained higher concentrations of C9-C14 PFCAs and related substances compared to the use of short chain alternatives or even fluorine free articles and mixtures.. Due to their long period of use, especially textiles may contribute to C9-C14 contamination from former uses of different perfluorinated compounds. Articles and mixtures containing more or less C9-C14

PFCA impurities are found in almost every household in the EU. This results in a wide dispersive release of these substances into air and into waste water e.g. laundry. It is impossible to gather all single release points, however WWTPs are a major source of the released C9-C14 PFCAs, their salts and related substances. C9-C14-PFCAs will not degrade in the WWTPs and therefore they will reach the effluent water or accumulate in sewage sludge. Moreover, C9-C14 PFCA related substances degrade in WWTPs to the corresponding perfluorinated acids (C9-C14 PFCAs). Thus, the amount of C9-C14 PFCAs is usualy higher in the effluent compared with the influent. Based on measured concentrations in effluent water and sludge and using data for default WWTPs according ECHA Guidance document, the release of C9-C14 PFCAs into the European environment was estimated. Different authors reported varying concentrations of C9-C14-PFCAs from below the detection limit up to several µg per kg sludge or effluent water. The concentrations of C9-C14 PFCAs depend on the shares of the water qualities to be treated, the technical equipment in the WWTPs, the treatment stages and further factors. Usually, the concentration of the PFCAs in the sludge is much higher than in effluent water. But, due to the enormous amount of effluent water (comparing to the small amount of sludge) the release of long-chain PFCAs (including C9-C14 PFCASs) to the environment via WWTP effluent water is not negligible. Because of several restriction measures, like for PFOA and PFOS, the content of C9-C14 PFCAs is noticeable decreasing in consumer articles and mixtures and as a consequence also in the WWTP effluent and sludge. It could be assumed, that about 0.005 t of C9-PFCA, about 0.099 t of C10-PFCA and 0.012 t of C12-PFCA are released cumulatively into the European environment via WWTP effluents (effluent water and sludge) between 2015 and 2022 (see annex B.9.1.2.2 for details).

Composting of organic waste and sludge represents an important and well established part of waste management in Europe. Composting and digestion of organic residues and application of compost to soils follow the principle of sustainability. Between 50% and 100% of accruing sludge from WWTPs is composted or directly used in European agriculture. On the basis of the evaluated data from the WWTPs, we assume that 35 -70 kg of C9, 10, 12-PFCA could be directly emitted to the soil from sludge until 2022.

A wide spread release of the C9-C14 PFCAs, their salts and their related substances into the environment has to be considered despite there are no intentional uses of long-chain PFCAs announced by European industries (see Annex A.2). Based on the assuming calculations and the expecting emissions from wide spread use of articles and mixtures that unintentionally contain C9-C14 PFCAs and related substances, 116 kg of C9-C14 PFCAs will be emitted to the European environment via WWTP until 2022. In this dossier we present a worst case scenario that bases on the extrapolation of measured values in WWTP. Evaluating the data, the degradation of precursors may still be underestimated. Moreover, C9-C14 PFCA related substances can be released additionally to the atmosphere from WWTPs. Additionally, particle-bound C9-C14 PFCAs can be released into the air. Thus, the releases of C9-C14 PFCAs and related substances from WWTPs may even be higher in Europe.

## 1.1.5.1.5. Trends of C9-C14 PFCAs in the environment

C9-C14 PFCAs and related substances are found ubiquitously in the environment including wildlife and remote areas. Examples are provided in Appendix B.2.

In European wildlife, the levels of C9-C14 PFCA have been found to increase during the last years. Significant increases have been observed for C9-C14-PFCAs in migratory birds, marine fish and their predators as well as in terrestrial mammals (details are presented in Annex B.4.2.5). In some studies a decreasing trend was indicated in samples from the most recent 2-3 sampling years. Decreasing trends of C9-C15-PFCAs in environmental samples have been reported by Ahrens et al. in harbour seals from the German Bight sampled between 1999 and 2008 (Ahrens et al., 2009b).

Trend studies performed by the German Speciman Bank show that levels and trends of C9-C11 PFCAs vary even for one species, depending on the sampling site. In bream from the

river Elbe C10-PFCA peaked in 2011, whereas in the river Rhine highest concentration were found in 2015 (the last sampling year).For deers in most sampling sites a decline of C9-PFCA and an increase of C10-PFCA until 2015 was shown.

Decreasing trends of C9-C14 PFCAs in German sewage sludge were reported during 2008 and 2013 (Ulrich et al., 2016). Nearly 5000 sludge samples derived from Bavarian municipal WWTPs were analysed between 2008 and 2013 for 11 PFASs. In general, there is a decreasing trend for all three substances in the time period analysed. The decrease of C9-C14 PFCAs in sludge might be used as an indiactor that also the release of C9-C14 PFCAs from WWTPs into surface water are decreasing similarly. This decreasing trend seems to correspond with the decreasing (unintentional) use and thus decreasing release of the substances during the last years.

### 1.1.5.2. Human exposure assessment

European human biomonitoring data, including remote locations such as Greenland, show that C9-C14 PFCA have been detected in various human body fluids such as serum and breast milk (Annex B.9.2 and Appendix I).

Overall, the concentrations of C9-PFCA, C10-PFCA and C11-PFCA in human serum are in the similar range of high pg/ml to low ng/ml in the respective studied population in the different countries. The levels of C12-PFCA, C13-PFCA and C14-PFCA in serum are slightly lower and in the pg/ml range.

Temporal trend studies show that the concentrations of C9-C13 PFCA in human serum have been increasing since the 1980s whereas the increase seem to level out or slightly decrease around 2010 (Yeung et al., 2013). The concentrations of C14-PFCA were too close to or below LOD for reliable temporal trend analyses (Gebbink et al. 2015, Yeung et al. 2013).

In breast milk the concentrations are lower than in serum. The concentrations of C9-C13 PFCA in breast milk are ranging from < LOD to low pg/ml (Antignac et al., 2013; Karrman et al., 2010). For C14-PFCA no concentrations > LOD were found.

### 1.1.5.3. Summary exposure assessment

Considering that during the manufacturing and use of PFOA, its salts and related substances C9-C14 PFCAs, their salts and related substances are manufactured unintentionally.

-   Manufacturing of PFOA and its salts: 0.21% C9-C14 PFCAs and their salts (Prevedouros et al., 2006)
-   Manufactuing of C8 relatated substances: 20-45% (mean 32.5%) C9-C14 PFCA related substances are manufactured unintentionally (stakeholder information)

Thus, applying the release factors presented in Table 1-10 approximately 12.26 t C9-C14 PFCA related substances are emitted per year within the EU from those uses during 2015 and 2020 until the PFOA restriction enters into force (see Table 1-10). After the PFOA restriction becomes binding in 2020 it is estimated that the release of C9-C14-PFCAs related substances from the remaining uses will be reduced to 1.4 t/year in the EU. These estimations are however highly uncertain and should be regarded as an indication.

Additionally, import of fluoropolymers such as PVDF, which may be manufactured by using the ammonium salt of C9-PFCA may be a further emission source for C9-C14 PFCAs. Further information on emissions are presented in chapter B.9 of the Annex.

PFOA-alternatives, the C6-based fluorochemicals also contain C9-C14 PFCAs as unintended byproduct:

- C6-related substances (transported isolated intermediates): low ppm range of C9-C14 PFCA related substances.
- C6-related substances (mixtures sold to industry): up to 260 ppb C9-C14 PFCA related substances.

Releases from those uses have not been estimated in this dossier because the estimation of manufacturing and import volumes of C6 based fluorochemicals was not in the scope of this dossier.

Additionally, it is estimated that about 116 kg of C9-C14 PFCAs are emitted in Europe into the environment by WWTPs until the year 2022. By using (composted) sludge as fertiliser, about 35 – 70 kg of C9-C14 PFCAs directly could be applied to soil.
European human biomonitoring data, including remote locations such as Greenland, show that C9-C14 PFCA are widely detected in body fluids such as serum and breast milk in human populations at pg/ml to ng/ml levels. Temporal trend studies show increasing levels from 1980s until approximately 2010 where the levels seem to level out or decrease.

Increasing levels of C9-C14 PFCAs in some European wildlife species and a decreasing trend in German WWTPs were reported. It is unclear why levels in wildlife are increasing, although the releases of the substances decline. It is possible that the levels in the studied species have reached the peak by now, but most recent data are not available.

*Table 1- 10: Estimated annual use volumes and releases of PFOA (red) and PFOA-related substances (blue), C9-C14-PFCAs (brown) and C9-C14 PFCA related substances (green) subject to the proposed restriction based on current use (worst case scenario) and post 2015 (more realistic scenario) based on the background document for the PFOA restriction (European Chemicals Agency, 2015a)*

| PFOA and PFOA-related substances in... | Volume used/imported t/a 'post 2015' | Release factor % | Emission estimate t/a 'post 2015' | Releases of C9-C14 PFCAs and related substances 'post 2015 | Releases of C9-C14 PFCAs and related substances 'post 2020 |
|---|---|---|---|---|---|
| Import of PFOA | 0 | 0.35 (70 x 0.5) | 0 | 0 | 0 |
| in articles | 3 | ? | ? | ? | ? |
| Fluoropolymers | | | | | |
| import and use of PTFE mixtures | 15 | 38 | 5.7 | 0.01* | 0 |
| (volume used outside EU) | (9 – 280) | (80) | (7.2 – 224) | (0.01-0.15) * | |
| Manufacture of PFOA-related substances (central estimate) | 30 -300 (165) | 0.05 | 0.015 – 0.15 (0.083) | 0$ | 0$ |
| Textiles (uses of C8 based chemicals | | | | | |
| Use in EU | 300 | 2* | 6 | 1.95§ | 0.2§ |
| Import in articles (central estimate) | 300 – 3,000 (1,500) | 1* | 3 – 30 (15) | 0.98– 9.8§ (5,4) § | 0.09-0.98§ (0.54) § |

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| PFOA and PFOA-related substances in… | Volume used/imported t/a 'post 2015' | Release factor % | Emission estimate t/a 'post 2015' | Releases of C9-C14 PFCAs and related substances 'post 2015 | Releases of C9-C14 PFCAs and related substances 'post 2020 |
|---|---|---|---|---|---|
| Fire-fighting foams (central estimate) | 15 – 30 (23) | 4.5** | 0.7 – 1.4 (1) | 0.23 – 0.46 (0.69) | 0.23 – 0.46 (0.69) |
| Paper (central estimate) | 45 – 60 (53) | 2* | 0.9 – 1.2 (1.1) | 0.29 – 0.39 (0.68) | 0 |
| Paints and inks (central estimate) | 15 – 30 (23) | 54.5** | 8.2 – 16.4 (12) | 2,67 – 5,33 (3,9) | 0 |
| Photographic applications | 0.001/0.1 | 0.02/? | 0.0000002/? | 0.000000065/? | 0.000000065/? |
| Semiconductors | 0/0.02 | -/3.8 | -/0.000076 | -/0.000025 | -/0.000025 |
| Total PFOA/C9-C14 PFCAs PFOA-related substances/C9-C14 PFCA related substances (central estimate) | 18/ 675 – 3,420*** (1,900) | > 32/ 1.7 -2.8 (1.9) | >5.7/ 18.8 – 55.2*** (35.2) | 0.01/ 6.12 – 17.9*** (12.62) | 0/ 0.52 – 1.64*** (1.43) |

* assuming that 0.1% of C9-PFCA and 0.01% of C10-C14 PFCA are unintentionally present (based on van der Putte et al 2010); $ manufacture ceased in 2015; § Estimate: 10% are still treated with C8

### 1.1.6. Risk characterisation

C9-C14-PFCAs were added to the REACH Candidate List as Substances of Very High Concern due to their PBT or vPvB-properties. C9- and C10-PFCA are additionally toxic for reproduction. Furthermore, C9-C14 PFCA-related substances can degrade to the corresponding perfluorinated acids and must therefore be considered as PBT/vPvB substances as well (Regulation No 1907/2006 Annex XIII) (in the same manner as PFOS-related substances have previously been treated under REACH (Regulation No 1907/2006 Annex XVII) and currently in the EU POPs regulation (Commission Regulation (EU) No 757/2010)) and PFOA-related substances under REACH (Commission Regulation (EU) No 2017/1000).

Derivation of PNECs is not applicable to substances with these properties (REACH recital 70/ Annex I, para 6.5). Exposure of the environment (and humans) with these substances should be reduced to the extent possible.

It was demonstrated in chapter 1.1.5 that the environment, including human population, is exposed to C9-C14 PFCAs, their salts and related substances via various exposure pathways (wide dispersive, mainly from releases in the past). Due to the PBT/vPvB-properties environmental risks cannot be quantified.

Available emission estimates (see 1.1.5.3 and annex B.9) and environmental monitoring data (details in annex B.4.2.5 and appendix B.2 are a proxy for an unacceptable risk.

# 1.2. Justification for an EU wide restriction measure

A large variety of emission sources contribute to the exposure of humans and the environment to C9-C14 PFCAs (see chapter B.4. and B.9. in the Annex). Human biomonitoring shows that the whole EU population is exposed to C9-C14 PFCAs (Appendix I) and monitoring studies show the ubiquitous presence of the substances in all environmental media. Thus, exposure to humans and the environment takes place in all EU-Member States. A restriction on C9-C14 PFCAs, their salts and related substances is the most appropriate way to limit the risks (due to further releases into the environment) for human health and the environment on an EU level (see more information in Annex C).

Therefore national regulatory actions will not adequately manage the risks of C9-C14 PFCAs and related substances.

The restriction on PFOA, PFOA-related substances and its salts will become binding in 2020 with certain derogations. This so called C8-chemistry represents the preferred choice of chain length for almost all fluorinated applications due to its superior properties with regard to quality and cost. A large part of the industry has already substituted C8-based chemicals towards C6-technology or fluorine free alternatives. It is believed that the vast majority of the remaining companies using C8-chemistry will substitute to C6 or fluorine free alternatives. However, it may be possible that companies may consider the use of C9-C14 PFCAs, their salts and related substances in the future, especially after the restriction on PFOA, its salts and related substances becomes binding in 2020. Thus, an EU-wide measure is necessary to prevent possible future manufacturing and use resulting in increasing releases into the environment.

The restriction will complement the decreasing trend in the use of C9-C14 PFCAs, its salts, and related substances triggered by the US-EPA PFOA Stewardship Program (see Annex E.1.1), the Canadian restriction on long-chain PFCAS, the Norwegian ban of PFOA in consumer articles and the EU-restriction of PFOA, its salts and related substances. An EU wide restriction

will prevent and reduce the releases of C9-C14 PFCAs, their salts and related substances within the EU in a hormonised manner. Moreover, a restriction within the EU may be the first step for global action.

# 1.3. Baseline

Trend analyses in organisms (see chapter Annex B.4.2.5) show that there are increasing trends for C9-C14-PFCAs in some species in Europe, such as migratory birds, marine fish and their predators, and terrestrial mammals. One study reported decreasing concentrations in harbour seals sampled in the German Bight between 1999 and 2008. C9-C14 PFCA related substances were found to increase in osprey eggs in Sweden. Temporal trend studies for human blood show that the concentrations of C9-C14 PFCA have been increasing since the 1980s until approximately 2010 when the increase seems to level out or slightly decrease (Annex B.9.2). Hence, there is a high potential that ongoing releases of these substances into the environment will result in long-term human and environmental exposure to C9-C14 PFCAs.

Since 2002, there is a trend amongst manufacturers in the USA, Canada, Europe and Japan to replace long-chain PFCAs and their potential precursors with chemicals containing shorter perfluoroalkyl chains or with non-perfluoroalkyl products. This decreasing use-trend for C9-C14 PFCAs, their salts and related substances is observed as well considering data obtained from the Swedish Products Register. Moreover, registrants inactivated REACH registration dossiers for long-chain PFCAs, including C9-C14 PFCAs and related substances in 2017 (see Annex A.1.1).

According to the results of the stakeholder consultation, no current intentional uses of C9-C14 PFCAs, their salts and related substances are known for companies located in the EU. The substances are mainly manufactured unintentionally during the manufacturing of PFCAs containing a carbon chain of less than 9 carbon atoms. For manufacturing PFOA, higher amounts of C9-C14 PFCAs are usually manufactured compared with the intentional manufacturing of alternatives containing a carbon chain of less than eight carbon atoms, such as perfluorohexanoic acid based substances (C6) (Annex B.2). C9-C14 PFCAs, their salts and related substances, thus, may occur as impurities in articles and mixtures if fluorinated substances containing a carbon chain of less than nine carbon atoms are used (see chapter Annex A.1). The availability of fluorine free alternatives for many sectors is growing (see chapter Annex E.2.3.2). However one intentional user has been found for imported semiconductors. The company reported the use of C10-PFCA in a small number of semiconductors imported into the EU. An alternative is available and will be used in the near future. Additionally there are hints that C9-C14 PFCAs are intentionally used outside the EU, such as the use of C9-C14 PFCAs in semiconductors.

The global market for fluoropolymers is growing. In the literature, C9-PFCA is described to be used as emulsifier for manufacturing polyvinylidene fluoride (PVDF). Stakeholders indicated a general transition trend to move from eight and nine carbon perfluorinated carboxylate polymerization aids (C8-PFCA/C9-PFCA) for manufacturing fluoropolymers to certain mono- or poly-fluoroether carboxylates or other shorter-chain fluorinated substances. According to the stakeholder consultation C9-C14 PFCAs, their salts and related substances are not used in EU for manufacturing fluoropolymers. It is possible that manufacturers outside the EU still use C9-C14 PFCAs, their salts and related substances for manufacturing fluoropolymers. Thus, imported articles may still contain these substances. The demand for thermoplastics (e.g. PVDF) is predicted to grow between 3.1 to 6% annually in EU until 2022. Considering the rising demand for fluoropolymers, an increase of imported articles containing C9-C14 PFCAs residues is possible.

The voluntary US-EPA 2010/2015 Stewardship Program and the Canadian restriction on long-chain PFCAs are the only existing measures to reduce the releases of C9-C14 PFCAs. However, indirectly, also the Norwegian ban of PFOA in textiles and the EU-restriction on PFOA have a reducing effect on the unintentional use of C9-C14 PFCAs. However, imported articles and mixtures may still contain higher amounts of C9-C14 PFCAs and their related substances because it is possible that outside the EU, e.g. in Asia, long-chain PFCAs including C9-C14 PFCAs are still used. C9-C14 PFCAs are listed in the Candidate List, which means there is a duty to inform in the supply chain on articles, which contain above 0.1% of either of these substances (Article 33). This could have an impact on use since an inclusion in the Candidate List clearly establish that the substances have properties for being considered as a substance of very high concern, which should be substituted wherever possible. However, when detected in articles the concentration is often below 0,1 % that means that the duty to inform in the supply chain is not applicable. In addition, C9-C14 PFCA related substances are not listed and therefore not covered by information requirements.

Moreover, it may be possible that without further regulation C9-C14 PFCAs their salts and related substances are used as C8- substitutes once the PFOA restrictions is enforced in 2020. However, to date there are no indications that this case would actually occur.

Considering that C9-C14 PFCAs and related substances are found as impurities in products based on shorter-chain PFCAs and their related substances, a continued exposure from those uses with a decreasing trend can be expected in the next years within the EU. No information are available on the scope of uses of C9-C14 PFCAs outside Europe. Therefore, we assume that uses are ongoing, meaning that imported goods may still contain C9-C14 PFCAs and emissions from those articles continue in the near future. Since the articles treated with long-chain PFCAs and their related substances have life-times from days to decades (e.g. wrapping paper vs. furniture), releases will continue although the uses have stopped.

# 2. Impact assessment

## 2.1. Introduction

When assessing the human health and the environmental impacts of the proposed restriction, the specific concerns of C9-C14 PFCAs, their salts and related substances as PBT/vPvB substances have to be taken into account. These concerns are particularly related to the potential of C9-C14 PFCAs to persist in the environment, which means that they do not degrade under normal environmental conditions (see more details in Annex B.4.1.). This means that even if the releases of C9-C14 PFCAs and elated substances will cease, it will not result in an immediate reduction of environmental concentrations. In addition to their extreme persistence, C9-C14 PFCAs are mobile in the environment and have the potential to be distributed over long distances, e.g. via long range atmospheric transport. As a consequence, C9-C14 PFCAs are present in the environment on a global scale, also in remote areas where releases of the substances are negligible (see Annex B.4.2.5). This implies that continuous releases may lead to rising concentrations in the environment and exposure of humans and the environment to C9-C14 PFCAs will continue and possibly increase. In combination with the potential of C9-C14 PFCAs to accumulate in living organisms (bioaccumulation) as well as the toxicological properties of C9- and C10 PFCAs (for details see Annex B.5. and Annex B.8), continuous use and releases of C9-C14 PFCAs and related substances may lead to adverse effects on human health and the environment arising from long-term exposure. These effects will be very difficult to reverse, once they have occurred.

Owing to lack of knowledge and data (in particular of long-term effects), the risks of PBT substances cannot be predicted and quantified by standard risk assessment methods. This means that the magnitude and extent of the risks of C9-C14 PFCAs and related substances

as PBT/vPvB substances remain uncertain. To inform risk management, the risks of PBT substances are qualitatively assessed taking into account the hazards as well as release patterns and exposure pathways.

Against this background, it is evident that also the physical impacts on human health and the environment of reducing the releases of C9-C14 PFCAs and related substances cannot be quantified.

The restriction is necessary to avoid the possibility that C9-C14 PFCAs, their salts and related substances are used as substitutes when the PFOA restriction becomes binding in 2020 and to reduce the environmental release of the substances present in imported articles and mixtures intentionally treated/manufactured with C9-C14 PFCAs, their salts and related substances.

# 2.2. Risk management options

## 2.2.1. Proposed options for restriction

Since the subtances are most probably not intentionally used within Europe and imported articles are a possible emission source of intentionally used C9-C14 PFCAs, their salts and related substances, a restriction on only single uses would not result in sufficient exposure reduction.

In terms of risk reduction capacity, a total phase out of manufacturing, use and contents in articles and mixtures (including imports) is needed

## 2.2.2. Proposed restriction

*Table 2- 1: Restriction on the manufacturing, use, placing on the market and import of C9-C14 PFCAs, their salts and related substances.*

| | |
|---|---|
| Perfluoroalkyl carboxylic acids (branched and/or linear) with the formula:<br><br>$CF3$-$(CF2)_n$-C, n=7 or 8 or 9 or 10 or 11 or 12 as structural elements including their salts and including all combinations thereof | 1. Shall not be<br><br>a) manufactured, or placed on the market as substances on their own;<br><br>b) used in the production of, or placed on the market in: |
| Perfluoroalkyl carboxylic acids (branched and/or linear) with the formula:<br><br>$CF_3$-$(CF_2)_n$-, n=8-13 as a structural element, including their salts |     i.    another substances, as a constituent,<br>    ii.   a mixture,<br>    iii.  an article or any parts thereof, |
| Any related substance (including its salts and polymers) with the above defined linear and/or branched perfluoroalkyl structural elements that can degrade to C9-C14 PFCA | in a concentration equal to or above 25 ppb for the sum of C9-C14 PFCAs and their salts or 260 ppb for the sum of C9-C14 PFCA related substances<br><br>2. Paragraph 1 shall apply 18 month from entry into force of the restriction |
| The following substances are excluded from this designation: | 3. Paragraph 1 shall not apply to |

| | |
|---|---|
| <ul><li>CF$_3$-(CF$_2$)$_n$-X, n > 7, where X= F, CI, Br<br>including any substance with linear and/or branched perfluoroalkyl elements and all mixtures thereof</li><li>CF$_3$-(CF$_2$)$_n$-SO2X', n > 7 where X'=any group, including salts</li><li>CF$_3$-(CF$_2$)$_n$-C(=O)OH, n > 12 including salts</li></ul> | a) the manufacture of a substance where this occurs as an unintended by-product of the manufacture of fluorochemicals with a carbon chain equal to or shorter than 8 atoms;<br><br>b) a substance that is to be used, or is used as a transported isolated intermediate, provided that the conditions in Article 18(4) lit. a) to f) of this Regulation are met;<br><br><br>4. Paragraph 1(b-iii) shall not apply to<br><br>a) Articles placed on the market before the restriction becomes effective |

The proposal restricts the manufacturing of C9-C14 PFCAs, their salts and related substances within the EU. Further the proposal restricts the use, placing on the market and import of C9-C14 PFCAs, their salts and related substances as substances on their own or in a mixture or in an article in a concentration equal to or above 25 ppb for the sum of C9-C14 PFCAs and their salts or 260 ppb for the sum of C9-C14 PFCA related substances.

C9-C14 PFCAs, their salts and related substances are mainly unintended by-products during the manufacturing of per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms, such as perfluorooctanoic acid (PFOA) based substances and perfluorohexanoic acid based substances. The latter are alternatives of the C8-based chemistry. It is the intention that this restriction should not apply to the manufacturing of these so called short-chain alternatives and a specific derogation is introduced.

The proposed restriction is defined as a ban on the use of C9-C14 PFCAs, their salts and related substances. This includes a restriction on the manufacturing, placing on the market and use of C9-C14 PFCAs, their salts and their related substances in the EU and the import of C9-C14 PFCAs, their salts and their related substances in articles into the EU.

This option will phase out the manufacturing, placing on the market and use of C9-C14 PFCAs, its salts, and related substances 18 months after entry into force. It is suggested to enforce this restriction together with the restriction of PFOA. The phase out will cover C9-C14 PFCAs, its salts, and related substances on its own, in mixtures and articles above a content of the proposed set of thresholds. It also covers imported articles and imported mixtures.

The proposed restriction does not cover the "second-hand" market (e.g. textiles). 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. Therefore a derogation for the second hand market is assessed as reasonable.

The consulted stakeholders stated that there are no intentional uses of C9-C14 PFCAs, their salts and related substances within the EU. It may, however, be possible that during the

public consultation more intentional uses may be reported. In this case possible derogations need to be assessed[2]. One company reported the use of C9-C14 PFCAs (in the low kg range) in a small number of semiconductors which are imported into the EU. The company requested a longer transitional period until 2023. However, C9-C14 PFCA levels in the articles were not reported. Thus, a transitional period for semiconductors and articles containing semiconductors until 2023 seems reasonable but cannot be justified based on the data provided.

Since the restriction of PFOA will be enforced in 2020 and the fact that there are no identified intentional uses of C9-C14 PFCAs a transitional period of 18 month after entry into force seems reasonable. This would mean the two restrictions would enter into force about the same time. As previously stated, a rather short transitional period is important to reduce the incentives that C9-C14 PFCAs, their salts and related substances are used as C8-substitutes when the PFOA restriction becomes binding.

**Threshold:**

Based on the information provided by industry, C9-C14 PFCAs, their salts and related substances occur as unintended by-product during manufacturing of PFCAS containing a carbon chain of less than nine carbon atoms . With the shift from C8 to short-chain alternatives, such as C6 and C4-based substances the amount of unintentional manufactured C9-C14 PFCAs is reduced. Industry stated to be able to comply with similar thresholds as set for the PFOA restriction, i.e. 25 ppb for the sum of C9-C14 PFCAs and the salts and 1000 ppb for the related substances.

- The Fluorocouncil suggested a threshold of 25 ppb for any of the acids or 1000 ppb for the sum of all substances related to any one of the individual acids covered by the restriction.
- However, further information were provided that a threshold for 260 ppb (for the sum of C9-C14 PFCA related substance is feasible for mixtures and articles placed on the EU market.

In transported isolated intermediates C9-C14 PFCAs, their salts and related substances are present in the low ppm range when intentionally using C6-based chemistries. To further allow the manufacturing and processing of the C6-based chemistries stakeholders asked either for a derogation of the transported isolated intermediates or for setting a higher threshold. Thus, based on the information provided, it is concluded that the following thresholds are feasible for mixtures and articles placed on the market:

- **25 ppb for the sum of C9-C14 PFCAs and their salts**
- **260 ppb for the sum of C9-C14 PFCA related substances**

Articles and mixtures tested for C9-C14 PFCAs, their salts and related substances in the past (see Annex B.2. for details) seem to mainly contain lower concentrations, thus the data presented suggest that the proposed threshold of 25/260 ppb is reasonable.

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[2] Assuming suitable justifications are provided
(https://echa.europa.eu/documents/10162/13641/public_consultation_guidance_en.pdf/7c4705d5-ad01-43ed-a611-06f1426a595c).

## 2.2.3. Justification of the selected scope of the proposed restriction

Releases of PBT/vPvB-substances into the environment need to be minimised. The following factors have to be considered for this case:

- C9-C14 PFCAs are ubiquitously present in the environment and in human blood and breast milk of the general population.

- C9-C14 PFCA related substances contribute to environmental concentrations of C9-C14 PFCAs

- Exposure pathways of C9-C14 PFCAs, their salts, and related substances are diverse, as described in Annex B.9, and include industrial sites (e.g. production and processing sites of per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms) as well as consumer articles and mixtures (wide dispersive use). Furthermore, imported articles and mixtures may contain intentionally used C9-C14 PFCAs, their salts, and related substances.

- Effects of PBT/vPvB substances on human health and environment cannot be predicted for the long term.

Thus, it is justified to include all substances into the restriction comprising the structural pattern of a 8 to 13 perfluorinated carbons in a row, i.e. C9-C14 PFCAs and their related substances.

Moreover, also the use of the so called C6 technology contains impurities of C9-C14 PFCAs, their salts and related substances as well. Thus, manufacturers of the C6 technology requested a derogation for manufacturing short-chain per- and polyfluorinated substances and for transported isolated intermediates during the stakeholder consultation.

The restriction proposal also includes recycled material and articles made from recycled materials. In this dossier, we have demonstrated that humans and the environment are exposed to C9-C14 PFCAs, its salts and related substances. Because of the extreme persistence of the substances, each release increases the environmental stock of C9-C14 PFCAs. When recycled materials contain these substances, releases are ongoing in the future.

This is in line with the Commission's regulation (EU) 2017/1000 on PFOA. As the Commission states in its detailed explanation for PFOA, 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. This, in our opinion, would also be the case for articles and mixtures containing C9-C14 PFCAs, its salts and related substances. In addition (as the Commission also states for PFOA), substances with POP properties, in line with the objectives of Regulation (EC) No 850/2004, should not be recycled. C9-C14 PFCAs, their salts and related substances have not yet been identified as POPs under the Stockholm Convention, however, their properties are similar to PFOA which is being discussed.

Articles and mixtures placed on the market before the proposed restriction enters into force (i.e. second hand articles) are excluded from the scope. There are primarily two reasons for this:

1. The second hand market is difficult to control, in many cases this involves one single article donated or sold by one consumer to a non-profit organisation, which in turn is purchased by another consumer. It would not be practical to revoke single articles from the market.

2. To use e.g. a jacket as long as possible before it turns into waste is a sustainable management of resources.

A short transitional period of 18 month after entry into force is reasonable. There are no reported uses within the EU and we propose a longer transitional period for the use in semiconductors.

# 2.3. Restriction scenario

C9-C14 PFCAs and related substances are found ubiquitously in the environment including wildlife and remote areas (see Annex B.4.2.5). As shown in Annex A.2.4., C9-C14 PFCAs, their salts, and related substances can be found in many (imported) articles and mixtures which to some part could explain the findings in the environment. Fluorine free alternatives are already available on the market and widely used in several branches (see Annex E.2.3.2).

Industry based in Europe has already shifted from the use of long-chain per- and polyfluorinated substances to either short chain homologues (such as C6-based chemistries) or fluorine free alternatives. Thus, there are no major effects foreseen for stakeholders. However, importers of articles may be effected by the restriction, (one stakeholder reported the use of C9-C14 PFCAs in imported semiconductors) because they have to make sure that the imported articles comply with the thresholds for C9-C14 PFCAs, their salts and related substances. This is still an area of uncertainty since we do not know to what extent C9-C14 PFCAs are included in imported articles. Part of the compliance cost which might occur can be shared with the PFOA restriction, since actions taken to comply with the PFOA restriction can reduce the compliance cost for this restriction. National authorities need to enforce the restriction, thus they need to control certain imported articles. Since C9-C14 PFCAs can be expected in similar articles as PFOA and the PFOA restriction will entry into force in 2020 we consider that this restriction will only imply a minor burden on national authorities.

# 2.4. Assessment of the restriction option

### 2.4.1. Economic impacts

Since no intentional usage of C9-C14 PFCAs and their related substances have been identified within the EU during the stakeholder consultation (except for one use in imported semiconductors) there are also few economic consequences which have been identified.

Regarding the use of PVDF-fluoropolymers for thermoplastics (see Annex A.2.2. for details) industry contacts stated that within the EU C9-C14 PFCAs and their salts are not used anymore for PVDF manufacturing. It is however assumed that some part of the industry, most certain located outside the EU may experience cost increases when transition is made to C9-C14-PFCA free production process.

In the EU C9-C14-PFCAs are manufactured as unintended side fraction during the manufacturing of per- and polyfluorinated chemicals containing a carbon chain of less than nine carbon atoms, e.g. based on a C6- per fluorinated carbon chain. During the manufacturing of C8-based substances, the amount of C9-C14 PFCAs as impurities is higher compared with the levels in the C6-based substances. In the EU, North America and Japan, the manufacturing and use of C8-based substances has been reduced drastically during the last decade. This transition may have started also in other countries, such as China and Russia. Imported articles may still contain higher unintended fractions of C9-C14 PFCAs compared with articles manufactured and treated with PFCAs containing a carbon chain of less than 9 carbon atoms in the EU. Costs might occur for importers, downstream users and

consumers if these articles can no longer be imported. Part of these compliance costs can potentially be shared with the PFOA restriction.

## Administrative costs

Some companies in the outdoor textile industry have indicated that they intend to send some of their products to independent laboratories for testing once a restriction is implemented. This is done to test the occurrence of C9-C14 PFCAs through unintended use. This will induce some costs for the companies (see annex E). Part of these testing costs can most probably be shared with the testing needed to comply with the PFOA restriction. Even though it has not been implied in the data collection process by any other stakeholder it cannot be ruled out that similar testing costs might be incurred on other type of companies.

## Substitute cost

No substitution costs have been identified since no use of C9-C14 PFCA has been identified in the EU, except for one example of C9-C14 PFCAs in imported semiconductors. Unless anything else is reported further along in the stakeholder consultation process, we assume that there are no substitution costs in the EU. In Annex E.2.3.2 some costs were provided to produce fluorine free articles. However, these costs apply for substituting PFOA and short chain per- and polyfluorinated substances, such as the C6-based chemistries.

## Comparison with other similar PBT & vPvB, PFAS cases

In cases with other similar PBT and vPvB substances, where concentrations have reached the recommended guidance level, for example PFAS in drinking water in Sweden (from firefighting foam), it has been proven (Swedish Chemicals Agency, 2016), to be a cost effective measure to regulate these substances in beforehand rather than paying for the abatement and substitution cost afterwards. This follows from the large replacement costs for a contaminated water source, which makes the cost of regulation in beforehand much smaller than replacing the water source afterwards. We argue (for a similar hypothetical case) that it would be cost effective to regulate the use of C9-C14 PFCA and their related substances in beforehand as well rather than abating or replacing a water source if, if recommended guidance levels where to be exceeded.

## Remediation costs of contaminated sites

In the US C9-PFCA was detected as the major component in ground water, surface water and drinking water near a fluoropolymer manufacturing site in New Jersey[3]. The reason for the contamination is historical uses of Surflon, S111 a mixture containing primarily C9-PFCA, between 1991 and 2010. It was reported that 86,6% of the 125 t used during this time period were released to the environment. Because of elevated C9-PFCA concentrations in ground water, local authorities developed specific ground water limit values for C9-PFCA. Remediation costs were not reported but are assumed to be high.

The use of chemistries containing C9-C14 PFCAs as (unintended) by-products and historical uses of the substances has contributed to the contamination of (drinking) water and soil with corresponding high costs of remediation. Most of these contaminations have been caused by the use of PFASs (including long-chain PFASs) in fire-fighting foams in fire events. The remediation costs are mainly related to the treatment of ground/drinking water and the excavation and disposal of contaminated soil. The severity and extent of the damage caused and the related costs entailed differ between the cases reported. In some cases the total remediation cost is not known yet or not reported. Those costs are, however, usually

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[3] http://www.state.nj.us/dep/dsr/pfna/

attributed to (historical) contamination with PFOA or PFOS. C9-C14 PFCAs are also present in those contaminated sites when PFOS or PFOA was used intentionally.

**Enforcement Cost**

Average enforcement costs have been identified in connection to the restriction on lead compounds in PVC for EU28 Member State Agencies to ensure compliance with EU regulation, with reference to Milleu, (2012) and RPA, (2012). In these reports ECHA assessed the administrative cost of member states to comply with restrictions to be approximately EUR 55 600 per year. This number should only be seen as an indications of the magnitude of the enforcement costs, since a variation in costs is observed for different restrictions. It is in general believed that the enforcement costs of this restriction will be lower than on average since some of these costs can be shared with the enforcement costs associated with the PFOA restriction. An inspection and the following testing for the occurrence of both PFOA and C9-C14 PFCA in articles at the same time is cheaper than dining two separate inspections and testing procedures. Thus, the costs described above can already in part be attributed to the enforcement of the PFOA-restriction.

**Competition**

It is anticipated that this restriction will have no effect at all on competition, since all companies on the common market are affected in the same way.

## 2.4.2. Human health and environmental impacts

### 2.4.2.1. Human health impacts

The human exposure to C9-C14 PFCAs, their salts and related substances have the potential to cause adverse health effects, considering the PBT or vPvB properties of these substances. The toxicological profile of C9-C14 PFCAs (described in Annex B.5.) lead to the classification of C9- and C10-PFCA i.e. as Repr. 1B. (See section 1.1.3 -1.1.6 for details).

In Annex B.9. and Appendix I it is demonstrated that there is an on-going human exposure to C9-C14 PFCAs their salts and related substances. C9-C14 PFCAs are detected in human blood and breast milk samples globally and in the EU, including remote locations such as Greenland. Consumers are exposed to C9-C14 PFCAs via food, drinking water and house dust. Food is the major source of exposure for the general population. Furthermore, drinking water exposure is dominant for populations near sources of contaminated drinking water.

Some of these detected C9-C14 PFCA levels in human blood and serum have also been seen to increase or level out despite a decreasing time trend for the use of C9-C14 PFCA in manufacture and production. Increasing time trends have also been observed in human breast milk (see Appendix I for details). One explanation for this may be their persistent and bioaccumulating properties.

To date only indications of serious human health risks are documented, but since these substances persist and accumulate in humans and wildlife, releases are not reversible. It may thus be possible that serious health concerns related to C9-C14-PFCAs-exposure may be documented in the future. Thus, it is important that releases are reduced to a minimum and possible future uses of the substances are prevented.

No monetary valuation of human health impacts has been possible since clear cause and effect relationship between C9-C14 PFCA levels and different health impacts have not been concluded.

## 2.4.2.2. Environmental impacts

Several studies indicate an increasing time trend for C9-C14 PFCAs in the environment, from 1980 until 2010, when the increase seem to level out in some studies (see Annex B.4.2.5 for details). Increasing levels have been seen in both migratory birds, marine fish and their predators as well as in terrestrial mammals. This indicates that C9-C14 PFCAs are spread worldwide over several types of ecosystems and that increasing or non-decreasing trends of concentrations are observed at different levels of these ecosystems. At the same time releases into the environment from imported articles as well as from (unintended) production and manufacturing of C9-C14 PFCAs has been seen to decrease, at least in the EU and Northern America.

The discrepancy between the observed trends in nature (and humans) and the reduced release into the environment from (unintentional) production and manufacture may be explained by the extreme persistence and bioaccumulation of C9-C14 PFCAs. The stock of the substance in the environment is still increasing with each emission despite a decrease of the flow of C9-C14 PFCA into the environment. Moreover, stockpiles of C9-C14 PFCAs, e.g. in landfills continue to be a source of release of C9-C14 PFCAs which is difficult to capture.

The PBT and vPvB – properties of C9-C14 PFCAs (described in detail in Annex B.8) make it important to decrease the releases into the environment even further by the implementation of this restriction.

A monetary valuation of the potential decrease of C9-C14 PFCAs due to the implementation of this restriction is not possible. Standard procedure for PBT and vPvB substances is to use the reduced volumes as a proxy for the value of the reduction in terms of risk reduction. In this case no clear definition of the volumes of C9-C14 PFCAs, which might be reduced has been possible. Therefore no clear volume reduction is available to base the valuation on.

## 2.4.3. Other impacts, practicability and monitorability

### 2.4.3.1. Implementability and manageability

The proposed restriction is considered to represent an implementable option for the actors involved within the timeframe of 18 months. As described in Annex E.2. it appears that the necessary technology, techniques and alternatives are available and economically feasible. The RMO is in line with the US-EPA Stewardship Program. Thus, many industry actors are already preparing for using different substances and technologies from 2015 on.

### 2.4.3.2. Enforceability

Enforcement authorities can set up efficient supervision mechanisms to monitor industry`s compliance with the proposed restriction. Although there are no standard analytical methods to measure the content of C9-C14 PFCAs, their salts and related substances in articles and mixtures yet available, those methods are being developed already for the restriction of PFOA and related substances. The same methods can be applied for testing C9-C14 PFCAs and related substances.

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. Nevertheless, the establishment of an EU standard method could make the routine implementation of these tests easier, but it would also imply expenditure of time and money. At the same time the efforts for the development of such a standardized method are minimized due to the fact that there is already a standardized method (under development) for the very similar restriction of PFOS.

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 long-chain perfluorinated and polyfluorinated substances in textile articles that include long-chain per- and polyfluorinated compounds from C7 – C14.

Articles and mixtures to be targeted by sampling for enforcement are listed in Annex A.2.4.

### 2.4.3.3. Monitorability

There are numerous analytical methods reported in the scientific literature to measure C9-C14 PFCAs and some related substances in almost all environmental media, e.g. water, air, biota, and in humans.

Furthermore, at least in Germany, there is a norm (DIN 38407-42) for analysing C9-C14 PFCAs (and other 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 unfiltered 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 C9-C14 PFCA-related substances without knowing every single substance is the conversion of these substances to the corresponding acids and subsequent analysis of C9-C14 PFCAs, for example in water samples. Oxidation can be performed with hydroxyl radicals (Houtz and Sedlak, 2012). These 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 C9-C14 PFCAs are persistent substances, which will remain in the environment for ages even if releases to the environment are 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 C9-C14 PFCAs and related substances in the environment should result in decreasing C9-C14 PFCAs concentrations in such a trend monitoring. It might be sufficient to measure C9-C14 PFCAs in such a trend monitoring, because C9-C14 PFCAs related substance will be degraded to C9-C14 PFCAs in the environment. Decreasing trends in releases 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 C9-C14 PFCAs from environmental sinks, like sediment, might bias time trend in some cases.

## 2.4.4. Proportionality

The restriction is proportionate. It has small costs (and benefits) due to the fact that only one user of C9-C14 PFCAs has been identified, (in imported semiconductors). It nevertheless has risk reducing properties which we argue outweigh the cost to society associated with the implementation of this restriction (see section E.4.3.). It is thus anticipated that the cost-benefit ratio is either unaffected, or slightly improved.

# 3. Assumptions, uncertainties and sensitivities

For the data collection process a questionnaire has been sent out to 69 chemical companies, downstream users and to relevant industrial interest organisations (see Annex G). For the industrial organisations it is not known how many companies they contacted through their networks, but it is believed that all relevant stakeholders have been contacted either directly through the questionnaire or through targeted interviews conducted in the data collection process. It is therefore assumed that all possible actions with regard to proportionally have been made.

The response rate to published questionnaire was very low. Companies were invited to an expert meeting at the German competent authority, but from 19 invited companies, only five responded to the invitation and three took part in the meeting. Telephone interviews were done from March to April 2017. Altogether 69 companies were consulted from various branches (especially, textile, paper, furniture, fire-fighting, paints, building sector). Although the Dossier Submitter tried its best to receive information on uses etc. it is possible that certain branches were not consulted and thus it is possible that intentional uses may exist within the EU. However, we assume that those uses would be rather small scale uses for specific applications.

The data retrieved from the Swedish Product Register is in part made up from the imports of substances to Sweden. As described in Annex A.1 and A.2 these data show a sharp downward trend and indicate a total phase out for several applications such as textile and paper treatment. Most applications for which a use was reported in 2015 also contain PFOA. It is believed that most of these uses will be affected and disappear once the PFOA restriction becomes binding. It has however not been possible to verify this with certainty. It has not been possible to verify how well this data from the Swedish Product Register represents the trend for the rest of EU.

The restriction on PFOA, PFOA-related substances and its salts will become binding in 2020 with the exception of certain derogations. C8-chemistry represents the preferred choice of chain length for almost all fluorinated applications due to its superior properties with regard to quality and cost. A large part of the industry has already substituted C8-based chemicals towards C6-technology or fluorine free alternatives. It is believed that the vast majority (if not all) of the remaining companies using C8-chemistry will substitute to C6 or fluorine free alternatives. There is however the possibility that some of the users of C8 chemistry may use C9-C14 PFCAs and related substances after the PFOA restriction becomes binding.

An example of this are some small-volume uses of C9-C14 PFCA related substances, which have been identified through the Swedish Product Register (too small volumes to be registered in REACH). It is in the SEA assumed that these volumes in large are by-products (impurities) and complements to the use of C8-chemistry. We do however believe that there is a small but positive probability that these volumes can become second best substitutes to PFOA and that a substitution process could take place once the PFOA restriction becomes binding. It is however not possible to say with any certainty how large this substitution can become (if any).

It is nonetheless possible to exemplify what kind of volumes this substitution might lead to, by doing a scenario analysis using the data from the PFOA dossier. This is here done using textiles as an example. This is a simplified example where we assume that a possible substitution scenario from C8 chemistry to C9-C14 occurs when five percent of the C8 textile users choose to substitute to C9-C14 (the remaining 95 percent are assumed to substitute to C6 chemistry or to fluorine free alternatives). Since we do not have a reference point in C9-C14 substitution costs it is however not possible to quantify the magnitude of the cost that could occur if it is not possible to substitute from C8 to C9-C14 due to this restriction on C9-

C14. It is however possible to illustrate with a scenario case from the PFOA dossier. If textile industry are (economic) rational they will only substitute from C8 to C9-C14 (rather than C6 chemistry or fluorinate free) if the benefit from that substitution is positive. Thus the cost of substitution for not being able to substitute from C8 to C9-C14 is always less than the worst case of substitution cost from the PFOA dossier (under the assumption of economic rationality). The worst case of cost in EUR per kilo of substitution for textile for C8 to C6 chemistry or fluorinate free is EUR 35/kg. Thus we can argue that the cost of not being able to substitute to C9-C14 from C8 is always less than 35 EUR/kg if the industry act rational. In table 3-1 below the volumes are exemplified if five percent of the C8 textile industry (post 2015 central estimate values) chooses to substitute to C9-C14. A similar argument can be made for all other uses of C8. Included in this table is therefore also an example with the total (post 2015, central estimate) volumes for C8 and the corresponding volumes for a five percent substitution scenario towards C9-C14 for all PFOA usage.

*Table 3- 1: Estimated use of C8-chemistry for textile treatment*

| | C8 volumes for, central estimate ton/year (post 2015). | Worst case scenario, 5% of C8 volumes substitutes to C9-C14, ton/year (post 2015). |
|---|---|---|
| **Textile treatments in the EU.** | 300 | 15 |
| **Imports of textiles.** | 1500 | 75 |
| **Total C8 tonnage.** | 1900 | 95 |

It is at the moment not possible to assess if second best substitution from C8 to C9-C14 might occur once the C8 restriction becomes binding. It can however be argued in a similar way, as is done in the example above for textiles that substitution to C9-C14 for other application areas will always be more cost effective than the worst case from the PFOA dossier. This holds if the industry are acting rational and only substitutes if there is a net benefit to be made from that substitution. The cost measured in EUR/kg will however differ depending on the application area. For a total overview of all of these cost measures we refer to the PFOA restriction dossier.

We also regard imports as a source of uncertainty, since we do not know with certainty to what degree C9-C14 PFCAs are included in imported articles (see chapter E.4.5.2).

# 4. Conclusion

C9-C14 PFCAs are substances of very high concern based on their PBT/vPvB properties. C9-C14 PFCAs related substances can degrade to the extreme persistent C9-C14 PFCAs. Thus they need to be considered as PBT/vPvB substances as well.

C9-C14 PFCAs, their salts and C9-C14 PFCA related substances do not occur naturally. However, they are ubiquitously present in the environment, also in remote areas, because they can be transported over long distances via water and air. This results in findings in rivers, oceans, drinking water, the atmosphere and biota. Moreover, C9-C14 PFCAs are present in human blood of the general population. Human exposure takes place via the environment, e.g. consumption of drinking water and food, or from emissions from articles and mixtures, e.g. via uptake of contaminated indoor dust. Numerous direct and indirect sources of C9-C14

PFCAs, their salts and C9-C14 PFCA related substances contribute to the overall environmental emissions of C9-C14 PFCAs.

Temporal trend studies for human blood show that the concentrations of C9-C14 PFCA have been increasing since the 1980s until approximately 2010 when the increase seems to level out or slightly decrease. The situation for environmental species is similar, although there are some studies where a decrease of the C9-C14 PFCA levels was not found yet. Hence, there is a high potential that ongoing releases of these substances into the environment will result in long-term human and environmental exposure to C9-C14 PFCAs.

Due to the extreme persistency of the substances, degradation under environmental conditions is not expected. Thus, every emission contributes to the environmental stock of the substances.

Interestingly, C9-C14 PFCAs, their salts and related substances are not used intentionally within the EU, according to the results of the stakeholder consultation. Since 2002, there is a trend amongst manufacturers in the USA, Canada, Europe and Japan to replace long-chain PFCAs, PFSAs and their potential precursors with chemicals containing shorter perfluoroalkyl chains or with non-perfluoroalkyl products. This decreasing use-trend for C9-C14 PFCAs, their salts and related substances is observed as well considering data obtained from the Swedish Products Register. Moreover, registrants inactivated REACH registration dossiers for long-chain PFCAs, including C9-C14 PFCAs and related substances in 2017. However, there are indications that imported articles may still contain the substances.

C9-C14 PFCAs, their salts and related substances occur as unintended fraction during the manufacturing of per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms, such as C8- and C6-based chemistries. This use may still occur outside the EU. Furthermore, it is possible that after the enforcement of the PFOA restriction in 2020, C9-C14 PFCAs and related substances may be used as second best option for certain uses. Thus, an EU-wide restriction seems reasonable to prevent those future uses and prevent increasing releases into the environment.

National regulatory actions will not adequately manage the risks of C9-C14 PFCAs and related substances. An EU wide restriction would create a more level playing field amongst companies operating on the EU market. A restriction on C9-C14 PFCAs, their salts and related precursors is the most appropriate way to limit the risks for human health and the environment on an EU level. Additionally, the proposed restriction is in-line with the US-EPA stewardship program and the restriction of long-chain per- and polyfluorinated substances in Canada. Moreover, a restriction within the EU may be the first step for global action.

Based on the information provided, it is concluded the following thresholds are feasible for mixtures and articles placed on the market:

- **25 ppb for the sum of C9-C14 PFCAs and their salts**
- **260 ppb for the sum of C9-C14 PFCA related substances**

A derogation for manufacturing C6-based chemistries should be considered to allow the manufacturing of these substances within the EU. Additionally a derogation for transported isolated intermediates should be granted to enable the processing of C6-based chemistries within the EU.

Semiconductors imported into the EU may contain C9-C14 PFCAs. The dossier submitter awaits additional information from the affecteded company to determine whether an extended transitional period for semiconductors is required.

Analytical methods to enforce the restriction and to monitor the effect are under development. The same methods could be used for the enforcement of the PFOA-restriction.

The costs for industry and enforcement agencies were assessed to be negligible. A transitional period of even less than 18 months seems to be manageable.

# Annexes

# Annex A: Manufacture and uses

## A.1. Manufacture, import and export

## A.1.1 REACH-Registrations

There are no registration dossiers for the single substances C9-C14-PFCAs.

One REACH registrant registered multi-constituent substances including C9-C14 PFCAs as shown in Table A.1- 1. During the stakeholder consultation the registrant explained that the C9-C14 PFCA their salts and related substances have never been manufactured intentionally, but occurred as unintended chemical by-product during the manufacturing of the C8-chemistry. The registrant manufactured and used three of the registered substances (see Table A.1- 1) until December 2015. In June 2017, the registrant deactivated these registrations because the registrant moved from manufacturing PFOA and related substances (so-called C8-chemistry) to short chain alternatives consisting of six perfluorinated carbon atoms, the C6-chemistry.

**Thus, to date no active registrations of C9-C14 PFCAs exist under REACH, therefore manufacture, import and export of these substances by companies in amounts above 1 t/a is not to be expected.**

*Table A.1- 1: Uses and tonnage bands of registered substances (source ECHA, 02.04.2017). The registrant switched from C8 manufacture to C6 based products.*

| CAS | Name | Tonnage band | Uses | Remarks |
|---|---|---|---|---|
| 85631-54-5 | 2-propenoic acid, γ-ω-perfluoro-C8-14-alkyl esters | 100-1000t/a | -Manufacture of another substance (use of intermediates). <br> - Manufacture of chemicals. <br> - Manufacturing of thermoplastics | Manufacturing and use ceased in December 2015 Registrant **deactivated** registration in June 2017 |
| 68391-08-2 | Alcohols, C8-14, γ-ω-perfluoro | < 1000 t/a | -Manufacture of another substance (use of intermediates) Manufacture of chemicals. | Manufacturing and use ceased in December 2015 Registrant **deactivated** registration in June 2017 |
| 85995-91-1 | Alkyl iodides, C8-14, γ-ω-perfluoro | > 1000 t/a | -Manufacture of another substance (use of intermediates). | Manufacturing and use ceased in December 2015 Registrant **deactivated** registration in June 2017 |
| 90622-71-2 | Alkyl iodides, C6-18, perfluoro | | -manufacture of another substance (use of intermediates) | Changes in registration planned, due to shift from C8 to C6 manufacturing |
| CAS -, EC 423-180-6 | Akyl diester (mixture) C6/C8/C10 perfluorinated | Conf. | Conf. | Changes in registration planned, due to shift from C8 to C6 manufacturing |

The following additional information is available:

- About two hundred C9-C14 PFCA related substances are found on the pre-registration list.

- C9-PFCA is on the list of pre-registered substances with a registration date of 30/11/2010. Also 132 of the 152 substances that may degrade into C9-PFCA were pre-registered (Posner et al., 2009).

- C10-PFCA was planned for registration on 30/11/2010 (three pre-registrations at >1000 tonnes/year), 31/05/2013 (two pre-registrations 100-1000 tonnes/year), and 31/05/2018 (three pre-registrations at 10-100 tonnes/year, and 11 pre-registrations at 1-10 tonnes/year).

- Ammonium nonadecafluorodecanoate (Ammonium salt of C10-PFCA) is pre-registered with an envisaged registration deadline on 31/05/2013.

It may be possible that some of these substances will be registered during the last registration period in 2018.

## Unintentional manufacturing of C9-C14 PFCAs and related substances

Perfluoroalkyl substances are in general manufactured via electrochemical fluorination or telomerisation (Buck et al., 2011). Both odd- and even-numbered PFCAs may be prepared from either process.

The raw material to manufacture perfluorinated chemicals via the telomerisation process is trifluoroethylene gas and iodine. The telomerisation process results in fluorotelomer iodide fractions (FTI). The telomere iodide fractions are separated by distillation into a C8/long-chain side fraction (approx. 20%) and a C6 iodide fraction (approx. 80 %). The C6 iodide fraction is further processed to C6 ethyl iodide, C6 fluorotelomer alcohol (FTOH) and the C6 monomers (i.e. fluorotelomer acrylate or methacrylate esters). These C6 monomers are the basis for polymerization reactions to manufacture mixtures containing C6 based polymers, which are than further used and processed by downstream users. These fractions still contain impurities of longer chain PFCAs, thus C9-C14 PFCAs occur as impurities in C6- based chemistries. According to (Prevedouros et al., 2006) during every step in production residues from the previous step remain. For example:

- 2% or less residual fluorotelomer iodide remains unreacted after the transformation from FTI to the fluorotelomer alcohol (FTOH) (Prevedouros et al., 2006). Additionally, 2-5 wt % by product fluorotelomer olefin (FTO) is formed, depending on the method used.
- The reaction of fluorotelomer alcohol to make fluorotelomer acrylate or methacrylate esters leaves 0.1-0.5 wt % unreacted residual FTOH.
- Alternatively, acrylate monomers can be manufactured by a reaction of fluorotelomer iodide and acrylic acid salt to form acrylate monomer resulting in 3-8 wt % FTO by-product

Moreover, longer chain fluorinated substances occur as impurities in all process steps (van der Putte et al., 2010) (Stakeholder consultation). Thus, C9-C14 PFCAs are manufactured unintentionally during the manufacturing of perfluorinated substances containing a carbon chain of less than nine carbon atoms. In the C6 production lines, the concentrations of these impurities are lower compared with the data provided in the current registration CAS 90622-71-2. The registrant will therefore update this registration (see Table below).

*Table A.1- 2: Estimated (unintentional) concentrations of C9-C14 PFCAs, their salts and related substances during manufacturing of other substances.*

| Process | Content of C9-C14 PFCAs and their salts | Content of C9-C14 PFCA related substances | Remarks | Ref. |
|---|---|---|---|---|
| Manufacturing C8 and C8 related substances | | | | |
| Manufacturing of APFO (C8-PFCA salts) | 0.21 % | | Ceased within the EU | Prevedouros et al. 2006 |
| Manufacturing of PFOA related substances (C8-PFCA related substances) | | 20-45 % | Ceased within the EU in 2015 | Stakeholder information |
| Manufacturing of C6 related substances | | | | |
| In the C8 fraction | | up to 30 % | This fraction is separated and reworked | Stakeholder information |
| In the C6-fraction | | Low ppm range | Transported isolated intermediates | Stakeholder information |
| | Up to 25 ppb | Up to 260 ppb | Mixtures sold to industry | Stakeholder information |

**Conclusion:** To date there is no active registration under REACH for C9-C14 PFCAs, their salts and related substances. The substances are however, still manufactured as unintended side fractions during the manufacturing of per- and polyfluorinated chemicals based on a C6-based chemistries . Pre-registrations exist for a number of C9-C14 PFCAs, their salts and related substances. It may be possible that these substances will be registered during the last registration period in 2018.

# A.1.2 Global manufacturing

The production of APFN – the ammonium salt of C9-PFCA – is believed to have started in about 1975. Prevedouros et al. estimated the total global production of C9-PFCA and its ammonium salt between 1975 and 2004 of 800 to 2300 t (Prevedouros et al., 2006). The estimated global annual production of C9-PFCA ammonium salt (APFN) in 2004 was between 15 and 75 tonnes (PERFORCE, 2004; Posner et al., 2009). Wang and co-workers estimated use rates of APFN during the period from 2011 to 2015 in the range from 17 to 107 t/a worldwide. The main use of APFN is manufacturing of polyvinylidene fluoride (PVDF), see Annex A.2 for further details. The authors consider that companies committed to the US-EPA Stewardship Program will have ceased the manufacturing of APFN and thus manufacturing volumes will decline (Wang et al., 2014) see table below.

*Table A.1- 3: Estimated global manufacturing volumes of APFN, the ammonium salt of C9-PFCA.*

| Time period | Globally manufactured APFN (estimates) [t] | Reference |
|---|---|---|
| 1975-2004 | 800-2300 | (Prevedouros et al., 2006) |
| 2004 | 15-75 | (Posner et al., 2009) |
| 2003-2005 | 11-99 | (Wang et al., 2014) |
| 2006-2010 | 13-105 | |
| 2011-2015 | 17-107 | |

According to Prevedouros et al., (2006) and Wang et al., (2014) ammonium perfluorononanoate (APFN) has been manufactured primarily in Japan by oxidation of a mixture of linear fluorotelomer olefins (FTOs) to the corresponding odd numbered PFCAs. Another possibility to manufacture APFN is fluorotelomer iodide carboxylation.

According to Wang et al., 2014 commercial C9-PFCA-based products are typically a mixture of the ammonium salts of C9-PFCA and other PFCA homologues. The product Surflon S-111 (CAS 72968-38-8) contains besides C9-PFCA, C-11-PFCA and C13-PFCA accounting for 20 and 5 percent of the mixture, respectively.

Although only limited data on manufacturing volumes for C9-C14 PFCAs, their salts and related substances are available, a number of classes are available on the world market (see Table below).

*Table A.1- 4: Chemical classes for C9-C14 PFCA precursors found on the world market (ordered in decreasing number of PFASs)*

| Number of C9-C14 PFASs | Chemical fluoro class |
|---|---|
| 127 | Fluorinated (meth)acrylate polymers |
| 93 | poly/perfluorinated PHOSPHOORGANICS |
| 52 | poly/perfluorinated ALKYL substances – not yet categorised |
| 35 | poly/perfluorinated ALKOHOLS |
| 34 | poly/perfluorinated IODIDES |
| 28 | poly/perfluorinated (METH)ACRYLATES |
| 20 | poly/perfluorinated ESTERS |
| 15 | poly/perfluorinated ALKANOYL/SULFONYL CHLORIDE or FLUORIDES |
| 15 | poly/perfluorinated SILOXANES/SILICONES/SILANES/SILICATES |
| 12 | Fluorinated urethanes polymers |
| 12 | Polyfluoro siloxanes and silicones polymers |
| 10 | poly/perfluorinated AMINES |
| 9 | poly/perfluorinated SULFONAMIDES |
| 9 | poly/perfluorinated AMMONIUM ORGANICS |
| 8 | poly/perfluorinated TIOLS |
| 7 | poly/perfluorinated OXIRANES |
| 6 | poly/perfluorinated POLYMERS – not yet categorised |
| 6 | Semifluorinated alkanes/alkenes |
| 5 | poly/perfluorinated SULFONIC/SULFINIC ACIDS |
| 4 | poly/perfluorinated ETHERS |
| 4 | poly/perfluorinated AMIDES |
| 2 | poly/perfluorinated ORGANICS – Other |
| 2 | poly/perfluorinated URETHANES |
| 1 | poly/perfluorinated ETHOXYLATES |

**Conclusion:** Only limited data are available for the global manufacturing of C9-C14 PFCAs. The global manufacturing volume of C9-PFCA ammonium salt was estimated to increase until

2015 to a maximum volume of 107 t. After 2016 the manufacturing volumes are expected to decline to zero, due to the results of the US-EPA Stewardship-Program. At least one company in Japan manufactured C9-PFCA ammonium salt. Products available on the global market i.e. Surflon S-111 (CAS 72968-38-8) contain a mixture of long-chain PFCAs, such as C9-PFCA, C-11-PFCA and C13-PFCA.

Data on manufacturing volumes for C9-C14 PFCA related substances are not available, but a number of substances seem to be available on the world market.

## A.2. Uses

## A.2.1 Overview on uses

**During the consultation, (see Annex G for further information) no current intentional use was reported by industry in Europe. This means, all the uses described below seem to be historical uses.**

There is no active registration under REACH for C9-C14 PFCAs their salts and related substances, as shown in Annex A.1. According the stakeholders consultation intentional uses of the substances were not reported by the consulted industries. Stakeholders also stated that the substances were not used intentionally in Europe in the past but rather occurred as unintended impurity in per- and polyfluorinated chemicals containing a carbon chain of less than nine carbon atoms. One stakeholder reported the use of the substances as analytical standard in the laboratory and for research and development purposes (gram to kg quantities). One stakeholder reported that it could not rule out for sure the use of the substances by suppliers outside the EU. One company reported the use of C9-C14 PFCA in semiconductors which are imported in articles into the EU. The volumes of the substances used is in the low kg range. The company reported to use an alternative from 2019 on. Thus, it may be possible that C9-C14-PFCA related substances are still imported in articles into the EU.

## A.2.2 Manufacturing of fluoropolymers

The ammonium salt of C9-PFCA (APFN) has been used for **fluoropolymer and fluoroelastomer production**, e.g. polyvinylidene fluoride – PVDF since the 1970's (van der Putte et al., 2010). However, during the stakeholder consultation, no company reported the manufacturing nor the use of the ammonium salt of C9-PFCA. Thus, it can be assumed that the ammonium salt of C9-PFCA is currently not used within the EU for the manufacturing of fluoropolymers.

The ammonium salt of C9-PFCA has been manufactured and used at least by one manufacturer in Japan but it is believed that the use has been ceased due to the US-EPA Stewardship Program. Some estimated manufacturing volumes of PVDF are available in the literature and summarised in the following table:

*Table A.2- 1: Estimated global manufacturing volumes of PVDF*

| Time period | Globally manufactured PVDF (estimates) | Reference |
|---|---|---|
| 2003-2005 | 15 – 26.5 kt | (Wang et al., 2014) |
| 2006-2010 | 17.5 – 28 kt | |
| 2011-2015 | 22.5 – 28.5 kt | |

C9-PFCA ammonium salt acts to solubilize fluorinated monomers to facilitate their aqueous polymerisation (Prevedouros et al., 2006).

C9-PFCA is the primary constituent of Surflon S-111 (CAS # 72968-38-8), a commercial mixture of linear perfluorinated carboxylic acids in ammonium salt form. It is commonly used as a polymerization aid in the production of fluoropolymers. According to van der Putte et al., 2010 this substance was imported in quantities of < 5 t/a during 2004 and 2008. This substance is not registered under REACH. The substance was pre-registered with an envisaged registration deadline 30/11/2010.

Worldwide, 41 000 t of PVDF have been used in 2015 (Krämer and Schlipf, 2016). This amount corresponds to 15 % of the world market of fluoropolymers. PVDF is the most important representative of the fluorothermoplastics. According to the study, PVDF represents the fastest growing fluoropolymer worldwide. For Europe, an annual growth of 3.0 % is predicted for fluorothermoplastics until 2020. It is used in more and more applications in automotive and aviation sectors. Another study predicts a 5.1% growth of PVDF demand in Europe until 2022 and concludes on a worldwide annual growth rate of 9.2% (2016 – 2022) (ReportLinker, 2016).

According to the global PVDF industry 2016 market research report the increasing demand for semiconductors, wire and cable insulation and artificial membrane in biomedical science will increase the demand for PVDF in the future. The study predicts a worldwide increase from 1,234 kt in 2014 to 1,952 kt in 2020 (Market Research Store, 2016). In 2014, chemical processing industry accounted for 35% share in the PVDF market. Construction and new energies application segments are being the fastest growing application segments due to high saturation in all the regions. The oil and gas industries are expected to show rapid growth in the future.

The study states that North America (followed by Asia-Pacific and Europe) was the leading region for PVDF market in 2014. China was the leading country in the consumption of PVDF. India and Japan are leading the Asia-Pacific PVDF market. Some of the key participants in the global polytetrafluoroethylene market include Solvay S.A., Arkema, Daikin Industries Ltd, Kureha Corporation, Dyneon GmbH, Shanghai 3F New Materials, Company Ltd, Zhuzhou Hongda Polymer Co. Ltd, Quadrant Engineering Plastics Products Inc, Zhejiang Fotech International Co. Ltd.and Shanghai Ofluorine Chemical Technology Co. ltd (Market Research Store, 2016)

C9-PFCA is not an intended component of PVDF and is present only at trace levels (100-200 ppm) in the PVDF fluoropolymer that is produced and used in commercial and industrial products (Prevedouros et al., 2006). According to information from the stakeholder consultation, the consulted companies do not use C9-14-PFCA or any related substance for manufacturing of PVDF in Europe. One company reported that the PVDF used is manufactured without any emulsifier, thus no use of C9-PFCA ammonium salt is needed.

PVDF is mechanically stronger than perfluorinated polymers such as polytetrafluoroethylene (PTFE). Similarly, it has higher abrasion resistance, and resistance to both creep under long-term stress and fatigue during cyclic loading. PVDF has good thermal stability, resistance to ultraviolet and higher energy radiation, and chemical resistance to most chemicals and solvents.

As described in Annex A.1 and Annex A.2.1 uses of C9-C14 PFCAs and their salts were not reported during the stakeholder consultation, thus, it can be assumed that PVDF manufactured in Europe does not contain C9-C14 PFCAs and their salts. However, it is possible that outside the EU fluoropolymers such as PVDF are still manufactured by using C9-PFCA ammonium salt. Thus, imported goods may containing C9-PFCA ammonium salt as impurity. According to Ebnessajjad (2013), PVDF is used in the following sectors:

- High-purity semiconductor market (low extractable values)

- – Pulp and paper industry (chemically resistant to halogens and acids)
- – Nuclear waste processing (radiation and hot-acid resistant)
- – General chemical processing industry (extreme chemical and temperature applications)
- – Water treatment membranes (industrial and potable water uses)

PVDF-resins can be fabricated into a wide range of components, e.g.:

- – Pipes, fittings, and valves
- – Pump assemblies
- – Wire and cable insulation
- – Sheet and stock shapes
- – Films
- – Tubing (flexible and rigid)
- – Tanks and vessels
- – Nozzles
- – Membranes and filter housing
- – Powder coatings
- – Foams
- – Polymer process aids

PVDF homopolymers and copolymers are used in the battery industry as binders for cathodes and anodes in lithium-ion batteries, and as battery separators in lithium-ion polymer batteries. PVDF powder coatings are applied to metals for corrosion resistance (Ebnesajjad, 2013). Ebnessajjad (2013)

PVDF films have been developed for use in the protection of back sheet and for front sheet glazing. KYNAR® film provides superior solar transmittance and also has excellent dirt shedding and fire-resistance properties(Ebnesajjad, 2013).

Other polymers:

Besides PVDF there are some other fluoro-copolymers used as membrane materials, such as poly (vinylidene fluorideco-hexafluoropropylene) (P (VDF-HFP)), poly (vinylidene difluoride-co-chlorotrifluoroethylene) (P (VDF-CTFE)), etc. P (VDF-HFP) can also be applied in the field of rechargeable lithium-ion battery as a separator material because P (VDF-HFP), contains more amorphous domains capable of trapping a large amount of liquid electrolytes. P(VDF-CTFE) membranes are modified by grafting of poly(styrene sulfonic acid) or poly(ethylene glycol) methyl ether methacrylate (PEGMA), which can be used for ultrafiltration membranes or proton conducting membranes (Liu et al., 2011a).

**Conclusion:** No intentional uses of C9-C14 PFCAs, their salts and related substances were reported during the stakeholder consultations. Thus, it can be assumed that manufacturing and use has been ceased in Europe. One company reported the use of C9-C14 PFCA in semiconductors which are imported in articles into the EU. One major (historical) use of the C9-PFCA ammonium salt (APFN) has been the manufacturing of polyvinylidene fluoride (PVDF). The global use of PVDF increases. However, as reported by industry, PVDF used in Europe is manufactured without APFN. There are no recent information available for other regions.

## A.2.3 Uses of C9-C14 PFCA related substances

Long-chain PFCA-related substances were used either as **non-polymeric substances** or as part of **side-chain fluorinated polymers**, such as fluoroacrylate polymers (OECD, 2013; van der Putte et al., 2010). The term long-chain PFCA does also include C8-PFCA (PFOA, perfluorooctanoic acid). A differentiation relative to chain lengths is not reported. For fluorotelomers, a term often used referring to substances produced with the telomerisation process, it was reported that 80% are used in side-chain fluorinated polymers and 20% in non-polymeric applications (Telomere Research Program Update, 2002) cited in (Ellis et al., 2003).

US-EPA (U.S.EPA, 2009) reports that the world-wide production of fluorotelomers (no separation of chain lengths) in 2006 was mainly used in:

– Textiles and apparel (50%) (largest share)

– Carpets and carpet care products (second largest share in consumer uses)

– Coatings, including those for paper products (third largest category of consumer product uses)

It is not clear whether that listing is focused on consumer uses only or if industrial applications are also considered.

According to the stakeholder consultation in 2017, the C9-C14 PFCA-related substances occurred as side products in the final product. The main component was C8-related substances, meaning structures with eight perfluorinated carbon atoms.

The use of C9-C14 PFCA-related substances has been analysed for a number of relevant uses by means of the Swedish Chemical Product Register. This data concerns small volumes, which do not require REACH registration. In part it is made up of imports (but it is hard to determine to what degree, since it is not known to what degree imports (to Sweden) from another EU country in turn has been imported from a non-EU country), either of articles or compounds used in other articles. We have looked at time trends for the use of C9-C14 PFCA-related substances in *textile application, paint and paper.* These are just used to exemplify time trends and has not been aggregated to an EU level. For this analysis, the share of the PFCA-related substance weight, which is made up of C9-C14 PFCA-related substances, has been calculated. Depending on the PFCA, related substance the share that is C9-C14 PFCA has varied between 68-80 percent of the total weight of the PFCA-related substance. The remaining 20-32 percent is made up of other chain length, for example C8. An average of 73 percent has been used where data is lacking. This is a worst-case scenario and other chain length than C9-C14 PFCA might be included in the calculated volume, since compounds with no identified chain length has been assumed C9-C14. The substance weight, which is C9-C14 PFCAs is therefore upward biased in the diagrams. It should also be noted that the Swedish Product Register is a rough-hewn data source. Double accounting can occur when data is generated from the Swedish Product Register. This follows from the way data is entered into the registry based on several different product characteristics. Therefore, this data and the diagrams shown here should be seen as rough estimates and not as accurate to the point. They indicate a rough trend, not be viewed as an exact time trend. Over all time series and for all years and all applications it seems as if all entries contain C8 chemistry. Thus, the information may in part support the stakeholder information that C9-C14 PFCAs, their salts and related substances were not used intentionally in the past within the EU, and only occurs as unintended impurities together with C8 chemistry. For imported goods there is however not enough information to conclude that C9-C14 PFCAs, their salts and related substances are only part of a C8 mixture as an impurity. It is therefore concluded that the possibility exist that C9-C14 PFCAs are used intentionally in mixtures with C8 chemistry for imports.

ANNEX XV RESTRICTION REPORT – C$_9$-C$_{14}$ PFCAs -including their salts and precursors-

In the diagrams below, the lower blue line represents the share of the PFCA-related substance weight, which have a chain length of C9-C14 and the upper red line represents the total weight of the PFCA-related substance. For textile application the use of C9-14 PFCA-related substances in Sweden reaches a peak in use in the year 2006 when 65 ton per year was used, it then decreases until the year 2010 when 4 ton C9-14 PFCA-related substances was used for textiles in Sweden. For 2015, (the latest available year) 8 ton per year is registered for textile application in Sweden.
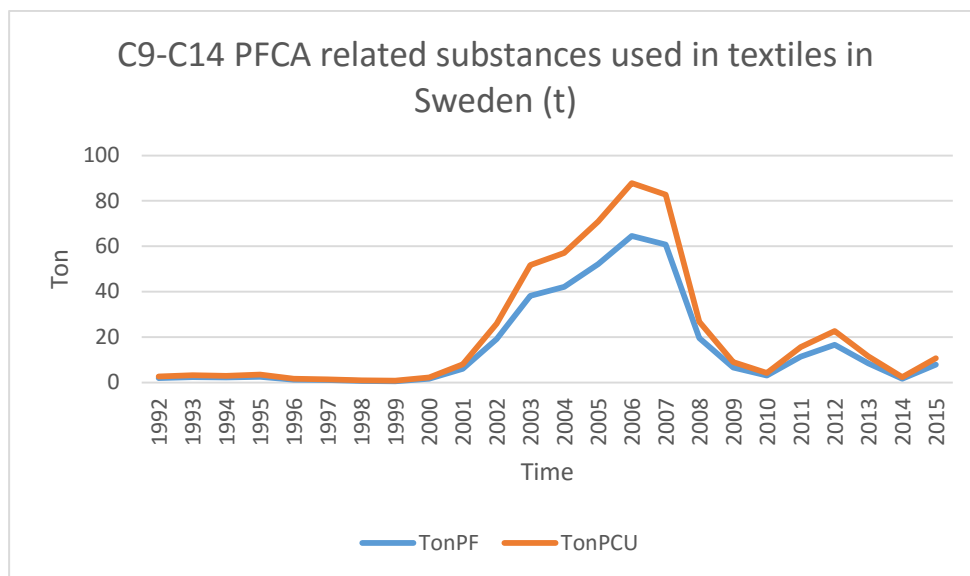


*Figure A.2- 1*: C9-C14 PFCA related substances used in textiles in Sweden, where ton PF= the share of the PFCA-related substance weight, which have a chain length of C9-C14 and ton PCU= the total weight of the PFCA-related substance (Swedish Product Register).

A similar decreasing time trend is seen for the use of PFCA C9-C14-related substances for paper in Sweden. For paper, the use of PFCA C9-C14 precursors in Sweden is showing a decreasing time trend for 1995-2005, but with a large increase in 2007-2010. For 2011-2015 only small volumes is registered. This time trend is however, sensitive to single entries since fewer entries are registered for paper compared to textile. See Figure A.2- 2, below.
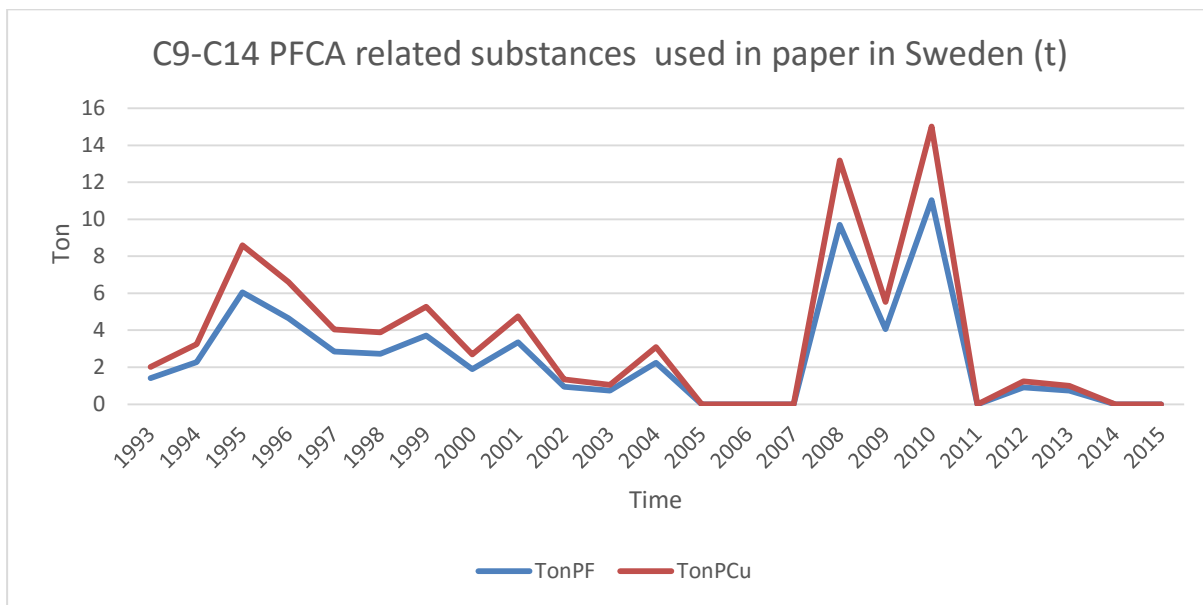
*Figure A.2- 2: C9-C14 PFCA related substances used in paper in Sweden, where ton PF= the share of the PFCA-related substance weight, which have a chain length of C9-C14 and ton PCU= the total weight of the PFCA-related substance (Swedish Product Register).*

For the use of PFCA C9-C14 precursors in paint, an increasing time trend is exposed for 1995-2011 (but with dips in the time trend in 2004 and 2009). After that, a sharp decrease is seen in the use of PFCA C9-C14 precursors in paint during 2011-2015.
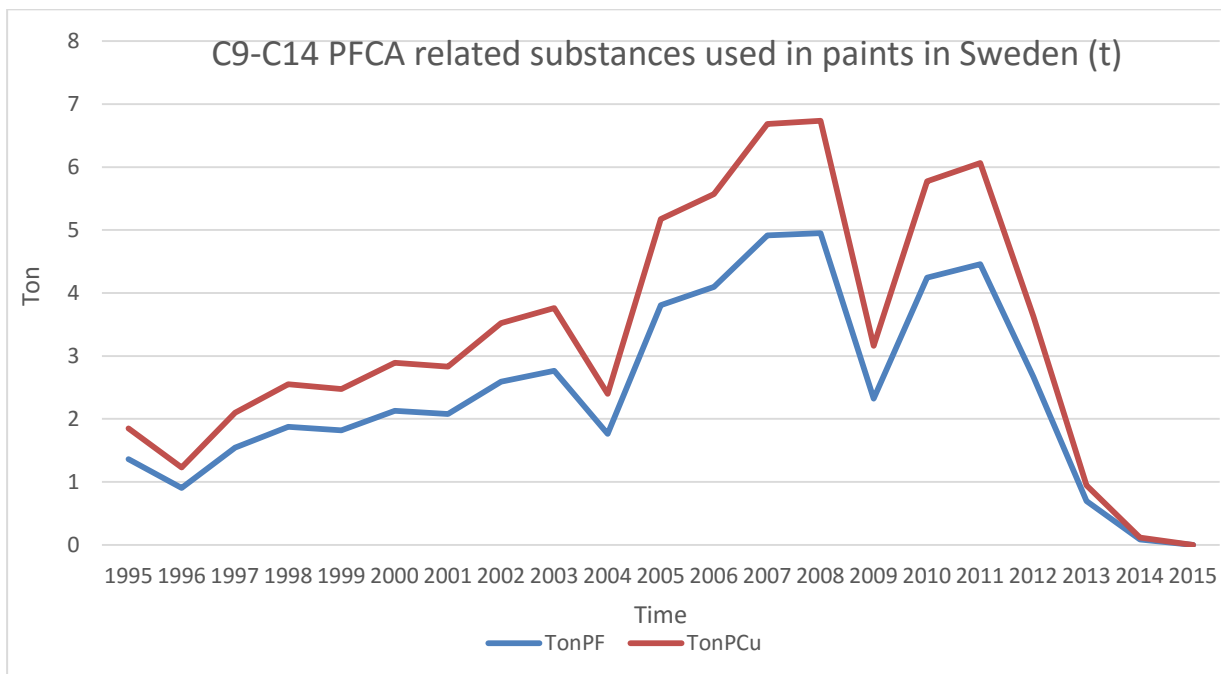


*Figure A.2- 3: C9-C14 PFCA related substances used in paints in Sweden, where ton PF= the share of the PFCA-related substance weight, which have a chain length of C9-C14 and ton PCU= the total weight of the PFCA-related substance (Swedish Product Register).*

Two stakeholders indicated that C9-C14 PFCAs, their salts and related substances are used intentionally in sites outside the EU and thus, imported articles and mixtures may contain the substances.

One stakeholder stated that small amounts (gram or kilogram quantities) of C9-C14 PFCAs its salts and related substances (there was no clarification which substances) are used in labs as analytical standards and for limited research and development purposes.

**Conclusion:** Only little information is available on the uses of C9-C14 PFCA related substances. According to stakeholders consulted, these substances are only unintentional impurities in per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms and are not used intentionally within the EU. One stakeholder has reported an active use for imported semiconductors or articles containing semicontoctors into the EU.. A search in the Swedish Product Register seems to clarify that the use of C9-C14 PFCA related substances is declining. The time trend examples from Sweden show that a substitution process or phasing out has taken place for the use of PFCA C9-C14 related substances in several important application areas. It is assumed that a similar substitution process has taken place or is under way in the rest of the EU. During the stakeholder consultation the PFOA restriction was reported as main driver to decrease the use of long-chain PFCAs including C9-C14-PFCA related substances.

One stakeholder reported the use of the substances as analytical standard in the laboratory and for research and development purposes (gram to kg quantities). Two stakeholder reported that the substances are used outside the EU. Thus, it may be possible that intentionally used C9-C14-PFCA related substances are still imported in articles into the EU.

## A.2.4 Findings in articles and mixtures

C9-C14 PFCAs their salts and related substances can occur as impurities in articles and mixtures manufactured with:

- – C4-chemistry

- – C6-chemistry

- – C8-chemistry

Since manufacturing of PFOA and other C8-based substances in the EU has ceased, production is still ongoing especially in China. Thus, imported articles and mixtures may still contain C9-C14 PFCAs as impurities above the proposed threshold. According to van der Putte (2010) up to 0.2 % C9-PFCA is present in PFOA (C8-PFCA) manufactured with the electrochemical fluorination (ECF). C10-C14-PFCAs may be present up to 0.01% in PFOA manufactured with ECF. Contaminations up to 0.01% C9-C14 PFCAs occur during PFOA manufacturing using the perfluorooctyl iodide oxidation (also called telomerisation process). Each compound of the C9-C13-PFCA can be present up to 0.01 % (van der Putte et al., 2010). Also for the manufacturing of the C6-chemistry (and even C4) long-chain PFASs may be present as impurities (see Annex A.1 for details).

In articles and mixtures treated with C6-chemistry C9- C14-PFCAs and related substances can occur as impurities. According to information provided during the stakeholder consultation, C9-C14 PFCA related substances are assumed in concentrations up to 260 ppb in mixtures sold to industry. Thus in final articles and mixtures used by consumers the concentrations of these impurities might be lower.

In conclusion, the C9-C14 PFCA, their salts and related substances may be present as impurities in all articles where other PFCAs containing a carbon chain of less than nine carbon atoms have been used or in articles which have been imported into the EU and manufactured with the C8-technology outside the EU. Examples are provided in the following chapters. It is however not possible to retrace of C9-C14 PFCAs their salts and related substances were used intentionally or unintentionally in the articles and mixtures.

## A.2.4.1 Textile and leather

In a study on PFASs in consumer articles, textiles (jackets, shoes) were collected in Sweden in 2015 and analysed for various PFASs including C9-C10 PFCA, 10:2 FTOH and 10:2 FTA (Borg and Ivarsson, 2017). The result showed that one out of eight textile samples contained C9-PFCA and C10-PFCA at 0.45 µg/kg and 2.7 µg/kg, respectively. 10:2 FTOH and 10:2 FTA was not detected in any product. PFOA was detected at 6.6 µg/kg in the same product. The study also included analysis of total organic fluorine (TOF) content. The comparisons between the sums of detected PFASs to the TOF concentrations showed that for most samples the analysed PFAS constituted only a very minor part of the TOF. One likely explanation is that many of the individual PFASs measured represent degradation products of PFAS related substances (e.g. C9-C14 PFCA related substances). This indicates that the content of C9-C14 PFCA related substances could be higher than regular studies show.

Gremmel et al., 2016 determined PFCAs in all Durable Water Repellent (DWR) jackets tested. Altogether 16 jackets were purchased in Germany – manufactured outside the EU - (15 outdoor jackets and one working jacket) in the period from August 2011 to March 2012 (Gremmel et al., 2016). One jacket was not treated with PFASs and declared as PFASs-free. From the PFASs analysed, only PFOA and C14-PFCA were found in this jacket in amounts of 0.02 and 0.01 µg/m$^2$. In all other jackets, C9-C14 PFCAs and related substances were found. Only one representative of the C9-C14 PFCA related substances, 10:2 FTOH was tested and found in all jackets (except the PFAS-free one) in higher concentrations compared with the C9-C14 PFCAs concentrations of the same sample (see table below).

*Table A.2- 2 C9-C14-PFCAs and relating substances analysed in Durable Water Repellent jackets (Gremmel et al., 2016).*

| Substance | Detected in no of jackets (>LOQ) | Range in µg/m$^2$ | Range in µg/kg |
|---|---|---|---|
| C9-PFCA | 15 (~94%) | 0.02- 27.7 | 0.14 – 62.9 |
| C10-PFCA | 13 (~81%) | 0.07 – 85.3 | 0.42 – 194 |
| C11-PFCA | 3 (~20%) | 0.36-20.3 | 2.37 – 46.1 |
| C12-PFCA | 6 (~38%) | 0.13– 80.9 | 0.47 – 184 |
| C13-PFCA | 4 (~25%) | 0.03– 3.7 | 0.13 – 8.4 |
| C14-PFCA | 7 (~44%) | 0.01 – 20.5 | 0.12 – 46.5 |
| 10:2 FTOH | 15 (~94%) | 1.34 – 182 | 6.57 - 1191 |

A German study from 2012 looked at various perfluorinated substances in work wear for medics, pilots and firemen which protect against cold, rain and fire (Zangl et al., 2012). C9-PFCA and C10-PFCA were detected in a number of analysed garments.

Kotthoff et al., 2015 analysed C9-C14-PFCAs and 10:2 FTOH as an example for the C9-14-PFCA- related substances in outdoor textiles (n=5), carpets (n= 14), gloves (n=3) and awning cloth (n=1) (Kotthoff et al., 2015). Articles were bought from German retailers in 2010. The results of the analysis are shown in the Figure below.
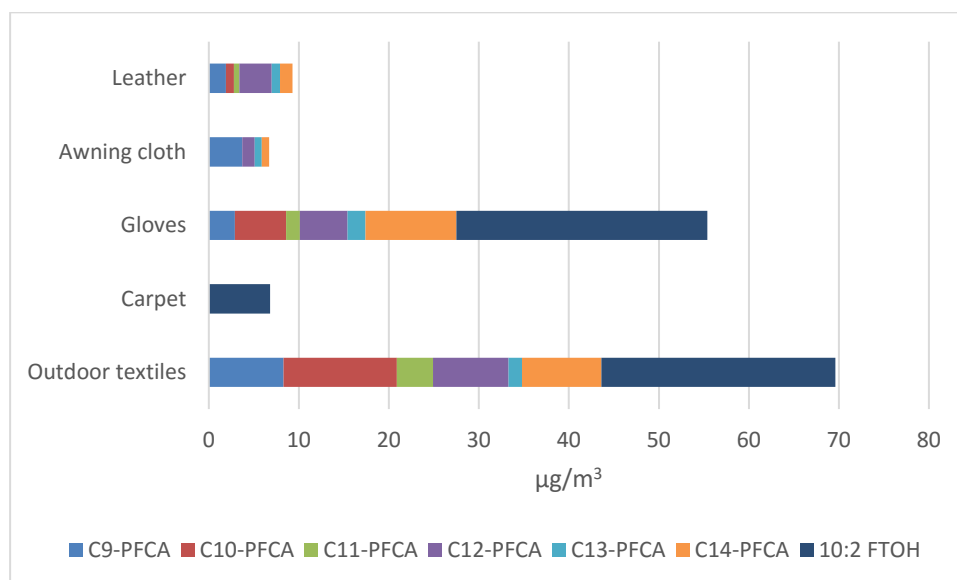
*Figure A.2- 4: C9-14-PFCAs in textile and leather samples (Kotthoff et al., 2015)*

## A.2.4.2 Paper and food-packaging

Kotthoff et al., (2015) found C9-C14-PFCAs and related substances in paper-based food contact material. The 33 samples were purchased in 2010. Median values are available for C9-, C10-, C12-, C14- PFCA of 0.5, 2.5, 2.0, and 1.3 mg/kg, respectively. 10:2 FTOH was found in 86% of the samples with a median value of 4.3 µg/kg (Kotthoff et al., 2015). Information from the Swedish Product Register, the IUCLID database and various inventory lists shows that on the global paper industry market there were a large number of polymers/polymer raw materials, mainly polyfluorinated/perfluorinated (meth)acryl polymers and monomers. Other major substance groups are poly/perfluorinated alkyl phosphorus compounds and polyfluorinated/perfluorinated (meth)acrylate (Swedish Chemicals Agency, 2015b).

Swedish Chemicals Agency states in its report form 2015 that nowadays side chain fluorinated polymers based on short-chain fluorotelomers are used. In a study on PFASs in consumer articles, paper- and food packaging (four microwave popcorn bags, one cupcake form) were collected in Sweden in 2016 and analysed for various PFASs including C9-C10 PFCA, 10:2 FTOH and 10:2 FTA (Borg and Ivarsson, 2017). The result showed that one popcorn bag contained C10-PFCA at 0.144 µg/kg. 10:2 FTOH and 10:2 FTA was not detected in any product.

In a study on PFASs in consumer articles, paper- and food packaging were collected in Norway in 2014 and analysed for various PFASs including C9-C14 PFCA ((Blom and Hanssen, 2015) Table A.2- 3). The result showed that one sandwich paper contained C9-C14 PFCA at levels above LOD, ranging from 0.063 µg/m$^2$ to 0.697 µg/m$^2$.

*Table A.2- 3: PFCA concentrations in samples of paper- and food packaging collected in Norway in 2014 (modified from (Blom and Hanssen, 2015)).*

| ID | Article | PFCAs (µg/m$^2$) | | | | | | |
|----|---------|------|------|------|------|------|------|------|
| | | C8 | C9 | C10 | C11 | C12 | C13 | C14 |
| 3 | Baking paper 1 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 4 | Baking paper 2 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 5 | Sandwich paper | 1,22 | 0,083 | 0,697 | 0,071 | 0,647 | 0,063 | 0,300 |

| 6 | Cupcake forms | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
|---|---|---|---|---|---|---|---|---|
| 7A | Popcorn paper 1 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 7B | Popcorn paper 2 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 22 | Non-stick silicon baking ware 1 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 23 | Non-stick silicon baking ware 2 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 24 | Non-stick cupcake baking ware, 1 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 25 | Non-stick cupcake baking ware 2 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 26 | Reusable baking liner 1 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |
| 27 | Reusable baking liner 2 | 0,268 | < LOD | < LOD | < LOD | < LOD | < LOD | < LOD |

## A.2.4.3 Impregnation agents

In a study on PFASs in consumer articles, impregnation agents for shoes, textiles and leather were collected in Sweden in 2016 and analysed for various PFASs including C9-C10 PFCA, 10:2 FTOH and 10:2 FTA (Borg and Ivarsson, 2017). The result showed that 1 out of 5 impregnating agents contained C10-PFCA at 0.447 µg/kg. 10:2 FTOH and 10:2 FTA was not detected in any product.

In a study on PFASs in consumer articles, impregnation agents for shoes and textiles were collected in Norway in 2014 and analysed for various PFASs including C9-C14 PFCA (Blom and Hanssen, 2015). None of the four tested impregnating agents contained C9-C14 PFCA.

There are a number of additional studies which show the content of various highly fluorinated substances in impregnating agents for textiles (Ye et al. 2014, Kotthoff et al. 2015, Liu 2014, Herzke et al. 2012, Fielder et al. 2010, Schulze and Norin 2007). 10:2 FTOH was detected in impregnation sprays (n = 16) with median values of 70,500 µg/kg. C9-C14-PFCAs were found in all samples with median values ranging from 0.5 to 8.1 µg/kg. The samples were purchased in 2010 (Kotthoff et al., 2015).

## A.2.4.4 Firefighting foam

PFAS-containing firefighting foams are usually used to extinguish liquid fires (class B), such as large storage tank fires and aircraft crashes.

According to the Nordon report (2013) mixtures of C8-C20 –γ-ω-perfluorotelomer thiols with acrylamide (CAS number 70969-47-0) were used in the most common fluorosurfactants in use in firefighting foams since the discontinuation of the PFOS based surfactants. According to the industry most of the manufacturers committed to continuing use of this chemistry until 2016 (Posner et al., 2013).

Recently, Dauchy and co-workers analysed nine different firefighting foam concentrates manufactured after 2002 by four different manufacturers (Dauchy et al., 2017). A number of PFAS were analysed, among them also C9-C13-PFCAs. The substances actually used in firefighting foams are unknown. Many related substances are difficult to analyse. Therefore, to mirror the presence of precursor-substances in firefighting foams, the authors oxidised the samples to transform the related substances into the end-stage products. Main degradation products were found to be short-chain PFAS, but C9-PFCA was found as well. The data indicate

that C9-PFCA related substances are present in firefighting foam concentrates, however the concentrations were lower compared with other substances. Similar results were reported in an earlier study by Houtz et al. (Houtz et al., 2013). Thus, C9-PFCA related substances may not be used as active ingredients, but rather occur as impurities. Most probably, these substances are unintended by-products generated during the manufacture of polyfluorinated substances containing a carbon chain of less than nine carbon atoms as reported during the stakeholder consultation.

In a chemical analysis of PFASs in selected fire-fighting foams on the Swedish market 2014, C9-C14 PFCA were detected in some of the sampled fire-fighting foams (Swedish Chemicals Agency, 2015a). However, the levels were significantly lower than e.g. C6-PFCA (C6-PFCA precursors are intentionally used) and likely represent impurities.

*Table Table A.2- 4: PFCA (µg/kg) in samples of fire-fighting foams on the Swedish market 2015. From (Swedish Chemicals Agency, 2015a).*

| Product | C4 PFBA | C5 PFPeA | C6 PFHxA | C7 PFHpA | C8 PFOA | C9 PFNA | C10 PFDA | C11 PFUnDA | C12 PFDoDA | C13 PFTrDA | C14 PFTDA |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OneSeven B-AR | 1485 | 1122 | 512 | 131 | 3 | <1 | <1 | <1 | <1 | <1 | <1 |
| ARC Miljö | 546 | 108 | 1074 | 20 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Towalex plus | <1 | 78 | 1481 | 23 | 70 | 7 | 26 | <1 | <1 | <1 | <1 |
| Towalex 3x3 | 1008 | 551 | 9770 | 134 | 239 | 20 | 63 | <1 | <1 | <1 | <1 |
| Towalex 3% super | <1 | <1 | 84 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Towalex 3% master | 1142 | 620 | 10352 | 149 | 344 | 21 | 79 | 8 | 26 | <1 | <1 |
| Sthamex AFFF-P 3% | 83 | 17 | 83 | <1 | <5 | <5 | <1 | <1 | <1 | <1 | <1 |

## A.2.4.5 Cosmetics

Fujii et al. 2013 reported the use of highly fluorinated substances in various cosmetic and hygiene products purchased in Japan (Fujii et al., 2013). This specifically concerns polyfluoroalkyl phosphonic acids (PAPs/diPAPs). These are used in sun creams, body lotions and other cosmetics to make the products oil- and water-repellent. Fujii et al. 2013 analysed various articles and mixtures that contained PAPs or other fluorine-based compounds (for example, polyfluoroalkyl silcylated mica) according to the international cosmetics database INCI (International Nomenclature of Cosmetic Ingredients). Various cosmetics for the face and nails were analysed, as well as sun creams from various manufacturers. The results show that besides PAPs the products also contained perfluorinated carboxylic acids, PFCA, among them C9-C14-PFCA. 87 percent of cosmetics samples (13 of 15) and 89 percent of sun creams (8 of 9) contained PFCA. The highest concentration of analysed $\sum_{C6-C14-PFCA}$ found was 5.9 µg/g in a foundation cream in powder form and 19 µg/g in a sun cream. The levels were generally higher in the sun creams. Also analysed were articles which, according to INCI, did not contain any fluorine-based substances (such as PAPs) but which came from the same manufacturer. These contained no detectable PFCA which, according to the study, indicates that PAPs are an important source of PFCA in articles and mixtures. However, this was a small study and more analyses would need to be performed before any reliable conclusions could be drawn. The study was performed with cosmetics purchased in Japan. The country of origin was mainly Japan, but two items originated from France and one from the Unites States. Since the cosmetics manufactured in France also contained C9-C14 PFCAs it may be assumed that cosmetics available in the EU also contain these substances.

ANNEX XV RESTRICTION REPORT – C$_9$-C$_{14}$ PFCAs -including their salts and precursors-

In the European Commission's public database on cosmetics CosIng a number of substances containing C9-C14-PFCAS and related substances were found. The results are shown in Table A.2- 5. The search was done with the word "perfluoro", thus the list may not be complete. Although no volumes used in cosmetics are given in the database, the number of entries seems to point to a rather important use of the substances in cosmetics.

*Table A.2- 5: Search results of uses C9-C14-PFCA and related substances in cosmetics. The search was done with the word "perfluoro". Source:* http://ec.europa.eu/growth/tools-databases/cosing/index.cfm?fuseaction=search.simple (5.12.2016)
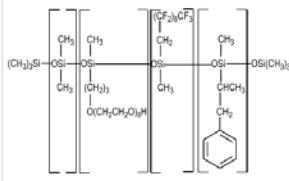
| INCI names (International Nomenclature Cosmetic Ingredient) | CAS | Function | Description |
|---|---|---|---|
| AMMONIUM C6-16 PERFLUOROALKYLETHYL PHOSPHATE | 65530-72-5 / 65530-71-4 / 65530-70-3 | Emulsifying | Phosphoric acid, esters with 2-(perfluoro-C6-16-alkyl)ethanol, ammonium salt |
| AMP-C8-18 PERFLUOROALKYLETHYL PHOSPHATE | | Emulsion stabilising, solvent, surfactant | |
| BUTYL ACRYLATE/C6-14 PERFLUOROALKYLETHYL ACRYLATE/MERCAPTOPROPYL DIMETHICONE COPOLYMER | | Film forming, pacifying | Butyl Acrylate/C6-14 Perfluoroalkylethyl Acrylate/Mercaptopropyl Dimethicone Copolymer is a copolymer of 2-(perfluoro(C6-14 alkyl)) ethyl acrylate, n-butyl acrylate and mercaptopropyl dimethicone monomers |
| C20-28 ALKYL PERFLUORODECYLETHOXY DIMETHICONE | | Film forming | |
| C4-14 PERFLUOROALKYLETHOXY DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 3-(2-perfluoro-C4-14-alkylethoxy)propyl methyl, dimethyl |
| C4-18 PERFLUOROALKYLETHYL THIOHYDROXYPROPYLTRIMONIUM CHLORIDE | 70983-60-7 EC 275-091-5 | Cleansing, surfactant | 1-Propanaminium, 2-hydroxy-N,N,N-trimethyl-, 3[(gamma-omega-perfluoro-C6-20-alkyl)thio] derivatives, chlorides |
| C6-12 PERFLUOROALKYLETHANOL | | Hair conditioning, skin conditioning, solvent | Perfluoro-C6-12-alkyl ethanol |

| | | | |
|---|---|---|---|
| C6-14 PERFLUOROALKYLETHYL ACRYLATE/HEMA COPOLYMER | | Film forming, viscosity controlling | C6-14 Perfluoroalkylethyl Acrylate/HEMA Copolymer is a copolymer of 2-(perfluoro(C6-14 alkyl)) ethyl acrylate and 2-hydroxyethyl methacrylate monomers |
| C9-15 FLUOROALCOHOL PHOSPHATE | 223239-92-7 | Skin conditioning | Perfluoro-C9-15-alkanol, esters with phosphoric acid |
| PERFLUORONONYL DIMETHICONE/METHICONE/AMODIMETHICONE CROSSPOLYMER | | Binding | Perfluorononyl Dimethicone/Methicone/Amodimethicone Crosspolymer is a crosslinked silicone polymer that is formed by reacting a copolymer of Perfluorononyl Dimethicone and Methicone with Methicone and Amodimethicone |
| PERFLUORONONYL OCTYLDODECYL GLYCOL GRAPESEEDATE | | Hair conditioning, skin conditioning | |
| PERFLUORONONYL OCTYLDODECYL GLYCOL MEADOWFOAMATE | | Hair conditioning, skin conditioning | Fatty acids, meadowfoam, esters with 1-perfluorononyl-2-octyldodecyloxy-ethan-1,2-diol |
| PERFLUORONONYLETHYL CARBOXY PEG-7 DIMETHICONE PHOSPHATE | | Hair conditioning | Perfluorononylethyl Carboxy PEG-7 Dimethicone Phosphate is the partial ester of phosphoric acid and a carboxylated derivative of perfluorononylethyl dimethicone containing an average of 7 moles of ethylene oxide |
| PERFLUORONONYLETHYL CARBOXYDECYL BEHENYL DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 11-(2-(nonafluorononyl)ethoxy)-11-oxoundecyl methyl, docosyl methyl, dimethyl |
| PERFLUORONONYLETHYL CARBOXYDECYL HEXACOSYL DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 11-(2-(nonafluorononyl)ethoxy)-11-oxoundecyl methyl, hexacosyl methyl, dimethyl |
| PERFLUORONONYLETHYL CARBOXYDECYL LAURYL DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 11-(2-(nonafluorononyl)ethoxy)-11-oxoundecyl methyl, dodecyl methyl, dimethyl |

| | | | |
|---|---|---|---|
| PERFLUORONONYLET HYL CARBOXYDECYL LAURYL/BEHENYL DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 11-(2-(nonafluorononyl)ethoxy)-11-oxoundecyl methyl, docosyl methyl, dodecyl methyl, dimethyl |
| PERFLUORONONYLET HYL CARBOXYDECYL PEG-10 DIMETHICONE | | Emulsifying, skin conditioning | Siloxanes and Silicones, 11-(2-(nonafluorononyl)ethoxy)-11-oxoundecyl methyl, 3-hydropoly(oxyethylene)oxypr opyl methyl, dimethyl (10 mol EO average molar ratio |
| PERFLUORONONYLET HYL CARBOXYDECYL PEG-8 DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 11-(2-(nonafluorononyl)ethoxy)-11-oxoundecyl methyl, 3-hydropoly(oxyethylene)oxypr opyl methyl, dimethyl (8 mol EO average molar ratio |
| PERFLUORONONYLET HYL DIMETHICONE/METH ICONE COPOLYMER | | Skin conditioning | Siloxanes and Silicones, 2-(nonafluorononyl)ethyl methyl, dimethyl. Hydrogen methyl |
| PERFLUORONONYLET HYL PEG-8 DIMETHICONE | | Skin conditioning | Siloxanes and Silicones, 2-(nonafluorononyl)ethyl methyl, 3-hydropoly(oxyethylene)oxypr opyl methyl, dimethyl (8 mol EO average molar ratio |
| PERFLUORONONYLET HYL PEG-8 PHENYLISOPROPYL DIMETHCONE | | Emollient, skin conditioning |  |
| PERFLUORONONYLET HYL STEARYL DIMETHICONE | | Film forming, skin conditioning | Siloxanes and silicones, di-Me, Me perfluorononylethyl, Me stearyl |
| TEA-C8-184 PERFLUOROALKYLET HYL PHOSPHATE | | Hair conditioning, skin sonditioning, surfactant | TEA-C8-18 Perfluoroalkylethyl Phosphate is the triethanolamine salt of a complex mixture of esters of phosphoric acid and a perfluoroalkylethyl alcohol containining 8 to 18 carbons in the alkyl chain |

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[4] Cosmetic restriction III/62

## A.4.2.6 Paints, printing inks, and lacquers, adhesives

Highly fluorinated substances such as C9-14-PFCAs can be used in paints and printing to improve wetting, smoothness and flow. The highly fluorinated substances are used to reduce surface tension in paints so that the surface on which the paint is applied is wetted. 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 and PFASs can be present at concentrations of about 1 percent (10 000 mg/kg). However, this figure is unreliable; in most cases there may be concentrations, around 0.05 percent (European Chemicals Agency, 2015a).

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).

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, 2012).

Swedish Chemicals Agency investigated a number of polymers and polymer appearing in raw materials in inventoried databases of paints and adhesives. 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 derivatives: (meth)acrylate polymers (C4-20), silicones/siloxanes (C8-14), and a smaller number of alkyl thiols (C4-20), iodides (C11), alkyl alcohols (C8-14),

Polyfluorinated silicones/siloxanes (C6-14), and poly/perfluorinated alkyl alcohols (C8-14) are used on the global market for printing inks

- Alcohols, C8-14, .gamma.-.omega.-perfluoro  (CAS : 0068391-08-2)

- Siloxanes and Silicones,(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)oxy Me, Me, Me octyl, ethers with polyethylene glycol mono-Me ether (CAS 0143372-54-7)

## A.4.2.7 Cleaning agents and polish

With regard to floor polish most manufacturers believe that fluorinated substances are necessary to give the product the desired properties (wetting, flowing and levelling evenly over the floor).

In a study on PFASs in consumer articles, shoe- and car waxes as well as floor and furniture polish were collected in Sweden in 2016 and analysed for various PFASs including C9-C10 PFCA, 10:2 FTOH and 10:2 FTA (Borg and Ivarsson, 2017). The result showed that none of the articles contained C9-C10 PFCA, 10:2 FTOH or 10:2 FTA

In a study on PFASs in consumer articles and mixtures, two car polishes were collected in Norway in 2014 and analysed for various PFASs including C9-C14 PFCA (Blom and Hanssen, 2015). The result showed that none of the articles contained C9-C14 PFCA,

A German study (Kotthoff et al. 2015) analysed nine different cleaning agents purchased in 2010. The results showed low or no content of perfluorinated carboxylic acids whereas levels of fluorotelomer alcohols were high (median 10:2 FTOH 23 mg/kg).

## A.4.2.8 Ski Wax

It is not certain what levels are present in the articles and mixtures themselves but ski waxes may contain mixtures of many different perfluoro-n-alkanes (C12-C24, C7 or C8) ((Posner et al., 2013).

In a study on PFASs in consumer articles, three ski waxes/gliders were collected in Norway in 2014 and analysed for various PFASs including C9-C14 PFCA (Blom and Hanssen, 2015). The result showed that none of the articles contained C9-C14 PFCA,

A study of 13 different ski waxes purchased in 2010 showed the presence of various perfluorinated substances in ski waxes, among them C9- and C10-PFCAs (Kotthoff et al. 2015).

Swedish Chemicals Agency reports that organofunctionalized silicone polymer, which contains at least one straight or branched, saturated or unsaturated perfluoro chain (C1-10) can be present in ski wax (Swedish Chemicals Agency 2015b).

## A.4.2.9 Electronic equipment and components

According to Swedish Chemicals Agency (2015b) highly fluorinated substances can be a component in dirt-repellent coatings which safeguard the transparency of glass surfaces on, for example, smartphones and solar cells (ACS 2009, US patent 8864897, Oct. 2014, USEPO 2015). These can consist of fluorosilanes with a perfluorinated dirt-repellent tail. The tail can consist of C1-20 perfluoro chains or polyethers (molecular weight > 1000, at least 20-30 Å thick). Besides their dirt repellent properties fluoro substances are colourless and do not interfere with the optical properties that are necessary for the functioning of an underlying anti reflex coating (US patent No. 6,277,485, USEPO 2015). (Meth)acrylates with straight (C1-9) perfluorocarbon chains are also mentioned in patents for this type of use (US patent 8231973 from 2012, USEPO 2015).

According to information provided by Swedish Chemicals Agency (2015b) the following C9-C14-PFCAs and related substances may be used in electronic articles:

- poly/perfluorinated amines (C4-18)
- poly/perfluorinated phosphoorganics (C4-9)
- poly/perfluorinated iodides (C4-20)

## A.4.2.10 Photographic surface layers

According to information from industry (European Chemicals Agency, 2015a) less than 0.1 ton PFOA and 0.1 ton PFOA-related substances are used in the EU per year for photographic applications. It is not known if C9-C14-PFCAs and related substances are used in this sector as well. It can be assumed that this may be a minor use.

## A.4.2.11 Semiconductors

According to one stakeholder, C9-C14 PFCAs (low kg range) are used for manufacturing a small part of semiconductors outside the EU. This use is decreasing. The company will stop using C9-C14 PFCAs in 2019. Imported articles contain traces of C9-C14 PFCAs , howecer a concentration was not reported.

## A.4.2.12 Medical devices

Fluorochemicals are used in medical devices and equipment. Textiles, for example surgical drapes and gowns are treated with side-chain fluorinated polymers to improve the surfaces and to enhance water-, oil- and dirt-resistance. The inert properties of fluoropolymers make

them suitable material for implants and other medical materials. Also highly fluorinated substances are used in the manufacture of x-ray film that is still needed for photo imaging with medical equipment (OECD, 2013).

According to Swedish Chemicals Agency (2015b) there is a Japanese patent available indicating that C9-C14-PFCAs and their related substances may be used for the manufacturing of contact lenses. The text of the patent refers to other patents in which PFAS are proposed as raw materials.

-   (meth)acrylate polymers (C1-4) and carboxylic acid esters (C1-20) (US patent 8,288,496, USEPO 2015).

C9-C14-PFCA related substances may also be used in UV-hardened dental restorative materials (Swedish Chemicals Agency 2015). The information is based on a German patent document from 2013 mentioning longer perfluorinated alkyl chains (C1-9 and C2-6) (US patent 8,466,210, USEPO 2015).

## A.4.2.13 Building materials

Fluoropolymers, such as PVDF, can be used as surface treatments in various building materials (for example, tiles and glass material) to impart fire- or weather-resistant properties. According to Swedish Chemicals Agency (2015b), there are reports that some fluorochemicals are used in various building and construction articles that have contact with lightweight concrete. Examples of these substances are thiols, C8-C20-γ-ω-perfluorotelomer thiols with acrylamide (CAS number 70969-47-0). This is found in Australia but it is not known whether this use also occurs in the EU and in the Nordic countries (Posner et al. 2013). The construction material in question here is often recovered, crushed and used as a filling material at landfill sites (Swedish Chemicals Agency 2015b).

# Annex B: Information on hazard and risk

## B.1. Identity of the substance(s) and physical and chemical properties

### B.1.1. Name and other identifiers of the substance(s)

### B.1.2. Composition of the substance(s)

### B.1.3. Physicochemical properties

The following tables summarise the physicochemical properties of the C9-C14 PFCAs.

*Table B.1- 1: Oerview of physicochemical properties of C9-PFCA*

| Property | Value | Remarks |
|---|---|---|
| **Physical state at 20°C and 101.3 kPa** | solid | (Yaws, 2008) |
| **Melting point** | 68 °C (at 1 atm) | (Yaws, 2008) |
| **Boiling point** | 218 ° C (at 1 atm) | (Yaws, 2008) |
| **Vapour pressure** | No data | |
| **Water solubility** | No data | |
| **Partition coefficient n-octanol/water (log value)** | 5.9 | (Wang et al., 2011b) Estimated using COSMOtherm C9-PFCA has surface active properties |
| **Dissociation constant** | < 1.6 0.82 (COSMOtherm) | (Vierke et al., 2013b) (Wang et al., 2011b) Estimated values |

*Table B.1- 2: Overview of physicochemical properties of C10-PFCA*

| Property | Value | Remarks |
|---|---|---|
| **Physical state at 20°C and 101.3 kPa** | solid | |
| **Melting point** | 87.4-88.2 °C | (Hare et al., 1954) |
| **Boiling point** | 218° C<br><br>203.4 °C<br>219.4 °C | (Kauck and Diesslin, 1951) (measured)<br>(Kaiser et al., 2005)<br>(Kaiser et al., 2005) (estimated) |
| **Vapour pressure** | 3.1 to 99.97 kPa (129.6 to 218.9 °C) | (Kaiser et al., 2005) (calculated) |
| **Water solubility** | 5.14 g/L at 25 °C | (Kauck and Diesslin, 1951) (measured) |

| | | |
|---|---|---|
| **Partition coefficient n-octanol/water (log value)** | 6.5 | (Wang et al., 2011b) Estimated using COSMOtherm C10-PFCA has surface active properties |
| **Dissociation constant** | < 1.6 2.58 (COSMOtherm) | (Vierke et al., 2013b) (Moroi et al., 2001) Estimated values |

*Table B.1- 3: Overview of physicochemical properties of C11-PFCA*

| Property | Value | Remarks |
|---|---|---|
| **Physical state at 20°C and 101.3 kPa** | solid | According to melting point |
| **Melting point** | 112-114 °C | (Huang et al., 1987) (measured) |
| **Boiling point** | 238.4 °C (at 101.325 kPa) | (Kaiser et al., 2005) (calculated) |
| **Vapour pressure** | 0.6 to 99.97 kPa (112 to 237.7 °C) | (Kaiser et al., 2005) (calculated) |
| **Water solubility** | 1.2E-4 g/L; pH 1 at 25°C 9.0E-4 g/L; pH 2 at 25°C 8.5E-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 using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Partition coefficient n-octanol/water (log value)** | 7.2 | (Wang et al., 2011b) Estimated using COSMOtherm C9-PFCA has surface active properties |
| **Dissociation constant** | < 1.6 0.52 ± 0.10 | (Vierke et al., 2013b) Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |

*Table B.1- 4: Overview of physicochemical properties of C12-PFCA*

| Property | Value | Remarks |
|---|---|---|
| **Physical state at 20°C and 101.3 kPa** | solid | According to melting point |
| **Melting point** | 112-114 °C | (Huang et al., 1987) (measured) |
| **Boiling point** | 249 °C | Data from SRC PhysProp Database, 02/2012 "PhysProp" data were obtained from Syracuse Research Corporation of Syracuse, New York (US) |
| **Vapour pressure** | 0.0043 mm Hg | Estimated value |

| | 9.40E-3 Torr at 25°C | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
|---|---|---|
| **Water solubility** | 4.81E-006 mg/L 2.9E-5 g/L pH 1 at 25°C 2.2E-4 g/L pH 2 at 25°C 2.0E-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 | Estimated value Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Partition coefficient n-octanol/water (log value)** | logP 9.363 ± 0.888 at 25°C 7.8 | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) *The value was most likely calculated for the non-ionised form.* (Wang et al., 2011b) Estimated using COSMOtherm C9-PFCA has surface active properties |
| **Dissociation constant** | 0.52 ± 0.10 | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |

*Table B.1- 5: Overview of physicochemical properties of C13-PFCA*

| Property | Value | Remarks |
|---|---|---|
| **Physical state at 20°C and 101.3 kPa** | solid | According to melting point |
| **Melting point** | 112-123 °C 117.5-122°C | (Aldrich) (Kunieda and Shinoda, 1976) |
| **Boiling point** | 260.7±35.0 °C (at 101.32 kPa) | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Vapour pressure** | 3.59E-3 Torr at 25°C = 0.479 Pa | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Water solubility** | 7.3E-6 g/L; pH 1 at 25 °C 5.5E-5 g/L; pH 2 at 25 °C 5.1E-4 g/L; pH 3 at 25 °C | Calculated using Advanced Chemistry Development |

| | | |
|---|---|---|
| | 3.5E-3 g/L; pH 4 at 25 °C<br>8.6E-3 g/L; pH 5 at 25 °C<br>0.0100 g/L; pH 6-10 at 25 °C | (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Partition coefficient n-octanol/water (log value)** | logP 10.093 ± 0.901 at 25°C<br><br><br><br><br><br>8.25 | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) *The value was most likely calculated for the non-ionised form.* (Wang et al., 2011b) Estimated using COSMOtherm C9-PFCA has surface active properties |
| **Dissociation constant** | 0.52 ± 0.10 | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |

*Table B.1- 6: Overview of physicochemical properties of C14-PFCA*

| Property | Value | Remarks |
|---|---|---|
| **Physical state at 20°C and 101.3 kPa** | solid | According to melting point |
| **Melting point** | 130 °C | (BIG Database) (Lehmler et al., 2001) (Kunieda and Shinoda, 1976) |
| **Boiling point** | 270 °C (at 98.6 kPa) | (BIG Database) |
| **Vapour pressure** | 1.37E-3 Torr at25 °C = 0.183 Pa | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Water solubility** | 1.9E-6 g/L; pH 1 at 25°C<br>1.4E-5 g/L; pH 2 at 25°C<br>1.3E-4 g/L; pH 3 at 25°C<br>9.3E-4 g/L; pH 4 at 25°C<br>2.2E-3 g/L; pH 5 at 25°C<br>2.6E-3 g/L; pH 6-10 at 25°C | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |
| **Partition coefficient n-octanol/water (log value)** | logP 10.823 ± 0.914 at 25°C<br><br><br><br><br>8.9 | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) *The value was most likely calculated for the non-ionised form.* (Wang et al., 2011b) |

| | | Estimated using COSMOtherm C9-PFCA has surface active properties |
|---|---|---|
| **Dissociation constant** | 0.52 ± 0.10 | Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) |

<u>Dissociation of C9-14-PFCAs and its salts in aqueous media</u>

Under environmental conditions in aqueous media the free perfluorinated carboxylic acids (PFCAs) stay in equilibrium with their conjugate bases, the perfluorinated carboxylates. The fraction of each species depends on the acid dissociation constant (pKa) and the pH of the environmental compartment. Salts of PFCAs, which are sometimes used in laboratory experiments, will be in equilibrium with the corresponding acid in aqueous phases as well. Currently used techniques for analysis and quantification of PFCAs in i.e. environmental samples are not able to distinguish between both of the species. Therefore, reported concentrations always include the acids as well as the bases. If reported concentrations are used for the determination of bioaccumulation factors or for experiments determining the persistency, aqueous phase concentrations include both species. Experimental determination of pKa is difficult for PFCAs, i.e. because of the surface active properties. Calculated values should be taken with care, because for most of the models it is unclear whether PFCAs are within their applicability domain. For assessing the intrinsic properties of the PFCA within this dossier the exact knowledge of the fraction of each species is not required, because both of the species will be available independently from the starting conditions.

# B.1.4. Justification for grouping

C9-C14-PFAC belong to the same substance category of long-chain 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 with experimental and estimated data, it can be concluded that with increasing chain length water solubility decreases and the sorption potential increases (see Table B.1- 7). It can be stated with sufficient reliability that the behaviour of the PFCAs follows a regular pattern.

*Table B.1- 7: 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, pentadecafluoro-** | **Nonanoic acid, heptadeca-fluoro-** | **Decanoic acid, nonadeca-fluoro-** | **Undecanoic acid, heneicosa-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 No | 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 | 414.09 | 464.08 | 514.08 | 564.0909 | 614.0984 | 664.1059 | 714.11 |
| Partitioning Coefficient log K$_{OW}$ | 2.82 (calc., COSMOtherm (temp. not specified) (Wang et al., 2011b)<br><br>3.39± 0.60 (calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02) | 3.48 (US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.11. Nov, 2012. Available from, as of Jan 11, 2015<br><br>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) |

| 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 |
| | | 4.99 ± 0.71 (calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02) | | | | | | | |
| log K$_{OA}$ | 6.04 (calc., COSMOtherm, Wang *et al.* 2011b) | 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) |
| log K$_{AW}$ | -3.23 (calc., COSMOtherm, Wang *et al.* 2011b) | -2.58 (calc., COSMOtherm, Wang *et al.* 2011b) | -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 | <1.6 (Vierke *et al.* 2013b)<br><br>0.85 (calc., COSMOtherm, Wang *et al.* 2011b) | <1.6 (Vierke *et al.* 2013b)<br><br>0.84 (calc., COSMOtherm, Wang *et al.* 2011b)<br><br>-0.16 (Zhao et al., 2014) | 0.5 (Vierke et al., 2013b) 2.5 (Ylinen *et al.* 1990) 2.8 in 50% aqueous ethanol (Brace, 1962)<br><br>1.3 (López-Fontán et al., 2005) | <1.6 (Vierke *et al.* 2013b)<br><br>0.82 (calc., COSMOtherm, Wang *et al.* 2011b) | <1.6 (Vierke *et al.* 2013b)<br><br>2.58 (Moroi *et al.* 2001) | <1.6 (Vierke *et al.* 2013b) | | | |
| Partition coefficients log | | | 0.04 (Ahrens *et al.* 2010)* | 0.6 (Ahrens *et al.* 2010) * | 1.8 (Ahrens *et al.* 2010) * | 3.0 (Ahrens *et al.* 2010) * | | | |

| 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 |
| K$_d$ (sediment and overlapping dissolved phase) | | | | | | | | | |
| Log Koc (sediment organic carbon-normalised distribution coefficient) | 1.88 (Guelfo and Higgins, 2013) | 1.31 (Guelfo and Higgins, 2013)<br><br>1.63 – 2.35 (Sepulvado et al., 2011) | 2.06 (Higgins and Luthy, 2006)#<br><br>1.09 (Ahrens *et al.* 2010)* | 2.39 (Higgins and Luthy, 2006)#<br><br>2.4 (Ahrens *et al.* 2010)* | 2.76 (Higgins and Luthy, 2006)#<br><br>3.6 (Ahrens *et al.* 2010)* | 3.3 (Higgins and Luthy, 2006)#<br><br>4.8 (Ahrens *et al.* 2010)* | | | |
| Water solubility | | 15.7 g/L (25°C)<br><br>(Zhao et al., 2014) | 9.5 g/L (25° C)<br><br>4.14 g/L (22°C)<br><br>(European Chemicals Agency, 2015a) | | 5.14 g/L at 25°C (Kauck and Diesslin, 1951) | 1.2E-4 g/L; pH 1 at 25°C<br><br>9.0E-4 g/L; pH 2 at 25°C<br><br>8.5E-3 g/L; pH 3 at 25°C<br><br>0.056 g/L; pH 4 at 25°C<br><br>0.14 g/L; pH 5 at 25°C<br><br>0.16 g/L; pH 6-10 at 25°C<br><br>(calculated) | 2.9E-5 g/L pH 1 at 25°C<br><br>2.2E-4 g/L pH 2 at 25°C<br><br>2.0E-3 g/L pH 3 at 25°C<br><br>0.014 g/L pH 4 at 25°C<br><br>0.034 g/L pH 5 at 25°C<br><br>0.039 g/L pH 6 at 25°C | 7.3E-6 g/L; pH 1 at 25 °C<br><br>5.5E-5 g/L; pH 2 at 25 °C<br><br>5.1E-4 g/L; pH 3 at 25 °C<br><br>3.5E-3 g/L; pH 4 at 25 °C<br><br>8.6E-3 g/L; pH 5 at 25 °C<br><br>0.0100 g/L; pH 6-10 at 25 °C | 1.9E-6 g/L; pH 1 at 25°C<br><br>1.4E-5 g/L; pH 2 at 25°C<br><br>1.3E-4 g/L; pH 3 at 25°C<br><br>9.3E-4 g/L; pH 4 at 25°C<br><br>2.2E-3 g/L; pH 5 at 25°C<br><br>2.6E-3 g/L; pH 6-10 at 25°C |

| 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 |
| | | | | | | (European Chemicals Agency, 2012b) | 0.040 g/L pH 7 at 25°C<br><br>0.041 g/L pH 8-10 at 25°C<br><br>(calculated)<br><br>(European Chemicals Agency, 2012e) | (calculated)<br><br>(European Chemicals Agency, 2012d) | (calculated)<br><br>(European Chemicals Agency, 2012c) |
| Vapour pressure | | 1.98 mm Hg at 25°C<br><br>US EPA; Estimation Program Interface (EPI) Suite. Ver. 4.11. Nov, 2012. Available from, as of Jan 11, 2015<br><br>Estimated (no experimental value available, unknown reliability of estimated value) | 4.2 Pa (25 °C) for C8-PFCA extrapolated from measured data<br><br>2.3Pa (20 °C) for C8-PFCA extrapolated from measured data<br><br>128 Pa (59.3 °C) for C8-PFCA measured<br><br>(European Chemicals | | 3.1 to 99.97 kPa (129.6 to 218.9 °C)<br><br>(calculated)<br><br>(Kaiser, 2005) | 0.6 to 99.97 kPa (112 to 237.7°C) (calculated)<br><br>(European Chemicals Agency, 2012b) | 1.25 Pa at 25°C (calculated)<br><br>(European Chemicals Agency, 2012e) | 0.48 Pa at 25°C (calculated)<br><br>(European Chemicals Agency, 2012d) | 0.18 Pa at 25 °C (calculated)<br><br>(European Chemicals Agency, 2012c) |

ANNEX XV RESTRICTION REPORT – C₉-C₁₄ PFCAs -including their salts and precursors-

| Abbreviation | C₄-PFCA | C₆-PFCA | C₈-PFCA | C₉-PFCA | C₁₀-PFCA | C₁₁-PFCA | C₁₂-PFCA | C₁₃-PFCA | C₁₄-PFCA |
|---|---|---|---|---|---|---|---|---|---|
| Acronym | PFBA | PFHxA | PFOA | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| | | | Agency, 2015a) Ammonium salt of PFOA: <0.1 hPa at 20 °C 0.012 Pa at 25 °C 0.0028 Pa at 25 °C (Nielsen, 2012) | | | | | | |
| Boiling point | | 157°C (Savu, 2000) | 189°C (Savu, 2000) | 218°C (Yaws, 2008) | 218°C measured (Kauck and Diesslin, 1951) | 238.4 °C (Kaiser et al., 2005) (calculated) | 249 °C SRC PhysProp Database | 260.7°C Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs) | 270 °C (BIG Database) |

*pH of the water samples analysed 7.1-8.3 Temp.: 15.3 – 17.7 °C

*Table B.1- 8: Information on degradation of C8-C14 PFCAs (European Chemicals Agency, 2012b; European Chemicals Agency, 2012c; European Chemicals Agency, 2012d; European Chemicals Agency, 2012e; European Chemicals Agency, 2013; European Chemicals Agency, 2015c; European Chemicals Agency, 2016b)*

| Abbreviation | C$_8$-PFCA | | C$_9$-PFCA | C$_{10}$-PFCA | C$_{11}$-PFCA | C$_{12}$-PFCA | C$_{13}$-PFCA | C$_{14}$-PFCA |
|---|---|---|---|---|---|---|---|---|
| Acronym | PFOA | APFO | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| Phototransformation in water DT50 | No photodegradation detected under relevant env. Conditions | No photodegradation detected under relevant env. Conditions | No photodegradation tested under relevant env. Conditions 100 % after 12 h by use of persulfate ion (S$_2$O$_8^{2-}$) in water | No photodegradation tested under relevant env. Conditions 100 % after 12 h by use of persulfate ion (S$_2$O$_8^{2-}$) in water | No photodegradation tested under relevant env. Conditions 77% after 12 h by use of persulfate ion (S$_2$O$_8^{2-}$) in water | | | |
| Hydrolysis DT50 | >97 yr | | No hydrolysis tested under relevant env. Conditions; 97% (absence of S$_2$O$_8^{2-}$) and 100% (by use of S$_2$O$_8^{2-}$) after 6 h in 80°C water | | | | | |
| Direct photolysis | | No photo-degradation | | | | | | |
| indirect photolysis | | No photo-degradation (H$_2$O$_2$; synthethic humic water, Fe$_2$O$_3$) estimated half-life > 349 days (Fe$_2$O$_3$) | | | | | | |
| ready biodegradability screening test | not readily biodegradable (OECD 301 C,F) | not readily biodegradable (OECD 301 B) | not readily biodegradable (OECD 301 F) | | | not readily biodegradable (OECD 301 C) | | not readily biodegradable (OECD 301 C) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Simulation tests | No elimination by metabolic processes, mineralization or adsorption | | | | | | | |
| Biodegradation in soil, sediment | No degradation detected | | | | | | | |

*Table B.1- 9: Information on bioaccumulation of C8-C14 PFCAs (European Chemicals Agency, 2012b; European Chemicals Agency, 2012c; European Chemicals Agency, 2012d; European Chemicals Agency, 2012e; European Chemicals Agency, 2013; European Chemicals Agency, 2015c; European Chemicals Agency, 2016b)*

| Abbreviation | $C_8$-PFCA | $C_9$-PFCA | $C_{10}$-PFCA | $C_{11}$-PFCA | $C_{12}$-PFCA | $C_{13}$-PFCA | $C_{14}$-PFCA |
|---|---|---|---|---|---|---|---|
| Acronym | PFOA | PFNA | PFDA | PFUnDA | PFDoDA | PFTrDA | PFTeDA |
| **BCF** | | | | | | | |
| Rainbow trout (carcass) | 4.5 ± 0.6 | - | 450 ± 62 | 2700 ± 400 | 18000 ± 2700 | - | 23000 ± 5300 |
| Rainbow trout (blood) | 27 ± 9.7 | - | 2700±350 | 11000 ±1400 | 40000 ± 4500 | - | 30000 ± 4200 |
| Rainbow trout (liver) | 8.0 ± 0.59 | - | 1100 ± 180 | 4900 ± 770 | 18000 ± 2900 | - | 30000 ± 6000 |
| Carp (whole) | 3.2-94 | - | - | 2300-3700 | 10000-16000 | - | 16000-17000 |
| **BAF** | 0.038-292 | 39-3981 | 714-158489 | 1409-1000000 | 10000-5011872 | - | 15857-19294 |
| **BMF** | 0.02-125 | 0.13-111 | 0.1-87 | 0.21-353 | 0.1-156 | 0.35-3.4 | 0.33-8.5 |
| **TMF** | 0.2-13 | 1.9-7.0 | 0.39-12.1 | 0.75-10.2 | 0.7-5.87 | 2.45 | 0.23-3.05 |

# B.2. Manufacture and uses (summary)

**Manufacturing**

To date there is no active registration under REACH of C9-C14 PFCAs, their salts and related substances. The substances are however, still manufactured as unintended side fraction during the manufacturing of per- and polyfluorinated chemicals containing a carbon chain of less than nine carbon atoms such as the C6- perfluorinated carbon chain. Pre-registrations exist for a number of C9-C14 PFCAs, their salts and related substances. It may be possible that these substances will be registered during the last registration period in 2018.

Only limited data are available for the global manufacturing of C9-C14 PFCAs. The global manufacturing volume of C9-PFCA ammonium salt was estimated to increase until 2015 to a maximum volume of 107 t. After 2016 the manufacturing volumes are expected to decline to zero, due to the results of the US-EPA Stewardship-Program. At least one company in Japan manufactured C9-PFCA ammonium salt in the past. Articles available on the global market i.e. Surflon S-111 (CAS 72968-38-8) contain a mixture of long-chain PFCAs, such as C9-PFCA, C11- and C13-PFCA. According to information from the internet this use has ceased.

Data on manufacturing volumes for C9-C14 PFCA related substances are not available, but a number of substances seem to be available on the world market.

C9-C14 PFCAs, their salts and related substances are mainly manufactured unintentionally. They occur as side fraction during the manufacturing of per- and polyfluorinated substances with carbon chains of less than 9 carbons.

**Uses**

No intentional uses of C9-C14 PFCAs, their salts and related substances were reported during the stakeholder consultations. Thus, it can be assumed that manufacturing and use has been ceased in Europe. One stakeholder has reported that small volumes of C9-C14 PFCAs (in the kg range) are used for manufacturing semiconductors outside the EU. The substacnes are used in Semiconductors or articles containing semicontoctors are imported into the EU. However the stakeholder will use a substitue from 2019 on. One major (historical) use of the C9-PFCA ammonium salt (APFN) has been the manufacturing of polyvinylidene fluoride (PVDF). The global use of PVDF increases. However, as reported by industry, PVDF used in Europe is manufactured without APFN. There are no recent information available for other regions.

Only little information is available on the uses of C9-C14 PFCA related substances. According to stakeholders consulted, these substances are only unintentional impurities in per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms and are not used intentionally within the EU. A search in the Swedish Product Register seems to clarify that the use of C9-C14 PFCA related substances is declining. The time trend examples from Sweden show that a substitution process or phasing out has taken place for the use of PFCA C9-C14 related substances in several important application areas. It is assumed that a similar substitution process has taken place or is under way in the rest of EU. Duringn the stakeholder consultation The PFOA restriction was reported as main driver to decrease the use of long-chain PFCAs including C9-C14-PFCA related substances.

One stakeholder reported the use of the substances as analytical standard in the laboratory and for research and development purposes (gram to kg quantities). One stakeholder reported that it could not rule out for sure the use of the substances by suppliers outside the

EU. Thus, it may be possible that C9-C14-PFCA related substances are still imported in articles and mixtures into the EU above the proposed threshold.

# B.3. Classification and labelling

See Chapter 1.1.3

# B.4. Environmental fate properties

## B.4.1. Degradation

### B.4.1.1 Degradation of C9-C14 PFCAs

C9-C14 PFCAs as well as the ammonium and sodium salts of C9-PFCA and C10-PFCA were included on the Candidate List as Substances of Very High Concern. All substances meet the P and vP-criteria of REACH Annex XIII based on the weight of evidence approach (European Chemicals Agency, 2012b; European Chemicals Agency, 2012c; European Chemicals Agency, 2012d; European Chemicals Agency, 2012e; European Chemicals Agency, 2015c; European Chemicals Agency, 2016b).

### B.4.1.2. Degradation of C9-C14 PFCA-related substances

Only limited degradation studies of C9-C14 PFCA-related substances are available. Therefore, read-across to C8, C6 and C4 PFCA-related substances was used. In general, the polyfluorinated substances (PFCAs) are degraded to perfluorinated acids. It can be assumed that the degradation mechanism for C9-C14 PFCA-related substances is similar to the homologues containing a carbon chain of less than nine 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 C9-C14 PFCAs 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.

## B.4.1.2.1 Fluorotelomere alcoholes (FTOHs)

*Table B.4- 1: Summary of formed PFCAs during degradation of FTOHs and the intermediate products (5:3 acid, fluorotelomer carboxylic acid (FTCA) and fluorotelomer unsaturated carboxylic acid (FTUCA)*

| Substance | Compartment | Study duration | C4-PFCA [%] | C5-PFCA [%] | C6-PFCA [%] | C7-PFCA [%] | C8-PFCA [%] | C9-PFCA [%] | C10-PFCA [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| 6:2 FTOH | Atmosphere | | + | + | + | + | | | | (Ellis et al., 2004b) |
| | 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., 2016) |
| 5:3 acid | WWTP-activated sludge | 90 d | | 0.8 mol% | 5.9 mol% | | | | | (Wang et al., 2012) |
| 8:2 FTOH | Atmosphere | | 0.1 | 0.1 | 0.24 | 0.32 | 1.5 | 1.6 | | (Ellis et al., 2004b) |
| | Aqueous photolysis – H2O2 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) |
| 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) |
| 10:2 FTOH | soil | 30 d | | | | | | 5.1 mol% | 4.3 mol% | 59.7 mol% | (Zhao and Zhu, 2017) |
| | Soil-earthworm | | | | | | | 8.7 mol% | 7.3 mol% | 74.9 mol% | |
| | Soil-wheat | | | | | | | 8.9 mol% | 5.9 mol% | 77.8 mol% | |
| | Soil-earthworm-wheat | | | | | | | 9.9 mol% | 6.0 mol% | 74.8 mol% | |
| 10:2 FTCA | Sediment-water system | 50 d | | | | | | | | 11 mol% (sed.) | (Myers and Mabury, 2010) |
| 10:2 FTUCA | Sediment-water system | 35 d | | | | | 0.37 mol% (sed.) | 1.9 mol% (sed.) | 1.1 mol% (water) 1.7mol% (sed.) | 6 mol% (water) 22 mol% (sed.) | (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 N2 or air, diluent at 296 +/- 2K. 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).

C6-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 (C7-PFCA, C6-PFCA, and C5-PFCA). These results provides 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 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%), C6-PFCA (4.5%), C5-PFCA (4.2%), and C4-PFCA (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 % C5-PFCA, 8.1% C6-PFCA, 1.8% C4-PFCA, 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 FT ketone were incubated with soil to elucidate the biodegradation pathway. 5:2 FT ketone yielded 5:2 sFTOH (78%), C6-PFCA (4%) and C5-PFCA (18%) after 90 days. Incubation with 5:2 sFTOH for 60 days yielded C6-PFCA (12%), C5-PFCA (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). C6-PFCA (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%), C6-PFCA (11 mol%), and C5-PFCA (4.4 mol%). C4-PFCA and C7-PFCA were not observed within two months. Another study investigated the biotransformation of 5:3 acid in activated sludge (Wang et al., 2012). After 90 days the 5:3 acid biotransformation yielded 4:3 acid (14.2 mol%), C5-PFCA (5.9 mol%) and C4-PFCA (0.8 mol%).

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% C5-PFCA, 8.4 mol% C6-PFCA, and 1.5 mol% C4-PFCA were detected. C7-PFCA was not observed. Most of the 5:3 acid formed bound residues with sediment organic components, which can only be recovered by NaOH 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 B.4- 1 illustrates the proposed biodegradation pathway of 6:2 FTOH in aerobic sediment systems.
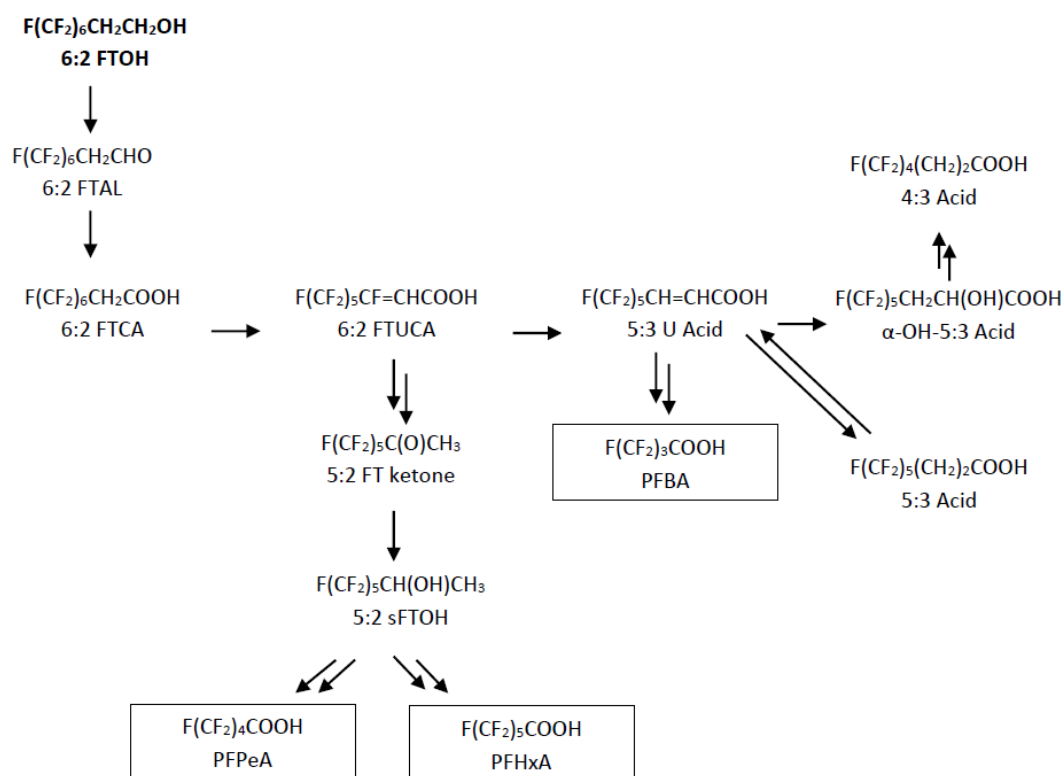


*Figure B.4- 1: Proposed 6:2 FTOH biotransformation pathways in aerobic sediment system. The single arrows indicate transformation steps based on observed transformation product and the double arrows indicate multiple transformation steps (based on (Zhao et al., 2013a)).*

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. C6-PFCA 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.

C8-FTOH

The following text was copied from the background document of the restriction proposal on perfluoroctanoin acid (C8-PFCA) (European Chemicals Agency, 2015a).

8:2 FTOH metabolism universally show the formation of C8-PFCA and, to a smaller fraction, C9-PFCA and lower-chain-length PFCAs (Butt et al., 2014).

Dinglasan et al. investigated biodegradation of 8:2 FTOH using mixed microbial system (Dinglasan et al., 2004). The enrichment culture was obtained from sediment and groundwater from a contaminated site. By day 81, C8-PFCA 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 major metabolite at day 81 (~50% of the total mass). Further degradation of 8:2 FTUCA may lead to an increase of C8-PFCA concentration (see Figure B.4- 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 C8-PFCA increased over 56 days and levelled off to 6% of the 14C 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 C8-PFCA (see Figure B.4- 2) (Wang et al., 2005a). In the activated sludge system 2.1% C8-PFCA and 33% sum of 8:2 FTUCA and 8:2 FTCA of the initial 14C mass have been identified after 28 days (Wang et al., 2005b). Similar degradation pathways were observed in aerobic soil, whereby formation of C8-PFCA were 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 C8-PFCA (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 C8-PFCA was not irreversibly bound to soils.
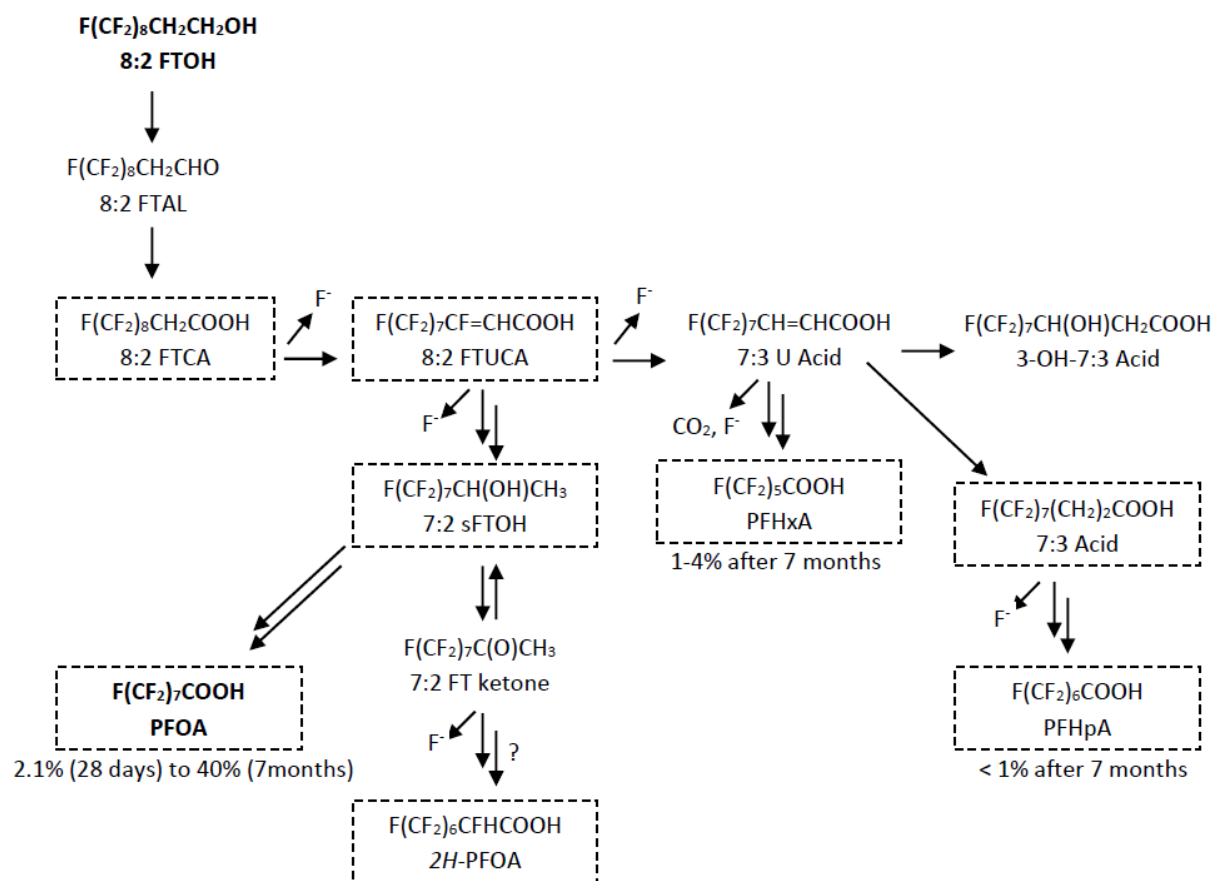
*Figure B.4- 2: Aerobic degradation pathways of 8:2 FTOH in soil and activated sludge (Figure based on (Liu and Mejia Avendano, 2013). The double arrows indicate multiple transformation steps. Defluorination reactions are indicated by release of fluoride ions (F−). Stable and semi-stable compounds are shown inside dashed boxes. 2H-PFOA (2H-C8-PFCA) has been proposed, but it has not been successfully validated as a C8-PFCA 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 [3-14C] 8:2 FTOH for 181 days. The half-life of 8:2 FTOH (primary degradation) is about 145 days. C8-PFCA formation was much lower compared with the results of the aerobic sludge and soil studies (0.3 mol% of initially applied [3-14C] 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.

Atmospheric degradation was further studied in a smog chamber (Ellis et al., 2004b). 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 C9-PFCA, C8-PFCA (1.5% C mass balance of 8:2 FTOH) and PFCAs containing a carbon chain of less than eight carbon atoms. The formation of C8-PFCA 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 C8-PFCA is small but significant and postulate that FTOH degradation is likely an important source of C8-PFCA 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 (10mM H$_2$O$_2$), 38.0 ± 6.0 hours (100µM H$_2$O$_2$), 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$_2$O$_2$ study after 10 hours were 8:2 FTCA (~60%) and C8-PFCA (~40%). During the experiment 8:2 FTAL was observed as a short-lived intermediate that underwent further photo-oxidation to C8-PFCA. 8:2 FTCA was shown to undergo aqueous phase photo-oxidation leading to C8-PFCA as the major product. It therefore appears that aqueous phase photo-oxidation of 8:2 FTOH will result in 75-100% C8-PFCA with time. In the other test systems 1-8% (after 140-146 hours; synthetic field water) and 18% C8-PFCA (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 C8-PFCA 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 C8-PFCA 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 C8-PFCA levels increased in a dose- and time dependent manner. The formation of C8-PFCA was around 10 times higher than that of C9-PFCA (Kudo et al., 2005). Similar results were observed in a study by Martin et al. (2005) were the formation of C8-PFCA was 10 times higher than that of C9-PFCA when measuredplasma 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 C8-PFCA 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> C8-PFCA >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 C8-PFCA decreased from 789 ± 41 to 668 ± 23 ng/ml and from 673 ± 23 to 587 ± 55 ng/g, respectively. C8-PFCA 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 C8-PFCA 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, 2007a).

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 C8-PFCA 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 C8-PFCA (median of 11 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 C8-PFCA (Nilsson et al., 2013). The

downside with this study is the lack of a control group showing possible background levels of FTOH-metabolites.

In conclusion, 8:2 FTOH mainly degrades to C8-PFCA in sludge, soil, water and air. In vertebrates, C8-PFCA is the main perfluoric acid formed by biotransformation of 8:2 FTOH. Emission and exposure of 8:2 FTOH will add to the overall blood concentration of C8-PFCA in human blood stream

10:2 FTOH

Zhao and Zhu investigated the behaviour of 10:2 FTOH in the systems of soil-earthworm (Eisenia fetida), soil-wheat (Triticum aestivum L.) and soil-earthworm-wheat, including degradation in soil, uptake and metabolism in wheat and earthworms (Zhao and Zhu, 2017). 10:2 FTOH was biodegraded by microorganisms to C8-PFCA, C9-PFCA and C10-PFCA. Assuming that the total molar mass of PFASs in the soils (soil, soil-earthworm, soil-wheat, soil-earthworm-wheat) was 100 mol%, the yields of the terminal metabolites were respectively as following: C8-PFCA (5.1, 8.7, 8.9, 9.9 mol% yield), C9-PFCA (4.3, 7.3, 5.9, 6.0 mol% yield) and C10-PFCA (59.7, 74.9, 77.8, 74.8 mol% yield). C10-PFCA was the primary degradation product in soil and the presence of earthworms and/or wheat stimulated the microbial degradation of 10:2 FTOH in soils.

10:2 FTOH could be taken up by wheat an earthworms from soil and biotransformed to PFCAs. C5-PFCA (~69-75 mol% yield), C6-PFCA (~22-25 mol% yield), and C10-PFCA (~2-6 mol% yield) were detected in root of wheat while C10-PFCA (~0-29 mol% yield) and C11-PFCA (70-99 mol% yield) were detected in shoot. C11-PFCA was only detected in shoot but not in roots and in soil, implying foliar uptake from the air with transformation of 10:2 FTOH. In earthworms C9-PFCA (11-19 mol% yield) and C10-PFCA (77-86 mol% yield) were detected as degradation products.

Fluorotelomer carboxylic acid (FTCA)/ fluorotelomer unsaturated carboxylic acid (FTUCA)

Fluorotelomer carboxylic acid (FTCA) and fluorotelomer unsaturated carboxylic acid (FTUCA) are intermediate transformation products during the transformation of FTOH to the corresponding PFCA (see Figure B.4- 1).

Myers and Mabury investigated the fate of fluortelomer carboxylic acids (FTCA) and the corresponding unsaturated acids (FTUCAs) in a simple sediment-water microcosm system (Myers and Mabury, 2010). 8:2 FTCA, 8:2 FTUCA, 10:2 FTCA and 10:2 FTUCA were monitored over time under different microcosm conditions: Control water microcosm (to monitor sorption to glass wall), sterile sediment microcosms (to monitor sorption on sediment) and active sediment microcosms. The bottles were spiked individually with a 0.1 g/L tap water solution of one of the above mentioned substances, to give a 1 μM concentration within each bottle. The fluorotelomer acids were rapidly degraded and sorption of the 10:2 telomer acid were greater compared with the corresponding 8:2 telomer acids.

In the 8:2 FTCA control and sterile microcosms, 22% of 8:2 FTCA was sorbed to glass walls by day 54 and 28% to sediment by day 32. In the 8:2 FTCA active sediment microcosm, no 8:2 FTCA was observed after 7 days either in the water or in the sediment. The only degradation product observed was C8-PFCA, approximately 30.3 mol% C8-PFCA was produced after 50 days (21 ± 3 mol% in water, 9.3 ±0.7 mol% in sediment).

In the 8:2 FTUCA control and sterile microcosms, no sorption to glass was observed, but 33±1.4 % 8:2 FTUCA sorbed to sediment by day 35. In the 8:2 FTUCA active sediment microcosm complete loss of 8:2 FTUCA in the water-phase was observed after 11 days, 22 mol% of 8:2 FTUCA remained in sediment. The following metabolites were observed: C8-PFCA (water phase: 27 ± 0.49 mol% at day 35; sediment: 9 mol% at day 35), C7-PFCA

(water phase: 12±0.16 mol% at day 22), C9-PFCA and C10-PFCA (both < 1 mol% in sediment).

In the 10:2 FTCA control and sterile microcosms, 66 mol% of 10:2 FTCA was sorbed to glass walls at day 54 and 55 mol% to sediment at day 32. Complete loss of 10:2 FTCA in the water-phase was observed at day 14 in the 10:2 FTCA active sediment microcosm. At day 2, 4, and 7 10:2 FTCA was found in sediment at an average molar recovery of 37 mol%, after which it was undetectable for the remaining time. C10-PFCA increased steadily in sediment to 11 mol% at day 50.

Each microcosm spiked with 10:2 FTUCA exhibited instability of the telomere acid, however, significant evidence of transformation products were observed only in the active sediment microcosm. In the 10:2 FUTCA active sediment microcosm, complete loss of 10:2 FTUCA in the water-phase was observed at day 22. 0.62 mol% of 8:2 FTUCA remained in sediment. By day 35, C10-PFCA was observed in the water-phase at 6 ± 0.65 mol% and in sediment at 22 ± 1.2 %. C9-PFCA was observed consistently in water and at day 35 with 1.1 mol%. After 35 days the following metabolites were also observed in sediment: 7:3 FTCA (2.1 ± 0.16 mol%), 9:3 FTCA (11mol%) 8:2 FTUCA (2.0 ± 0.15 mol%), C7-PFCA (0.37 ±0.049 mol%), C8-PFCA (1.9 ± 0.22 mol%), and C9-PFCA (1.7 ± 0.16 mol%).

All active sediment microcosm show significant losses in analyte molar balance. The authors indicate two possible explanations: a) irreversible sorption to sediment, b) FTUCA reactivity toward nucleophiles in the sediment, which would produce unidentified or unextractable covalently bound adducts. Nevertheless, the results indicate that degradation of the telomer acids in sediment occurs via biological activity and leads to formation of PFCAs.

***Conclusion: Based on the available data it can be expected 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 %/a. It can be assumed that the degradation mechanisms are independent from the chain length. Consequently, the degradation mechanisms shown in Figure B.4- 1 and Figure B.4- 2 are also transferable to n:2 FTOH (n = 10, 12, 14).***

## B.4.1.2.2 Fluorotelomer derivates

*Table B.4- 2: Summary of formed PFCAs during degradation of fluorotelomer derivates*

| Substance | Compartment | Study duration | C4-PFCA [%] | C5-PFCA [%] | C6-PFCA [%] | C7-PFCA [%] | C8-PFCA [%] | C9-PFCA [%] | C10-PFCA [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| **Fluorotelomer iodide (FTI)** | | | | | | | | | | |
| 6:2 FTI | Soil | 91 d | - | 20 mol% | 3.8 mol% | 16 mol% | | | | (Ruan et al., 2010) |
| 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) |
| 8:2 FTA | Soil | 105 d | | | <0.4 mol% | 1.3 mol% | 8 mol% | | | (Royer et al., 2015) |

| Substance | Compartment | Study duration | C4-PFCA [%] | C5-PFCA [%] | C6-PFCA [%] | C7-PFCA [%] | C8-PFCA [%] | C9-PFCA [%] | C10-PFCA [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| 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, 2011a) |
| 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 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 | | | |
| 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) |
| *Polyfluorinated amides* | | | | | | | | | | |
| N-ethyl-perfluoro-butyramide (NEtFBA) | Atmosphere | | | 16 | | | | | | (Jackson et al., 2013) |

| Substance | Compartment | Study duration | C4-PFCA [%] | C5-PFCA [%] | C6-PFCA [%] | C7-PFCA [%] | C8-PFCA [%] | C9-PFCA [%] | C10-PFCA [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| N-ethyl-N-(2-hydroxyethyl)perfluorooctaneamide (NEtFOA) | Hydrolysis pH14 pH 8.5 | 24h 8 d | | | | | 98 - | | | (Jackson and Mabury, 2013) |
| N-ethyl perfluorobutanesulfonamide (NEtFBSA) | 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% | | | |
| *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) |

| Substance | Compartment | Study duration | C4-PFCA [%] | C5-PFCA [%] | C6-PFCA [%] | C7-PFCA [%] | C8-PFCA [%] | C9-PFCA [%] | C10-PFCA [%] | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| 6:2 FTS | Aerobic sediment | 90 d | - | 21 mol% | 20 mol% | 0.55 mol% | | | | (Zhang et al., 2016) |
| | Anaerobic sediment | 100 d | - | - | - | - | | | | |
| *Fluorotelomer thioether amido sulfonate (FTTAoS)* | | | | | | | | | | |
| n:2 FTTAoS (n=4,6,8) | Soil amende with an AFFF solution | 60 d | + | + | + | + | | | | (Harding-Marjanovic et al., 2015) |
| *Perfluoroalkyl phosphinic acids (PFPiAs)* | | | | | | | | | | |
| PFPiAs | | | hydrolyze to PFPAs and CnF2n+1H (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 a atmospheric lifetime of approximately 1 day with respect to photolysis and approximaltey 20 days with respect to reaction with OH-radicals. The oxidation of perfluoroaldehyde lead to the formation of PFCA (e.g. for 4:2 FTI C3-C5 PFCAs). 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 C8-PFCA (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 C5-PFCA (20 mol%), C6-PFCA (3.8 mol%), 5:3 acid (16 mol%), and 4:3 acid (3 mol%). Furthermore, a significant level of C7-PFCA (16 mol%) was formed, perhaps via the intermediate 6:2 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 %/a.***

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 2 days. Subsequent degradation was monitored. Similar reaction products as shown in Figure B.4- 2 were found. C8-PFCA, which was the major terminal product, consistently increased over time reaching 1.7 mol% by day 80. C8-PFCA concentration has not reached plateau until day 80. Furthermore, C7-PFCA (0.38 mol%) and C6-PFCA (0.16 mol%) were detected as terminal product. C9-PFCA was also observed and increased over time (0.009 mol% on day 80). C9-PFCA 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 C8-PFCA 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 C8-PFCA (4 mol% at 94 days). Further terminal metabolites were C7-PFCA (0.9 mol%) and C6-PFCA (0.2 mol%). C8-PFCA 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 1. 4 mol% C8-PFCA, 0.2 mol% C6-PFCA, and 0.8 mol% C7-PFCA 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 %/a.***

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 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$_2$)$_n$CH=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).

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 B.4- 2). 8 mol% C8-PFCA was formed in FTA-amended

soil, and 10.3 mol% C8-PFCA was formed in FTMA-amended soil after 105 days, respectively. Besides the stable metabolites like C8-PFCA, C7-PFCA (1.3-3.4 mol%), C6-PFCA (< 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 %/a._**

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 C7-PFCA (8.4 mol% and 7.3 mol% expressed as percent PAP present in the aqueous phase at the start of the experiment), C6-PFCA (2.1 mol% and 6.2 mol%), C5-PFCA (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 C8-PFCA. The authors suggest that exposure in rats to either 8:2 monoPAPs or 8:2 diPAPs will result in increased C8-PFCA 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 C8-PFCA (D'eon and Mabury, 2011a).

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 100mg 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 %. Analysis 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: C6-PFCA > 5:3 acid > C5-PFCA > 6:2 FTUCA = 6:2 FTCA > C4-PFCA > 5:3 Uacid = C7-PFCA. C4-PFCA was the PFCA with the highest concentration in the plants after 5.5 months followed by C6-PFCA, C5-PFCA and C7-PFCA.

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 solution pH, 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% C6-PFCA, 6.4% C5-PFCA, 0.73% C4-PFCA 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% C8-PFCA, 0.25% C7-PFCA, 0.34% C6-PFCA 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.

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 C8-PFCA 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 %/a.***

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.***

Polyfluorinated amides

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 C8-PFCA was observed after 8 days at pH 8.5. Rapid degradation was observed in the borate buffer, but not to C8-PFCA. At pH 14 and at room temperature a quantitative (98%) conversion of EtFOA to C8-PFCA was observed after 24 hours. Hydrolysis from NEtFOA to C8-PFCA under environmental conditions will be negligible. The environmental fate of polyfluorinated amides is suggested to be volatilization to the atmosphere followed by oxidation by hydroxyl radical 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$_3$F$_7$C(O)NHCH$_2$CH$_3$) as a more volatile surrogate for longer chained polyfluorinated amides and identified C$_3$F$_7$C(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% C4-PFCA, 0.3% perfluoropropanoic acid and 0.3% trifluoroacetic acid). The authors predict similar reaction kinetic 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 C8-PFCA.

Martin et al. studied the atmospheric photo-oxidation (smog chamber experiment) of N-ethyl perfluorobutanesulfonamide (NEtFBSA, C$_4$F$_9$S(O)$_2$NHCH$_2$CH$_3$) and identified C$_4$F$_9$S(O)$_2$NHC(O)CH$_3$, C$_4$F$_9$S(O)$_2$NHCH$_2$CHOand C$_4$F$_9$S(O)$_2$NHCHO as intermediates, and SO$_2$, COF$_2$ and PFCAs as stable products (Martin et al., 2006). Three PFCAs were detected above the level of the blank: 0.33% C4-PFCA, 0.11% perfluoropropanoic acid, and 0.09 trifluoroacetic acid 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). The authors suggest that it is evident that analogous perfluorooctane sulfonamide is a potential source for C8-PFCA. They presented a general mechanism based on the observed product distribution. The atmospheric lifetime of NEtFBSA in the gas-phase (reaction with OH radicals) is estimated to be 20-50 days.

***Conclusion: Based on the available data it can be expected that polyfluorinated amides will be abiotic degraded and transformed into corresponding PFCAs in individual amounts greater than 0.1 %/a.***

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 C8-PFCA was observed. Nevertheless, the authors assume that the C8-PFCA 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 analog, 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 C8-PFCA, 0.11 mol% C7-PFCA, 0.07 C6-PFCA and 0.11mol% 8:2 FTOH were formed after 117 days. In the study with HMU 0.94 mol% C8-PFCA, 0.14 mol% C7-

PFCA, 0.06 mol% C6-PFCA, 0.88 mol% 7:2 sFTOH and 0.14 mol% 8:2 FTOH were observed at day 180. The authors estimated (KinKUii) final % C8-PFCA yields from FTU and HMU are 1.5-1.9 % and 3-5.2 %, respectively. In the experiments with forest soil C8-PFCA resulted from transformation of the 8:2 fluorotelomer urethane, since C8-PFCA 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 %/a.***

Fluorotelomer ethoxylates (FTEO)

Biotransformation of fluorotelomer ethoxylates was reported by Frömel & 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 12 and a degree of ethoxylation between 0 and 18 was analysed. Fluorotelomer ethoxylates were rapidly degraded (half-life (primary degradation = 1d). One significant metabolite was formed within the study duration of up to 48 days: Fluorotelomer ethoxylate carboxylate. The formation of 0.3 mol% C8-PFCA and 2.5 mol% C6-PFCA 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 de-sulfonation of 6:2 FTS may be the rate-limiting step. At day 90, 1.5% C5-PFCA, 1.1% C6-PFCA, 0.14% C4-PFCA 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 C7-PFHCA 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., 2016). In aerobic sediment 6:2 FTS was rapidly biotransformed with a half-life of less than 5 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 de-sulfonation. After 90 days 20 mol% C6-PFCA, 21 mol% C5-PFCA, 0.55 mol% C7-PFCA, 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 de-sulfonation, 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 0.6mol% C6-PFCA within 100 days in anaerobic sediment. These results confirm that the anaerobic experimental system was metabolically active and 6:2 FTS molecular structure 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 %/a.***

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 an 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, and C4 to C8 PFCAs. 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.

***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 hydrolyze to yield perfluoralkyl phosphonic acid (PFPAs) and CnF2n+1H. CnF2n+1H can be oxidized to from corresponding PFCAs (e.g. via reaction with OH radicals at high temperature or with alkaline conditions). Similary to PFCAs, PFPAs show high restiance 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 CnF2n+1H 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 chain covalently bonded to the polymer backbone may be transformed to PFCAs. The test substance itself was not directly measured, instead, terminal transformation products like C8-PFCA, C9-PFCA, C10-PFCA and C11-PFCA 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). C8-C11 PFCAs 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 C8-PFCA 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 C8-PFCA concentration ranged from 1.8 to 2.1 µmol C8-PFCA/kg soil. The residual amount of C8-PFCA in the test substance was 0.019 µmol C8-PFCA/kg soil. Hence, C8-PFCA is formed from degradation of residuals and possibly also from degradation of the side chains in the polymer. The maximum experimental C8-PFCA concentrations are 24-28% of the theoretical amount that could be derived from 100% conversion of the residuals alone (7.55 µmol C8-PFCA/kg soil). If all 8:2 related analytes are summed 25-32% of the theoretical amount of C8-PFCA 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 PFCA with longer chains. Similar to C8-PFCA the concentrations of C9-C11-PFCAs rise with time. The measurement of concentrations of higher PFCA-homologues (≥C12-PFCA) were not included in this study. The maximum concentrations after 728 days ranged from 0.089 to 0.218 µmol C9-PFCA/kg soil, 0.227 to 0.689 µmol C10-PFCA/kg soil and 0.016 to 0.045 µmol C12-PFCA/kg soil, respectively. Nevertheless, the amounts of longer chain FTOHs in the polymer were lower compared to 8:2 FTOH. Hence, lower concentrations of C9-C11-PFCA are not unexpected.

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 C8-PFCA 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 C8-PFCA. The maximum concentrations of C8-PFCA (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 C8-PFCA = 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 C8-PFCA formation from residuals was negligible in this study. Hence, the C8-PFCA formation resulted from biodegradation of the fluorotelomer-based urethane polymer. C9-C11-PFCAs were also formed during the experiment, but modelling of the polymer degradation only considered C8-PFCA formation.

Washington et al. also investigated the degradability of an acrylate-linked fluorotelomer polymer in soil (Washington et al., 2009). 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 C8-PFCA via the intermediate 8:2 FTOH. Estimated half-life of the tested coarse-grained polymer 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 C8-PFCA with an estimated half-life of 130 days. However, this result is contradictory to other studies which stated that C8-PFCA is 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 fluorotelomerbased 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 fluorotelomerbased 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 FTAC containing hydrogen and hexadecylthiol end groups and have primarily between 2 and 16 fluorotelomer appendages. The estimated half-lives ranged from 8 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 C6-PFCA, C7-PFCA, and C8-PFCA concurrently with the reduction of 8:2 FTCA and 8:2 FTUCA. C8-PFCA 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 < 1year under landfill conditions (40-50 °C and pH 4-9). Under some saturated landfill conditions abiotic hydrolytic degradation of fluorotelomer acrylates could be occur resulting in significant fluxes of FTOHs and their degradation products (e.g. C8-PFCA) into ground water and surface water.

Waste incineration of fluorotelomer-based polymers as a potential source of C8-PFCA 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 2 s at a mean gas temperature of 1000°C. No detectable levels of C8-PFCA 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 C8-PFCA 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 C9-C14 PFCA percursors and UVCBs

Other potential C9-C14 PFCA precursors and UVCBs cannot in general be classified as classes of substances leading to release of C9-C14 PFCAs. However, substances containing F(CF2)n(CH2)2-groups will most probably result in release of n:2 FTOHs in the environment. Thus, using the weigth of evidence approach they can be considered as a class of substances leading to release of C9-C14 PFCAs.

**Conclusion on degradation of C9-C14 PFCA-related substances**

In conclusion, all the presented C9-C14 PFCA-related substances are degraded to C9-C14 PFCAs 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 the substances will most probably be degraded in a similar way. Thus, based on the weight of evidence approach C9-C14 PFCAs will most probably be released in the environment. Hence, these substances need to be considered as important sources of C9-C14 PFCA in the environment. Furthermore, they need, according to REACH, be considered as PBT-substances as well.

# B.4.2. Environmental distribution

## B.4.2.1 Adsorption/desorption

The standard procedure to determine the sediment–water partitioning coefficient ($K_d$) is to calculate the ratio of the concentration in the sediment (ng kg$-1$ dw) to the concentration in the dissolved phase (ng L$-1$). The sediment–water partitioning coefficient normalized to carbon content ($K_{OC}$) is then derived from the following equation: $K_{OC} = K_d \times 100 / f_{OC}$ where $f_{OC}$ is the sediment organic carbon fraction.

**C9-C14 PFCAs**

Higgins and Luthy studied the sorption of various PFAS to natural sediments of varying iron oxide and organic carbon content (Higgins and Luthy, 2006). PFASs surfactant sorption was influenced by both sediment-specific and solution-specific parameters. Sediment organic carbon, rather than sediment iron oxide content, was the dominant sediment-parameter affecting sorption, indicating the importance of hydrophobic interactions. However, sorption also increased with increasing solution [Ca2+] and decreasing pH, suggesting that

electrostatic interactions play a role. According to Higgins et al., 2006 the perfluorocarbon chain length was the dominant structural feature influencing sorption, with each CF2 moiety contributing 0.50-0.60 log units to the measured distribution coefficients.

Kwadijk et al investigated field based the sediment–water distribution coefficients (K$_d$) for five PFASs (Kwadijk et al., 2010). K$_d$-values of 1.83, 2.89 and 2.87 were measured for C8-, C9- and C10-PFCA, respectively. The authors explain that the high standard derivation for C9-PFCA (0.53) compared with the much lower standard variation of 0.23 for C10-PFCA, meaning that they would expect a higher log K$_d$-value for the substance with a higher chain length.

The particulate associated fraction on the suspended particulate matter (SPM) was analysed by Ahrens et al. (Ahrens et al., 2010b). Using two depth profiles of seawater and two sediment cores from Tokyo Bay the partition coefficients of PFASs between SPM and the dissolved phase and sediment and dissolved phase were calculated. Moreover, the corresponding organic carbon normalised partition coefficients were analysed as well. Among a number of PFASs C9-C12 PFCAs and C14-PFCAs were analysed within this study. In the SPM fraction C9-11-PFCAs were detected. C9-PFCA was among the predominant substances with a contribution of 25%. C9-C12- and C14-PFCA were detected in the surface sediment (0-3 cm). In sediment concentrations of PFASs were much lower compared to SPM. C11-PFCA was among the PFASs with a greatest contribution with 16 %. Concentration levels in the sediment were by a factor of 30–40 lower than for the SPM fraction. However, the samples cannot be compared directly, as the surface sediment concentration represents a time period of 3 years (2006–2008) while the SPM fraction was collected on one specific date. The authors conclude that the long-chain PFCAs are distributed in the surface sediment, which could act as a sink for PFASs. The highest particulate associated fraction was observed for C11-PFCA with 62% in the study. This fraction decreased exponentially with decreasing perfluoroalkyl chain length. K$_d$-values increased with increasing chain length, indicating decreasing desorption behaviour. The authors conclude further that in general longer-chain PFCAs have a stronger potential to interact with SPM, which could be lead to sedimentation and accumulation in the sediment.

Zhao et al. analysed the sorption of PFASs to two sediments from different geographical locations (Zhao et al., 2012). The two sediments were fractionated according to their size and density and the distribution of PFASs in each fraction was investigated. Furthermore, desorption experiments were conducted to illustrate the bioavailability of sediment-associated PFASs.

Arvaniti et al. investigated the sorption of C8-PFCA, C10-PFCA and C11-PFCA onto different types of sewage sludge (Arvaniti et al., 2014). To determine the K$_d$ and K$_{OC}$ values for primary, secondary and digested sludge, batch experiments were conducted. The sorption equilibrium was reached after 8 h. The K$_d$ and K$_{OC}$ values for C8-, 10-, 11-PFCA are included in the following table. The values increase with increasing chain length.

Vierke et al. simulated riverbank filtration and set up a water-saturated sediment column to investigated the transport of several PFASs under near-natural conditions (Vierke et al., 2014). The enclosure with a length of 1m and a surface area of 1 m$^2$ of was embedded in a natural slow sand filter basin and fed by surrounding surface water. The water was pumped continuously through the sediment column with a velocity in the range of values often encountered in riverbank filtration systems. Water samples were taken an analysed from the supernatant, and at a depth of 40 and 80 cm. Interestingly, the partition coefficient of C9-PFCA was slightly lower than the one for C8-PFCA. The authors conclude, that the PFOA-value might have been overestimated due to a tailing peak of PFOA. The K$_d$-values reported by Vierke et al (2014) are lower than those reported in other studies. The authors conclude that sorption may be overestimated in batch studies due to lower sold:water ratios and because of break-up of aggregates resulting in larger surface areas accessible for sorption. However, also Ahrens et al., 2010 reported a similarly low log K$_d$-value of 0.6 for C9-PFCA calculated from infield studies.

Chen and Co-workers (2016) investigated the reversible and irreversible sorption of PFASs to bed sediments from an urban reservoir. Among a number of short-chain PFCAs and sulfonic acids, C9- and C10-PFCA have been studied. The sorption isotherms for C9- and C10-PFCA were nearly linear which implies a partition like-process. Irreversibility increased with chain-length and was nearly complete for C10-PFCA. The authors conclude that for strong adsorbing PFASs in the test C9- and C10-PFCAs bed sediments may act predominantly as irreversible sinks (Chen et al., 2016).

Hellsing et al. (2016) analysed the sorption of four PFASs including C9-PFCA to two types of minerals. It was shown that C9-PFCA adsorbs to alumina but not silica. This is explained by the difference in surface charge between alumina (positive) and silica, which is negatively charged. The authors conclude that the sorption to the solid mineral surface may be driven by electrostatic interactions between the negatively charged PFAS functional group and the mineral surface. Hellsing and co-workers conclude that PFASs sorb strongly to soils being rich in alumina (Al2O3) and other positively charged minerals (Hellsing et al., 2016).

Munoz et al. investigated the special distribution and partitioning of PFASs in 133 selected rivers and lakes in France (Munoz et al., 2015). Water and sediment samples were therefore collected and analysed. C9-C14 PFCAs were detected in the dissolved phase. However, the detection frequency decreased with increasing chain length. C9-PFCA was detected in 66 % and C13-PFCA in only 0.6% of the samples and C14-PFCA was not detected at all in the water samples. In sediment, however, all substances were detected in 33 – 47% of the samples. The measured concentrations of the C9-C14 PFCAs were relatively low (dissolved phase: up to 30ng/L and sediment up to 5 ng/g). K$_d$ and K$_{OC}$ values were calculated and are in agreement with those reported in other studies.

*Table B.4- 3: Sorption coefficients for C8-C14-PFCAs. Because only minor data on C12-C13 PFCAs and no data on C14 PFCA is available data for C8-PFCA are displayed as well for a trend analysis.*

| Type of adsorption coefficient | Media | C8-PFCA | C9-PFCA | C10-PFCA | C11-PFCA | C12-PFCA | C13-PFCA | Reference |
|---|---|---|---|---|---|---|---|---|
| Log K$_{OC}$ | Sediment | 2.11 | 2.50 | 2.92 | 3.30 | | | (Higgins and Luthy, 2006) |
| Log K$_d$ | Sediment | 1.83 | 2.89 | 2.87 | | | | (Kwadijk et al., 2010) |
| Log K$_{OC}$ | Suspended particulate matter | 3.50 | 4.00 | 4.60 | 5.10 | | | (Ahrens et al., 2010b) |
| | Sediment | 1.90 | 2.40 | 3.60 | 4.80 | | | |
| Log K$_d$ | Suspended particulate matter | 2.40 | 2.90 | 3.50 | 4.20 | | | |
| | Sediment | 0.04 | 0.60 | 1.80 | 3.00 | | | |
| Log K$_{OC}$ | Sediment | 2.09 2.17 | 2.50 2.35 | 3.23 2.78 | 3.80 3.65 | | | (Zhao et al., 2012) |
| Log K$_{OC}$ | Primary sludge | 2.85 | | 3.53 | 4.11 | | | (Arvaniti et al., 2014) |
| | Secondary sludge | 2.96 | | 3.98 | 4.68 | | | |
| | Digested sludge | 2.67 | | 3.88 | 4.53 | | | |
| Log K$_d$ | Primary sludge | 2.52 | | 3.20 | 3.78 | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Secondary sludge | 2.52 | | 3.54 | 4.24 | | | |
| | Digested sludge | 2.20 | | 3.41 | 4.07 | | | |
| Log $K_{OC}$ | Sediment 40 cm | 4,00 | 3,80 | | | | | (Vierke et al., 2014) |
| | Sediment 80 cm | 3.90 | 3.80 | | | | | |
| Log $K_d$ | Sediment 40 cm | 0.82 | 0.65 | | | | | |
| | Sediment 80 cm | 0.69 | 0.62 | | | | | |
| Log $K_{OC}$ | Sediment | 2.05 | 2.81 | 3.58 | | | | (Chen et al., 2016) |
| Log $K_d$ | | 0.45 | 1.21 | 1.98 | | | | |
| Log $K_{OC}$ | Sediment | 3.00 | 3.60 | 3.70 | 4.10 | 3.80 | 5.20 | (Munoz et al., 2015) |
| Log $K_d$ | | 1.90 | 2.50 | 2.60 | 3.00 | 2.70 | 4.10 | |
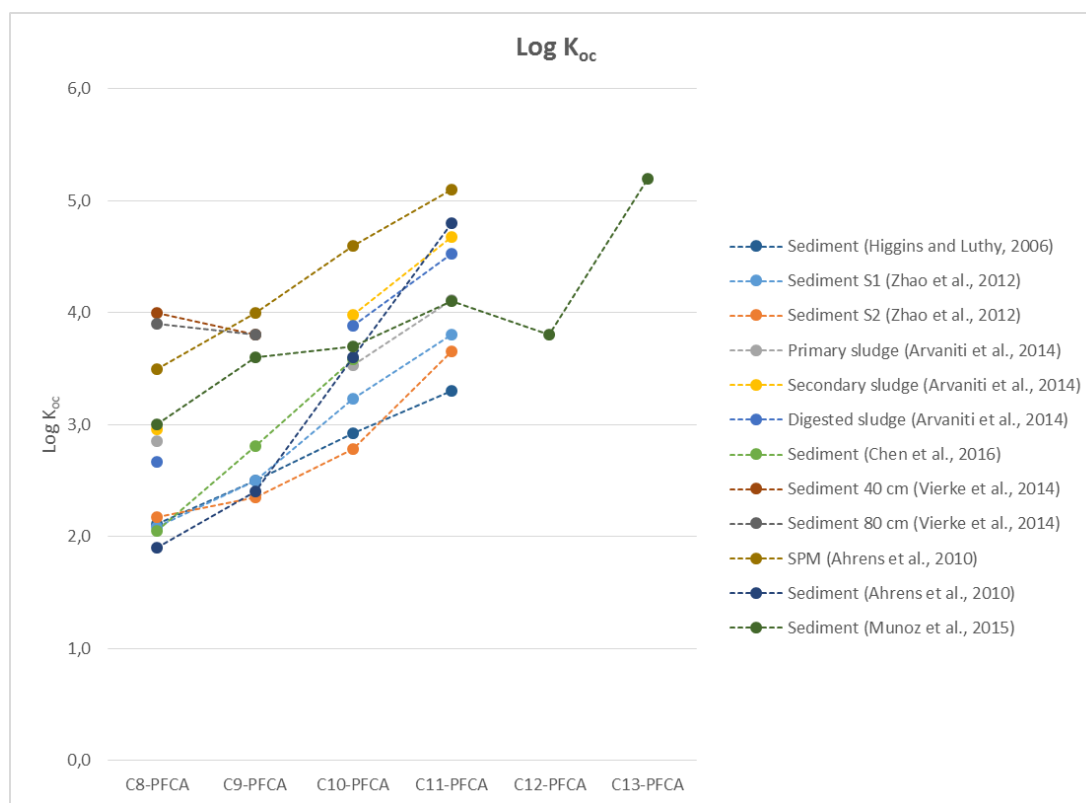


Figure B.4- 3: Trend of Log $K_{OC}$ with increasing chain length
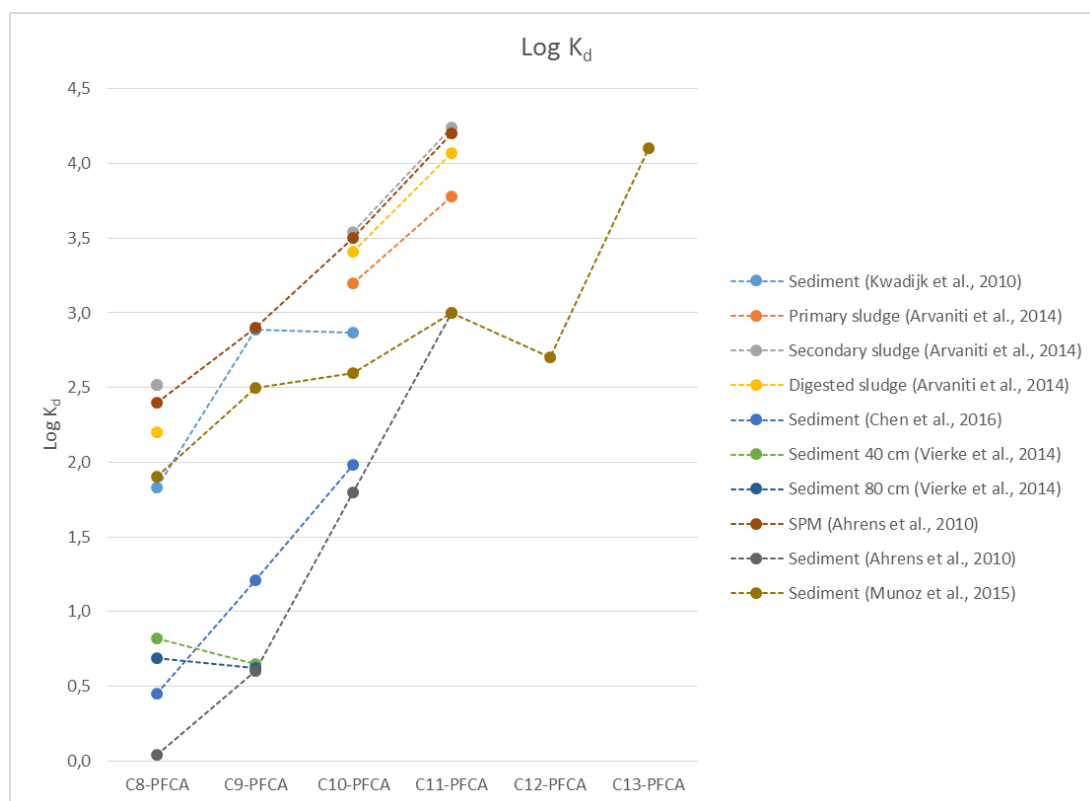
*Figure B.4- 4: Trend of Log K_d with increasing chain length*

## C9-C14-PFCA related substances

To the best of our knowledge no experimental data on adsorption/desorption are available for C9-C14 PFCA related substances. No data are provided by the registrants. However, some data are available for C8-PFCA related substances, such as 8:2 FTOH.

## 8:2 FTOH

Sorption studies with 8:2 FTOH have been performed by Liu and Lee and Arp et al. ((Arp et al., 2006; Liu and Lee, 2005) both cited in (Stock et al., 2010)). Liu and Lee determined a log $K_{OC}$-value of 4.13 for 8:2 FTOH by considering five soils. This indicates that adsorption to soil might be relevant. The substance has been found in sludge applied soils (Yoo et al., 2010).

Arp et al. measured adsorption coefficients at 15 °C on quartz, $Al_2O_3$ and $CaCO_3$ which could be used as laboratory surrogate for natural surfaces such as minerals (Arp et al., 2006). 8:2 FTOH showed the highest $K_{surface/air}$ value on $Al_2O_3$ ($4.22 \times 10^{-1}$).

## Conclusion

The sorption affinity of PFASs increases with increasing perfluoroalalkyl chain length. For C11-PFCA the particulate associated fraction was 62% (Ahrens et al., 2010b). Desorption decreases with increasing chain lengths.

In the literature, limited data is only available for C9 – C13-PFCAs. However, the trend of increasing sorption with increasing chain length was observed in all studies, thus it seems conclusive that this trend would also be followed by the C14-PFCA.

Thus, C9-C14-PFCAs sorb easily to surfaces and sediments are considered as a sink for C9-C14-PFCAs. The mobility in soil decreases with increasing chain length. Moreover soils containing positively charged minerals seem to have a stronger binding affect to C9-PFCA

compared with negatively charged minerals. Thus, it can be assumed that soils can be a long-term source of C9-C14 PFCAs to underlying groundwater.

No information is available on distribution coefficients of C9-C14 PFCA related substances. However, for 8:2 FTOH which can be regarded as a similar substance with a shorter perfluoroalkyl chain, adsorption to soil and sludge might play an important role. Thus it may be concluded that this could also be the case for the longer chain representatives.

## B.4.2.2 Volatilisation

Vapour pressures are available for C10-C14 PFCAs (see Annex B.1.3 and B.1.4). Vapour pressures decrease with increasing chain length. C9-C14-PFCAs are not expected to volatilise.

The $K_{AW}$ is proportional to the vapour pressure of a chemical divided by its aqueous solubility. For the longer chain PFCAs, Kaiser et al. measured a decreasing vapour pressure with increasing chain length (Kaiser et al., 2005). Similarly, a decreasing aqueous solubility with increasing chain length has been predicted (Rayne and Forest, 2009).

Vierke et al. measured air concentrations and particle-gas partitioning of PFASs at a wastewater treatment plant. Samples were collected at an aeration tank and a secondary clarifier using both active high volume samplers and passive samplers comprising sorbent-impregnated polyurethane foam (SIP) disks. C9-C14 PFCAs were detected in the particle phase as well as in much smaller concentrations in the air samples (Vierke et al., 2011).

C9-C13 PFCAs were mainly particle-associated in air: C9-PFCA (~88%), C10-PFCA (~95%), C11-PFCA (~89%), C12-PFCA (~80%), C13-PFCA (100%). The concentrations in air analysed above the aeration tank are shown in the table below.

One representative of the C9-C14 PFCA related substance was also analysed in this study. 10:2 FTOH was found in the gas phase as well as in the particulate phase. However, the concentration in the gas phase were much higher compared with the particulate phase. (see table below)

*Table B.4- 4: Concentration of C9-C13 PFCAs and 10:2 FTOH in the gas-phase and particle-phase and from SIP disk passive air samplers at the aeration tank (Vierke et al., 2011)*

| Substance | Gas phase [pg/m3] | Conc. Range in particulate phase (aeration tank) [pg/m3] | SIP disk passive air samples [pg/m3 |
|---|---|---|---|
| C9-PFCA | 0.69-9.3 | 3.0-48 | 1.1-1.2 |
| C10-PFCA | 0.25-2.8 | 4.0-110 | 2.0-2.2 |
| C11-PFCA | 0.03-9.0 | 0.59-47 | 1.2 |
| C12-PFCA | 0.09-0.64 | 0.09-4.7 | 0.15-0.21 |
| C13-PFCA | 0.004 | 0.02-2.2 | 0.01 |
| 10:2 FTOH | 72-3100 | 2.5-21 | 780-860 |

Vierke et al. investigated the air-water distribution (QAW) of PFCAs, including C9-C12-PFCAs (Vierke et al., 2013a). In situ measurements at a WWTP were used to investigate partitioning between the particle and dissolved phase for PFAS. One result of the study was that an overall tendency of decreasing QAW with increasing chain length. The QAWs were calculated using different pKA values, which were available in the literature. The QAWs for the C9-C14 PFCAs vary by two orders of magnitude, because of the variation of reported pKA values.

**Conclusion:**

C9-C14 PFCAs, are not expected to volatilise. C9-C13 PFCAs are mainly particle-associated in air. C9-C14 PFCA-related substances are volatile, remain predominantly in the gas phase.


## B.4.2.4 Distribution modelling and long range transport potential of C9-14 PFCAs and related substances

**Distribution modelling**

**C9-C14 PFCAs**

The acid functional group is hydrophilic and due to its low pKa the acids are completely dissociated in the aqueous phase at neutral pH. However, due to their hydrophobic perfluoroalkyl moiety, PFCAs have surfactant properties. As the length of the perfluorinated chain increases, the PFCA molecule will likely become more hydrophobic and its water solubility diminishes (Ellis et al., 2004a; Ellis et al., 2004b). As they cannot be applied to ionisable surfactants, widely accepted environmental fate models cannot be conducted for long-chain PFCAs. Addtionally, the octanol-water partition coefficient is a problematic parameter for surfactants, because they tend to aggregate at the interface of a liquid-liquid system, and therefore cannot be measured directly.

Thus, distribution modelling is challenging because of the dependence on distribution coefficients. Determination of these coefficients by experimental setups is difficult especially for the conjugate bases of C9-C14 PFCAs. Reasons for these difficulties are surface active properties and micelle building of C9-C14 PFCAs during the experiments. Therefore there is a lack of reliable distribution coefficients under controlled conditions in the laboratory. Nevertheless, a recent study shows that sediment-water distribution coefficients and bioconcentration factors (biota-water distribution) are proportional for PFOA and other perfluoroalkyl acids (Webster and Ellis, 2011).
The authors used a measured bioconcentration factor to predict a sediment-water distribution coefficient. The comparison of the predicted versus the measured values showed good agreement (within one order of magnitude). Therefore, the applicability of equilibrium models for C9-C14 PFCAs and other perfluorinated substances is validated (Webster and Ellis, 2011). For distribution modelling it has to be considered that the conjugate bases (i.e. perfluorononanoate, - decanoate) and the corresponding acids (perfluorononanoic acid, perfluorodecanoic acid) are in equilibrium. This equilibrium in dependence of the pH needs to be included in the models because of the different properties of the species (base versus acid form), i.e. vapour pressure. Therefore, a p$K_a$ is needed.

Some measured as well as estimated p$K_a$ values for C9-C14 PFCAs are reported in the literature and are summarized in Table B.4- 5.  For C11 and C13-PFCAs no pKa-values were found. There is a high variance in reported p$K_a$ values for a single substance (up to four log units), whereas highest reported data based on measurements and lower p$K_a$ values are estimations from models. Under environmental conditions at pH 7 99.9 % of C10-PFCA is present as conjugate base with a p$K_a$ of 6.17, whereas with a p$K_a$ of 0 > 99.999 % is present as conjugate base. Because of the dominance of the conjugate base in combination with its high solubility and negligible vapour pressure aqueous phases are expected to be of importance.


*Table B.4- 5: pKa values of C9-C14 PFCAs reported in the literature*

| Substance | pKa | Method | Reference |
|-----------|-----|--------|-----------|
| C9-PFCA | 0.82 | Modelled, COSMOTHERM | (Wang et al., 2011) |

| | | | |
|---|---|---|---|
| C9-PFCA | -0.21 | Modelled, SPARC | (Steinle-Darling and Reinhard, 2008) |
| C10-PFCA | 6.17 | Experimental, measured in 50/50 v/v ethanol/water | (Brace, 1962; Kissa, 2001) |
| C10-PFCA | -0.21 | Modelled, SPARC | (Steinle-Darling and Reinhard, 2008) |
| C11-PFCA | | | |
| C11-PFCA | -0.21 | Modelled, SPARC | (Steinle-Darling and Reinhard, 2008) |
| C12-PFCA | 6.13 | Experimental, measured in 50/50 v/v ethanol/water | (Brace, 1962; Kissa, 2001) |
| C12-PFCA | -0.2 | Modelled, SPARC | (Goss, 2008) |
| | 0.8 | Modelled, COSMO-RS | |
| C12-PFCA | -0.21 | Modelled, SPARC | (Steinle-Darling and Reinhard, 2008) |
| C13-PFCA | | | |
| C14-PFCA | -0.21 | Modelled, SPARC | (Steinle-Darling and Reinhard, 2008) |

## C9-C14 PFCA related substances

A number of substances can degrade to C9-C14 PFCAs (see Annex B.4.1.2 for details).

However, due to missing data and large uncertainties regarding physical-chemical properties, partitioning behaviour and degradation half-lives makes it difficult to model environmental distribution of C9-C14 PFCA related substances. Nevertheless, some studies considering global distribution of 8:2FTOH exist (e. g. (Stemmler and Lammel, 2010; Wallington et al., 2006)). Although information on environmental distribution of other C9-C14 PFCA related substances is rare, the substances are notwithstanding found in different environmental media (as it can be seen in Appendix B.2). For example in the study of Shoeib et al. (Shoeib et al., 2006), 10:2 FTOH, a C10-PFCA precursor, has been found in various air samples from North Atlantic and Canadian Archipelago (reviewed in (Butt et al., 2010)). Cai et al., found 12:2 FTOH, 10:2 FTOH, and 10:2 FTA (all C9-C14 PFCA related substances) in the atmosphere along the cruise track from the Japan Sea to the Arctic Ocean (Cai et al., 2012). During a cruise of the R/V Polarstern from October 2010 to January 2011 from Germany to the Antarctic individual PFASs in the marine atmosphere were measured with high volume air sampling sites. C9-C14 PFCA related substances, namely 10:2 FTOH and 12:2 FTOH were found in concentrations of 0.37 - 11.35 and 0.43 - 6.07 pg/m$^3$ air, respectively. 10:2 FTOH and 12:2 FTOH were also found in snow of the Antarctic Peninsula in average concentrations of 24 +/- 8.3 and 13 +/- 4.1 pg/L, respectively (Wang et al., 2015).

## Long-range transport potential

C9-C14 PFCAs, have been detected in remote areas of the world in monitoring programs involving various abiotic and biotic samples (Butt et al., 2010). For example, C9-C14 PFCAs have been measured in biota such as polar bears and seals in the Canadian Arctic.

Some examples for C9-C14 PFCA concentrations in remote areas are summarized in Table B.4- 6 (see more in Appendix B.2).

*Table B.4- 6: Concentration of C9-C14 PFCAs in remote areas*

| Sample | Substance | Value | Reference |
|---|---|---|---|
| Fish liver from Greenland and Faroe Islands | C9-PFCA | 0.12 – 3.32 ng/g ww | (Bossi et al., 2015) |
| | C10-PFCA | 0.17 – 2.92 ng/g ww | |
| | C11-PFCA | 0.39 – 10.9 ng/g ww | |
| | C12-PFCA | 0.43 – 4.45 ng/g ww | |
| | C13-PFCA | 0.9 – 11.9 ng/g ww | |
| | C14-PFCA | 0.51 – 2.8 ng/g ww | |
| Wolf liver remote area in Northern Canada | C9-PFCA | 4.7 – 7.4 ng/g ww | (Müller et al., 2011) |
| | C10-PFCA | 2.0 – 3.2 ng/g ww | |
| | C11-PFCA | 2.5 – 6.4 ng/g ww | |
| | C12-PFCA | 0.42 – 0.72 ng/g ww | |
| | C13-PFCA | 0.35 – 0.55 ng/g ww | |
| | C14-PFCA | n.a. | |
| Remote alpine lake sediment (Lake Oesa sediments) | C9-PFCA | 11 pg/g | (Benskin et al., 2011) |
| | C10-PFCA | n-d. pg/g | |
| | C11-PFCA | 69 pg/g | |
| | C12-PFCA | 28 pg/g | |
| | C13-PFCA | 70 pg/g | |
| | C14-PFCA | 12 pg/g | |
| Surface water of the Central Arctic Sea | C9-PFCA | 13 pg/L | (Yeung et al., 2017) |
| Snow/meltpond water | C9-PFCA | 107 pg/L | |
| Surface Water remote Area<br><br>Several lakes (2003 – 2005) | C9-PFCA | n.d. – 6.1 ng/L | (Stock et al., 2007) |
| | C10-PFCA | n.d. – 29 ng/L | |
| | C11-PFCA | 0.2 – 5.9 ng/L | |
| | C12-PFCA | n.d. – 2.3 ng /L | |
| | C13-PFCA | n.a | |
| | C14-PFCA | n.a | |
| Snow Antarctic Peninsula | 10:2 FTOH | 24 +/- 8.3 pg/L | (Wang et al., 2015) |
| | 12:2 FTOH | 13 +/- 4.1 pg/L | |

No information is available about current or historical use of C9-C14 PFCAs or related substances in the Arctic. A possible explanation for this finding is the long-range transport of either C9-C14 PFCAs or their potential precursors. Two possible transportation pathways include atmospheric and aquatic transport. It is generally assumed that transport pathways are similar to the ones described for C8-PFCA (PFOA) (European Chemicals Agency, 2015a). C9-C14 PFCA related substances are volatile substances which are transported via air currents. The substances and their degradation products (C9-C14 PFCAs) are deposited via precipitation to the water and soil surfaces. C9-C14 PFCAs and their salts are mainly translocated globally via ocean currents (Butt et al., 2010; OECD, 2013; Prevedouros et al., 2006; Taniyasu et al., 2013). The processes are described in more detail below.

**Aquatic Transport**

C9-C14 PFCAs have been reported in seawater from oceanic (Benskin et al., 2012; Gonzalez-Gaya et al., 2014) and coastal regions (Ahrens et al., 2010a; Cai et al., 2012). C8-PFCA is noticeably influenced by marine currents (Stemmler and Lammel, 2010; Yamashita et al., 2008).

The Antarctic Circumpolar Current acts as a natural barrier encircling Antarctica due to the weak north−south exchange of seawater that is thought to restrict the marine transport of PFASs. PFASs can also undergo atmospheric transport and deposition, and for inland areas as well as for neutral PFASs, this is arguably the main long-range transport mechanism. These

neutral PFASs may act as precursors of the ionizable PFASs through atmospheric oxidation or may be metabolized to ionizable PFASs following deposition to aquatic and terrestrial environments. Although PFCA and PFSA concentrations in remote snow and soils are clearly dependent on the atmospheric transport and deposition of PFASs, the extent to which atmospheric deposition and oceanic currents influence remote coastal areas remains unclear. Remarkably high concentrations of neutral PFASs have been reported for the Southern Ocean around the Antarctic Peninsula, and these could lead to an introduction of neutral and ionizable PFAS to Antarctic waters through atmospheric deposition (Casal et al., 2017).

Gonzalález-Gaya and co-workers studied a number of PFASs including C9- and C10-PFCAs in 92 surface water samples taken during during the Malaspina 2010 expedition which covered all the tropical and subtropical Atlantic, Pacific and Indian oceans. C9- and C10 PFCA were found in all oceanic basins (Gonzalez-Gaya et al., 2014).
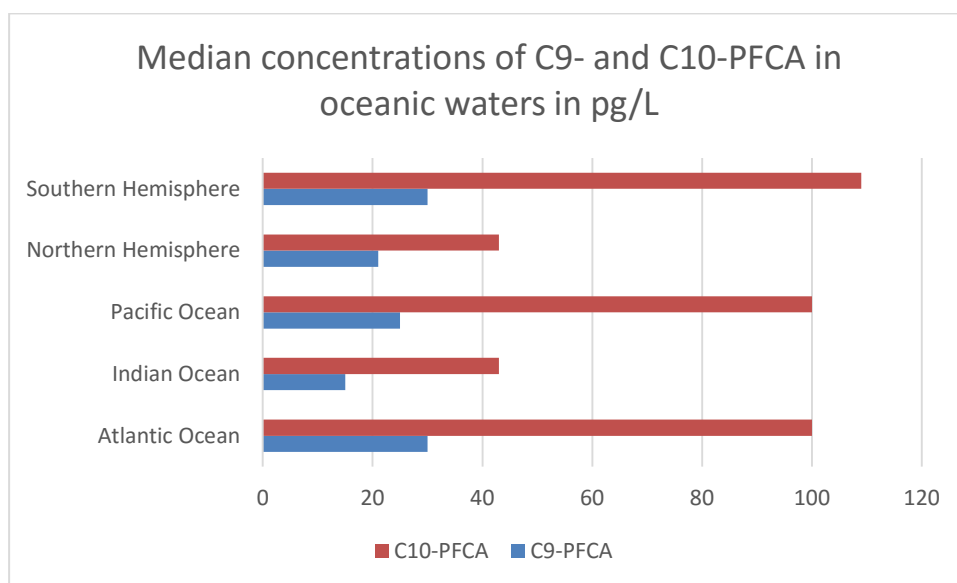


*Figure B.4- 5:: Median concentrations of C9- an C10 PFCA in oceanic waters, reported by Gonzalález-Gaya et al., 2014.*

Gonzalález-Gaya et al., 2014 reported the ubiquitous occurrence of PFCAs, in the global ocean. The potential factors affecting their distribution patterns were assessed including the distance to coastal regions, oceanic subtropical gyres, currents and biogeochemical processes. The authors suggest that a number of physical and biogeochemical processes collectively drive the oceanic occurrence and fate of PFASs in a complex manner.

PFASs (among them also the C9C14 PFCAs) in costal areas are 1-2 magnitudes higher than in open-ocean waters (Ahrens, 2011; Ahrens et al., 2010a; Kim and Kannan, 2007). Their sources in the marine environment have been identified to be mostly terrestrial through wastewater and riverine inputs, and directly linked to population density (Ahrens, 2011).

**Atmospheric transport and wet deposition**

Atmospheric life-time of FTOHs was calculated to be 20 days. Moreover, the authors stressed that FTOHs will be transported downwind long distances from its point of emission (up to 7000 km in 20 d by considering a global average wind speed of 13.8 km/h). Ellis et al. concluded that FTOHs are degraded in the atmosphere by reaction with OH radicals (Ellis et al., 2003).

Piekarz et al. estimated that atmospheric residence times of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were 50, 80 and 70 days, respectively (Piekarz et al., 2007).

Rankin et al. analysed a number of PFAS including C9-C14 PFCAs in surface soils at 62 locations representing all continents (Rankin et al., 2016). The authors conclude that atmospheric long-range transport (LRT) of neutral PFASs followed by oxidation and deposition are a significant source of PFCAs and PFSAs to soils, because all the soils were collected from locations absent of direct human activity.

Wang et al. analysed typical neutral PFASs in the atmosphere across the Atlantic as well as their air-snow exchange at the Antarctic Peninsula (Wang et al., 2015). FTOHs were dominant in both air and snow. The sum of PFASs was higher above the northern Atlantic compared to the southern Atlantic. Levels in the southern Atlantic were the lowest. High atmospheric PFAS levels around the Antarctic Peninsula were the results of a combination of air mass, weak elimination processes and air-snow exchange of PFASs. Higher ratios of 8:2 to 10:2 to 6:2 FTOH were observed in the southern hemisphere, especially around the Antarctic Peninsula, suggesting that PFASs in the region were mainly from the long-range atmospheric transport. 10:2 FTOH as well as 12:2 FTOH were found in both media, air and snow. The authors conclude that the substances are transported into the Antarctic via long range atmospheric transport. Interestingly, elevated PFAS levels have been found at the Antarctic Peninsula. Weak elimination processes, such as less intensity (or reaction rates) of photochemicals oxidation and less rainfall are primary reasons resulting in higher PFAS levels around the Antarctic Peninsula. Revolitilized from snow of the Antarctic Peninsula was discussed by the authors as well. Additionally, air mass back trajectories analysis showed that air mass originated or passed over the Peninsula for most time during sampling around the Antarctic Peninsula. The authors discussed as well that scientific research bases could be another potential source of PFAS in this area.

Conclusion:

C9-C14 PFCAs are transported over long distances via atmosphere and aquatic environment via rivers and oceans. C9-C14 PFCA relates substances, such as 10:2 FTOH have a high vapour pressure and are transported mainly via air. In the atmosphere C9-C14 PFCA related substances can be degraded to C9-C14 PFCAs. Subsequently, C9-C14 PFCAs are deposited on water and soil. As a consequence, C9-C14 related substances may be a significant long-term source of C9-C14 PFCAs in remote regions like the Arctic. Here, C9-C14 PFCAs are found in the environment and biota including top predator species like polar bears and seals.

## B.4.2.3 Distribution via sewage sludge and effluents from wate water treatment plants (WWTP)

Several studies showed that conventional wastewater treatment has a limited efficiency in removing C9-C14 PFCAs from aqueous waste streams. C9-C14 PFCAs accumulate in sludge and are released to receiving waters via WWTP effluents (Arvaniti and Stasinakis, 2015).

Generally, based on the physic-chemical properties of the substances, C9-C14 PFCAs rather tend to adsorb to sludge but they are also found in effluents. The adsorption rate increases with increasing chain length. Interestingly, usually higher concentrations of the perfluorinated acids are found in sludge and effluent compared with the influent. This is explained by the presence of precursor substances (PFCA related substances) in the influent which are degraded in the WWTP to the end-products, the PFCAs. A review on concentrations of different PFASs in WWTPs from USA, Europe, Australia, and Asia has recently been published (Arvaniti and Stasinakis, 2015) C9- and C10 PFCAs were found in almost all studies, summarized in this review. C11-C14 PFCAs were not analysed in all studies. The concentration of C9-C14 PFCAs in sludge were usually higher compared with water samples of influent and effluent (Arvaniti and Stasinakis, 2015).

Huset et al., 2008 found C9-PFCA and C10-PFCA in sludge and effluents only occasionally and in low concentrations in Swiss WWTPs. In most effluents and sludge samples the substances were not detected with the analytics used (Huset et al., 2008). In a study from Sinclair and Kannan (2006) effluent waters of six activated sludge wastewater treatment plants. The study analysed a number of PFASs among them C9-C11 PFCAs. C9-,C10- and C11-PFCA were found in effluents above LOQ of two, four and three plants, respectively. The sludge of two plants was investigated towards their PFASs content. In primary sludge of two plants with highest PFASs concentration in effluent, C9-C11 PFCAs were analysed. In one plant C9-C11 PFCAs were found, in the other only C9-PFCA was measured in primary sludge. The effect of primary and secondary treatment was described as well showing that the amount of the single PFCAs increased, because of the degradation of precursors (PFCA related substances) (Sinclair and Kannan, 2006)

Gomez-Canela and co-workers analysed sewage sludge from 15 differently operating WWTPs situated in Spain and Germany (Gomez-Canela et al., 2012). The WWTPs received both urban and industrial waters. Five PFASs were measured, including C9-PFCA. C9-PFCA was measured in sludge. Centrifuged sludge and sludge from the anaerobic digester contained higher levels as primary sludge. The reason might be degradation processes from C9-PFCA related substances. Different sludge residence times in the reactors and dewatering techniques determine the evolution of PFCAs within the sludge treatment process. The authors conclude that PFAS loads in sludge may pose future environmental risk if the sludge is used as fertiliser in agriculture.

Arvaniti et al. analysed C9-C14 PFCAs in wastewater and sludge from two different WWTPs in Greece (Arvaniti et al., 2012). During the sampling campaigns altogether 24 samples were collected from influents and effluents. C-9 and C-11 PFCA were found in five and seven samples respectively. C-10, C-12-C14 PFCAs were detected sporadically. The plant receiving municipal as well as industrial waste water showed higher PFASs concentration compared with the plant receiving only municipal waste water. Daily loads of C9-C14 PFCAs were calculated and were in the range from 820 to 7.580 mg/d for the single compounds in one plant and in the range of 0 to 1.438 mg/d in the other plant. In the sludge samples, C11-PFCA was detected in 12 out of 18 dewatered samples, and only in a few samples C9, C12,-C14 PFCAs were found.

## B.4.2.5 Monitoring and trends

C9-C14 PFCAs and related substances are found ubiquitously in the environment including wildlife and remote areas. Examples are provided in Appendix B.2.

C13-PFCA accounted for 40 – 70 % of the sum of PFAS in fish liver samples in a Norwegian study. C13-PFCA concentrations in the liver samples are in the range of 22 – 87 ng/g w.w., with the highest levels in lake Femunden and lowest in lake Mjøsa. In fish muscle samples, five different PFAS-compounds could be found in quantifiable concentrations. For C14-PFCA, the average liver concentrations were six times higher than the muscle concentrations, but there was a large variation around the means. The differences between muscle and liver concentrations seemed to increase with decreasing carbon chain length. The high levels in Lake Femunden are somewhat surprising since this lake is considered a remote location with barely any permanent residents in the area. However, it is a popular area for forest cabins. In contrast, Lake Mjøsa has a high level of human activity all around its shoreline. C13-isotope analysis indicates that the trout from Lake Femunden feeds on insects/ terrestrial organisms to a higher degree than the trout from Lake Mjøsa which has a more rich foodchain. This could explain the higher levels of PFAS observed in trout from lake Femunden compared to trout from lake Mjøsa (Norwegian Institute for Water Research, 2016).

PFOS and C9-C14 PFCAs dominated the sumPFAS found in earthworm, eggs from fieldfare and sparrowhawk, and liver from red fox in Norway. For earthworm, there is a major contribution of PFOS, C12- and C14-PFCAs in samples from Oslo, while C13-PFCA, followed by PFOS dominates the samples from the reference site. This was also observed in earthworms in another report from 2013 (Herzke et al., 2015) as well as in the fieldfare eggs. The differences were significant for sumPFAS (P = 0.001) PFOS (P = 0.007) and C14-PFCA (P= 0.004) only (M-W U). However, when comparing the different sampling locations for earthworms in the urban site, Oslo, PFAS is dominating in all sites, but is most abundant at Voksenkollen. Voksenkollen is heavily used for ski competitions and cross-country exercises in the winter time and we might see the impact of application of fluorinated skiwax in these earthworms (Norwegian Institute of Air Research, 2016).

Liver samples from otter (Lutra lutra) from Sweden and Norway were analysed for various PFAS. C9-PFCA was the predominant PFCA (up to 640 ng/g wet weight) closely followed by C10- and C11-PFCA. A temporal trend study was performed on otters from southern Sweden collected between 1972 and 2011. C9-14-PFCAs showed significantly increasing trend (Figure B.4- 6). When considering only the values from 2002 to 2011, the increasing trend is still significant with doubling times of 6.8 years (C9-PFCA), 5.1 years (C10-PFCA), 9.8 years (C11-PFCA), 4.6 years (C12-PFCA), 17 years (C13-PFCA), and 2.6 years (C14-PFCA), respectively . The yearly increase for the different PFCAs was in the range of 4.1–27% for the time period of 2002-2011. During the last 10 years C9-, 10-, 12, and 14-PFCAs increased even at a faster rate during recent years compared to the whole study period. The authors stated that no significant upward or downward trend of any of the PFSAs was detected between 2002 and 2011. Interestingly, although a decreasing trend of most PFASs has been reported, the otters still show increasing values of PFASs in their livers. The reason for the fast increase of the PFCAs in otters is not known. The authors discuss the possibility of an extraordinary long half-live of PFASs in otters. There was no correlation with age of the otters or any indications of a change in their diet (Roos et al., 2013).
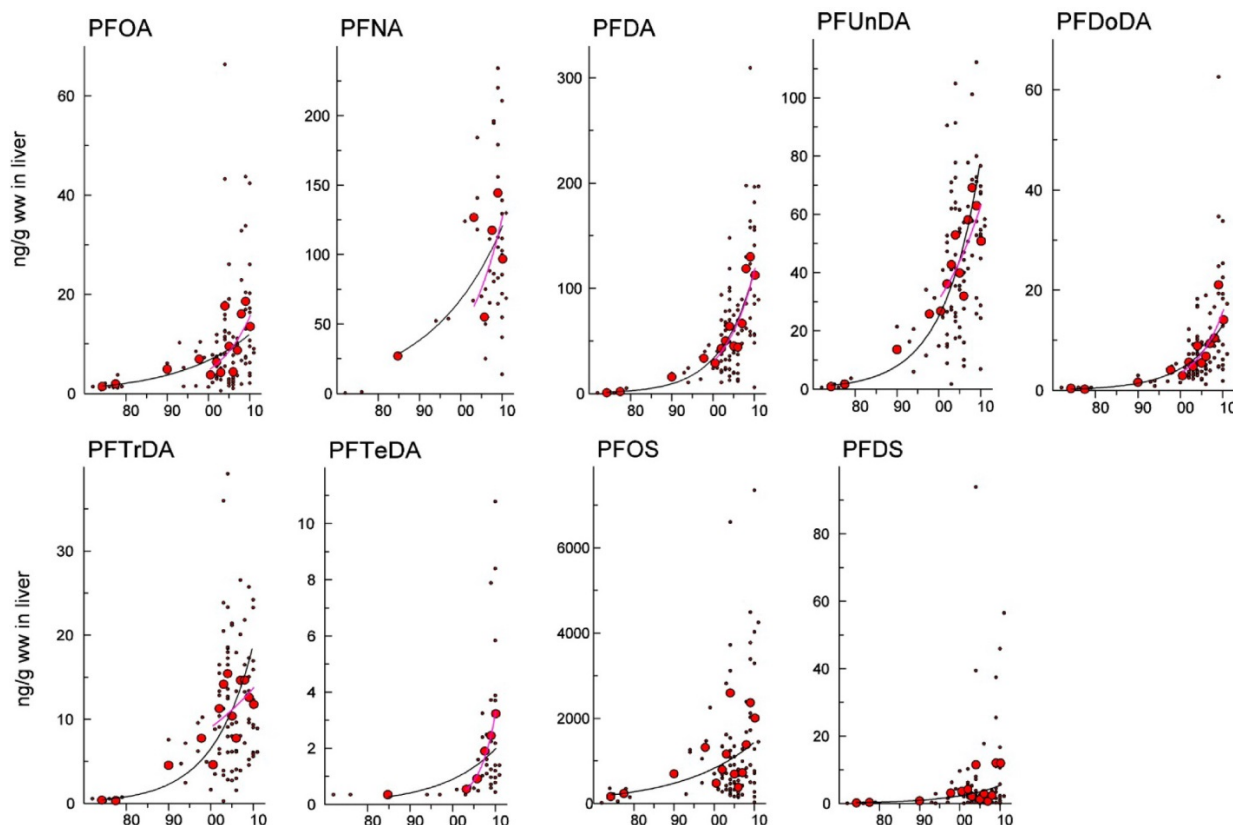
*Figure B.4- 6: Time trends of PFAA concentrations (ng/g ww) in livers from otters from southern Sweden collected between 1972 and 2011. Red circles represent annual geometric means. Black solid lines show the results of linear regression on log-transformed annual means for PFAAs displaying significantly increasing levels, and red solid lines show the results from the last 10 years, if the linear regression analysis was significant. Some extreme individual values are outside the ranges of the graphs. (reprinted with permission from (Roos et al., 2013). Copyright (2013) American Chemical Society)*

Bytingsvik and co-workers (2012) analysed PFAS in plasma levels of polar bear mothers and their cups sampled in 1998 and 2008 from Svalbard (Figure B.4- 7). In 2008 the values for C9-C14-PFCAs were significantly higher than in 1998 both in mothers and cups except for C14-PFCA which was not detected in cubs. Interestingly, a decreasing trend for PFOA was reported. The study results show that the concentrations of C9-11 PFCA are higher than PFOA. C9-PFCA was the predominant PFCA with mean concentrations of 27.5 ng/g ww (1998) to 38.1 ng/g ww in 2008 followed by C11- and C10-PFCA (Bytingsvik et al., 2012).
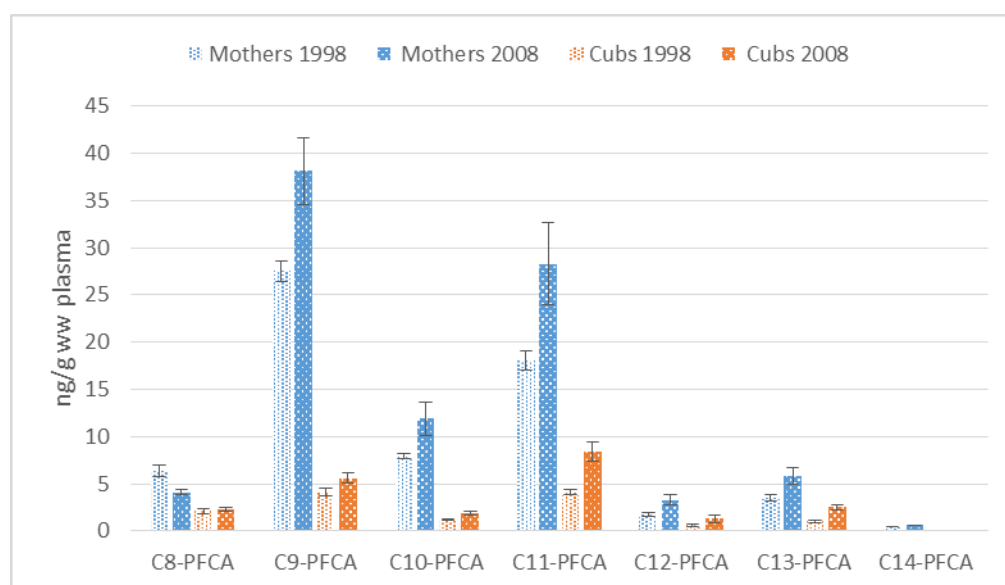


*Figure B.4- 7: Mean plasma concentration (ng/g ww) and standard error of mean (SEM) bars of individual PFCAs, in polar bear mothers and cubs from 1998 (n=12) and 2008 (n=9) from Svalbard, Norway. (according to (Bytingsvik et al., 2012))*

A significant increase for C9-14-PFCAs in osprey eggs from Sweden in the time period from 1997-2001 and 2008 to 2009 was reported by Eriksson et al., 2016 (Figure B.4- 8). There was no significant increase in the PFCA-concentrations between 2008/2009 to 2013. Over the years, the concentrations of C9-14 PFCAs increased in osprey, except for C13-PFCA, which decreased in the last few years (Eriksson et al., 2016).
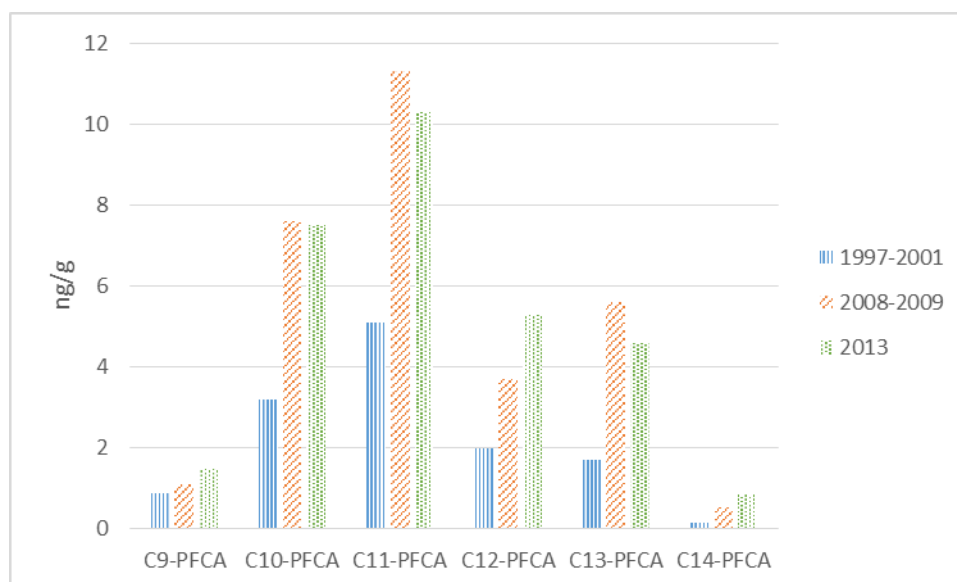
*Figure B.4- 8: Temporal trend of PFCAs in osprey eggs (ng/g, median, n=10 for each time point). (According to (Eriksson et al., 2016))*

Temporal trends of PFASs were also analysed in Baltic Sea herring and white-tailed sea eagle (WTSE) eggs from different sites in Sweden. Trends of most quantifiable PFASs increased over the monitoring period (1980 – 2014 in herring and 1960/1980s – 2010 in the WTSE). No decreasing trends were observed for the most recent years for any substance. The concentrations of long-chain PFCA (8 to 13 carbons atoms) increased over the whole time period in herring from all sites. Annual increase was 3 – 8% for PFOA and 7 – 10% for C9-C13 PFCAs. No trends were observed in the most recent ten years (Figure B.4- 9). Concentrations of C10-C15 PFCAs increased over the whole time period in all four WTSE sampling areas. Annual increases of C10-C15 PFCAs were lower for the inland samples (6 – 8%) compared to the other areas (10 – 15%). Comparable to the herring, no trends were observed in the most recent ten years (Figure B.4- 9). However, samples from the most recent 2-3 years appear to have lower concentrations compared to previous years (Faxneld et al., 2016).
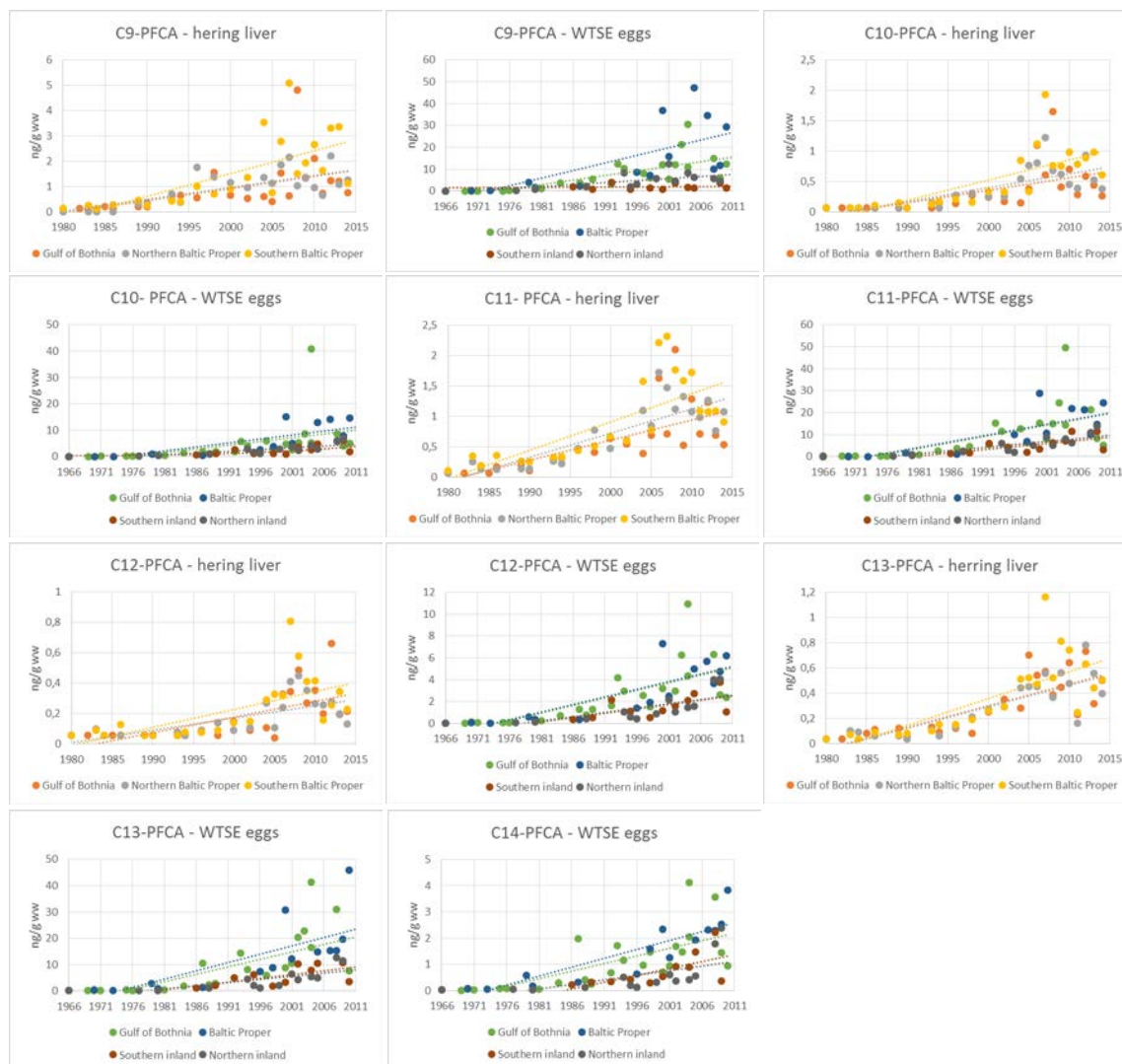
*Figure B.4- 9: Trends of C9-C14 PFCAs (concentration ng/g ww, geometric mean) in herring liver from Angskarsklubb (Gulf of Bothnia), Landsort and Utlangan (Baltic Proper) and in WTSE eggs from Gulf of Bothnia, Baltic Proper, northern Inland, and southern Inland (according to (Faxneld et al., 2016))*

Rigét et al. analysed C9-C11 PFCAs in livers from ringed seal liver and polar bear from 1980 to 2010 from different locations in Greenland (Riget et al., 2013). For polar bears from East Greenland the maximum values for C9- and C10-PFCA were found in the samples from 2006 with mean concentrations of 206 ng/g ww and 88 ng/g ww respectively. The maximum value for C11-PFCA was reported in 2008 with 111 ng/g ww. Samples collected later showed significantly lower values, indicating a decreasing trend in polar bears from East Greenland (Figure B.4- 10). In ringed seals from East Greenland the highest concentration of C9-PFCA was measured in the samples from 2008 with 8.1 ng/g ww. The sample analysed in 2010 showed slightly lower values (7.6 ng/g ww). For C10- and C11-PFCA, however, the highest values of the study were reported in 2010 with 8.4 ng/g ww and 19.9 ng/g ww, respectively. Interestingly, ringed seals from West Greenland showed peak levels of 10 already in 2006 (5.7 ng/g ww) and for C9 and C11-PFCA in 2008 with concentrations of 4,5 ng/g ww and 11.0 ng/g ww , respectively (Figure B.4- 10). The authors conclude that the distance to emission hot-spots and differences in long-range transport to the Arctic may be a reason for the different time trend results in polar bears and ringed seals from East Greenland and ringed seals from West Greenland.
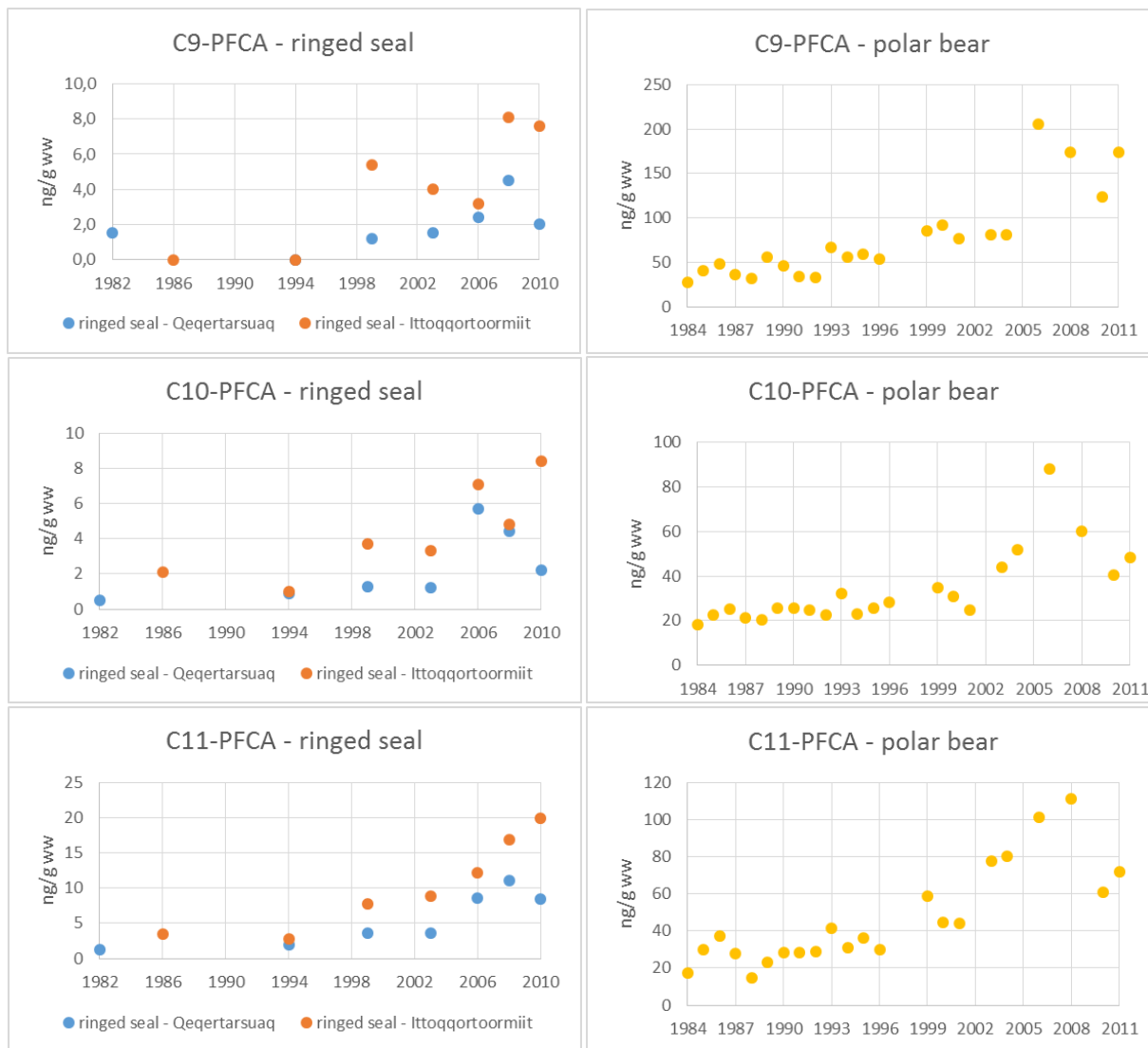
*Figure B.4- 10: Temporal trends of C9-C11 PFCAs (ng/g ww, annual average) in liver tissue of ringed seals from Qeqertarsuaq (West Greenland), Ittoqqortoormiit (East Greenland) and polar bears from Ittoqqortoormiit (East Greenland). (according to (Riget et al., 2013))*

Decreasing trends of C9-C15-PFCAs in environmental samples have been reported by Ahrens et al. in harbour seals from the German Bight sampled between 1999 and 2008 (Ahrens et al., 2009b).

The German specimen bank analysed a number of species from various areas according to their levels of C9-C14 PFCAs in a retrospective way. Some of the data are shown below. Interestingly, the trends and levels strongly depend on the sampling site. In Figure B.4-11 levels of C10-PFCA in Bream filet from the river Elbe and the river Rhine are shown. In the Breams from the river Elbe highest concentrations of C10-PFCA were found in 2007, whereas the highest value in Breams from the Rhine were measured in 2015.
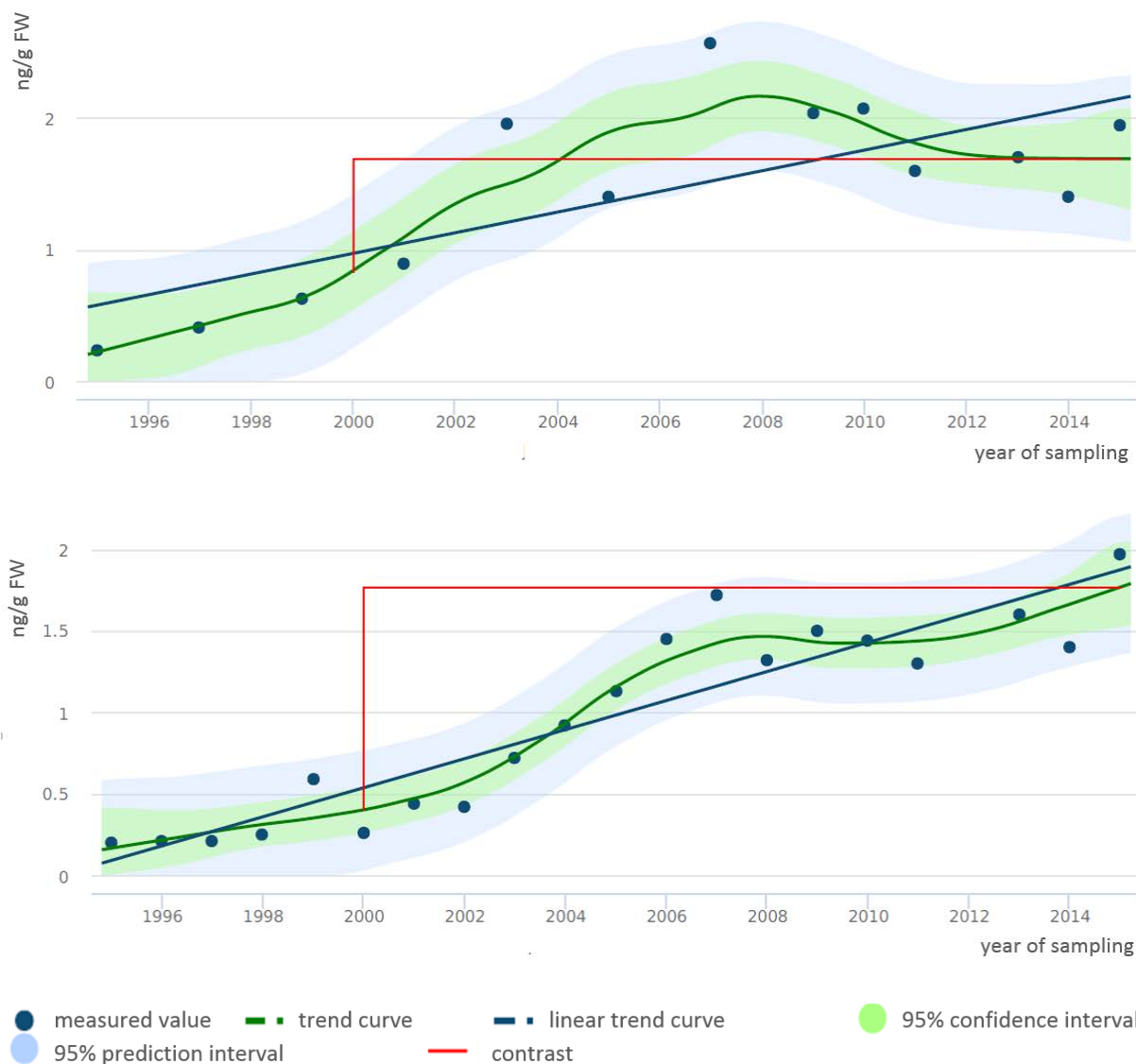
*Figure B.4- 11: Retrospective monitoring of C10–PFCA in bream filet (fresh wight) from German fresh waters; river Elbe, Barby (above) and, river Rhine, Iffezheim in ng/g ww.*

C9- and C10-PFCA were also monitored in deer meat. The different colours in Figure B.4-12 represent different sampling sites in Germany. The C9- levels in dear meat are slightly decreasing, wheras the C10-PFCA levels show a statistically significant increasing trend in dear meat from most sampling sites.
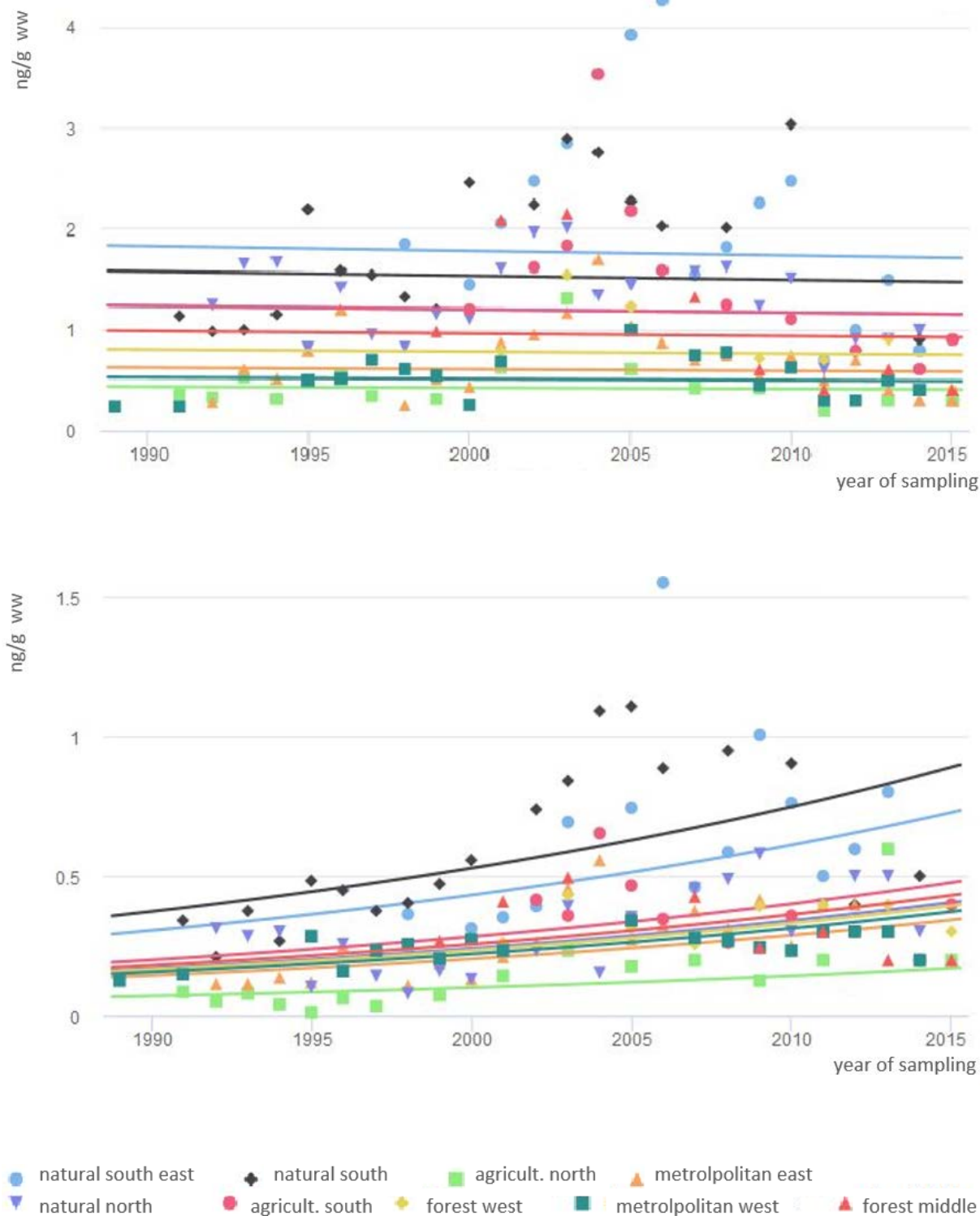
*Figure B.4- 12: Retrospective monitoring of C9–PFCA (above) and C10-PFCA (below) in deer meat from different areas in Germany in ng/g ww.*

C9-C11 PFCA levels were also analysed in herring gull eggs from three different locations in Germany (Figure B.4-13). Levels for C9-PFCA seem to decline during the last years. For C10-PFCA highest concentrations at Trischen and Heuwiese were measured between 2005 and 2010. In herring gull eggs from Mellum, however, levels still seem to increase. The

concentrations of C11-PFCA in herring gull eggs seem to level off at around 1-2 ng/g ww since 2005.
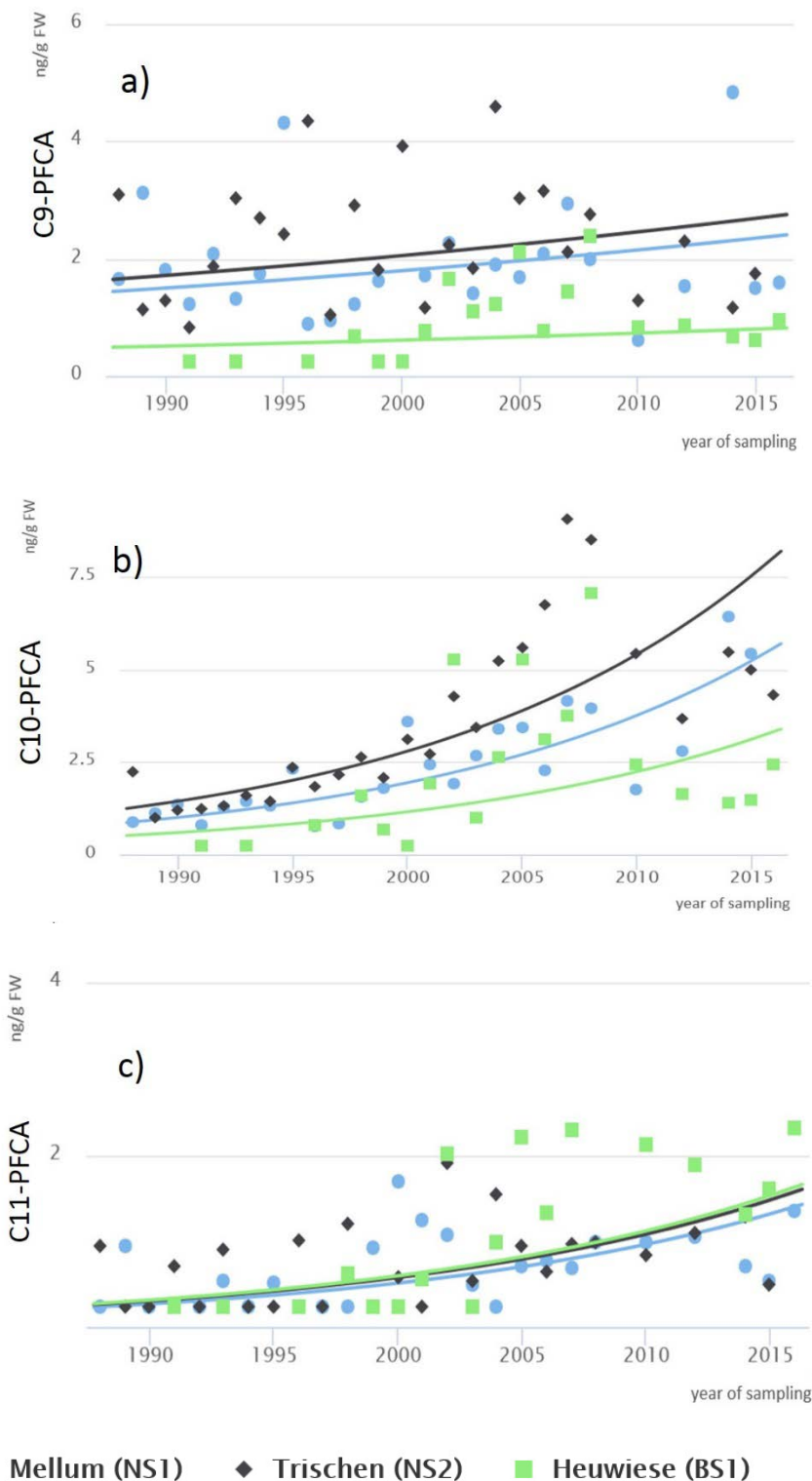


Figure B.4- 13: Retrospective monitoring of a) C9–PFCA, b) C10-PFCA and c) C11-PFCA in herring gull eggs from three different locations (North Sea (Mellum, Trischen) and Baltic Sea

(Heuwiese) in ng/g ww.    Increasing concentrations were identified for suspended solid samples of Lake Ontario and Niagara River for C9-12-PFCA and C14-PFCA (Myers et al., 2012). The concentrations of the substances increased from 2001 to 2006 with concentrations ranging 0.30–0.40 ng/g in 2006.

A further study analysed various PFASs in limed Class B biosolids from a municipal water resource recovery facility (WRRF), also know as a wastewater treatment plant. The biosolids are used for land application due to their richness in phosphate. The highest mean concentrations observed over the study period was 25.1 ng/g dw, for C9-PFCA. And these compounds were detected at concentrations 2.5–5 times higher than the remaining, detectable PFASs (Armstrong et al., 2016).

In a Chinese study, among other PFAS, C9-C14-PFCAs were analysed in liver samples of marine mammals (Lam et al., 2016). The authors reported increasing concentrations for C9-10 PFCA, C12-PFCA and C14-PFCA and a decreasing concentration for C11-PFCA in Indo-Pacific humpback dolphin (Sousa chinensis) from 2004 to 2014. In finless porpoise (Neophocaena phocaenoides), increasing concentrations were reported for C9- and C10-PFCA, whereas the concentration of C11-, 12-, 14-PFCA decreased. The concentrations of C9- and C10-PFCAs in cetacean samples of the present study were greater than other marine mammal samples. (Lam et al., 2016 EnvSci Techn.).

Ishibashi and co-workers measured PFAS in livers of Baikal seals (Pusa sibirica) collected from Lake Baikal in Russia in 2005 (Ishibashi et al., 2008). Among the 10 PFAS compounds measured C9-PFCA showed highest concentrations (3.3 – 72 ng/g wet wt) in the Baikal seal livers. The authors report that the residue levels of C9-, C10- and C11-PFCA were significantly higher in liver than in serum. Temporal trend analyses (1992-2005) showed that the animals collected in recent years showed higher concentrations of C9- and C10-PFCA indicating ongoing sources of PFC contamination in Lake Baikal.

Ulrich and co-workers  reported decreasing trends of C9-C14 PFCAs in German sewage sludge (Ulrich et al., 2016). Nearly 5000 sludge samples derived from Bavarian municipal WWTPs were analysed between 2008 and 2013 for 11 PFASs. In the table below data representing the concentration of C9-, C10- and C12-PFCA are shown. In general, there is a decreasing trend for all three substances in the time period analysed.

*Table B.4- 7:  Concentration of C9-, 10 and 12-PFCA in sludge from Bavarian municipal WWTPs collected during 2008 and 2013 (Ulrich et al., 2016).*

|      | C9-PFCA | C10-PFCA | C12-PFCA |
|------|---------|----------|----------|
| 2008 | 1,4 ng/g-11 ng/g | 9,2 ng/g-16 ng/g | 2,5 ng/g-12 ng/g |
| 2009 | 0,63 ng/g-10 ng/g | 6,9 ng/g-14 ng/g | 2,1 ng/g-11 ng/g |
| 2010 | 0,31 ng/g-10 ng/g | 4,3 ng/g-12 ng/g | 1,4 ng/g-11 ng/g |
| 2011 | 0,43 ng/g-10 ng/g | 3,4 ng/g-12 ng/g | 0,89-11 ng/g |
| 2012 | 0,23 ng/g – 10 ng/g | 2,8 ng/g-11 ng/g | 0,34 ng/g-10 ng/g |
| 2013 | 0,08 ng/g-10 ng/g | 1,3 ng/g-11 ng/g | 0,24 ng/g-10 ng/g |

**C9-14-related substances**

Various diPAPs (6:2/10:2 diPAP, 8:2/10:2 diPAP, 10:2 diPAP; 8:2/12:2 diPAP) were analysed by Eriksson and coworkers in osprey eggs (n = 10) sampled in Sweden. The substances were found in all samples. The data indicate an increase of the substances in eggs sampled in the period from 1997-2001 to those sampled in 2008-2009 (Figure B.4- 14). Eggs, collected in 2013 contained lower diPAP concentrations compared to those, collected in 2008-2009 (Eriksson et al., 2016).
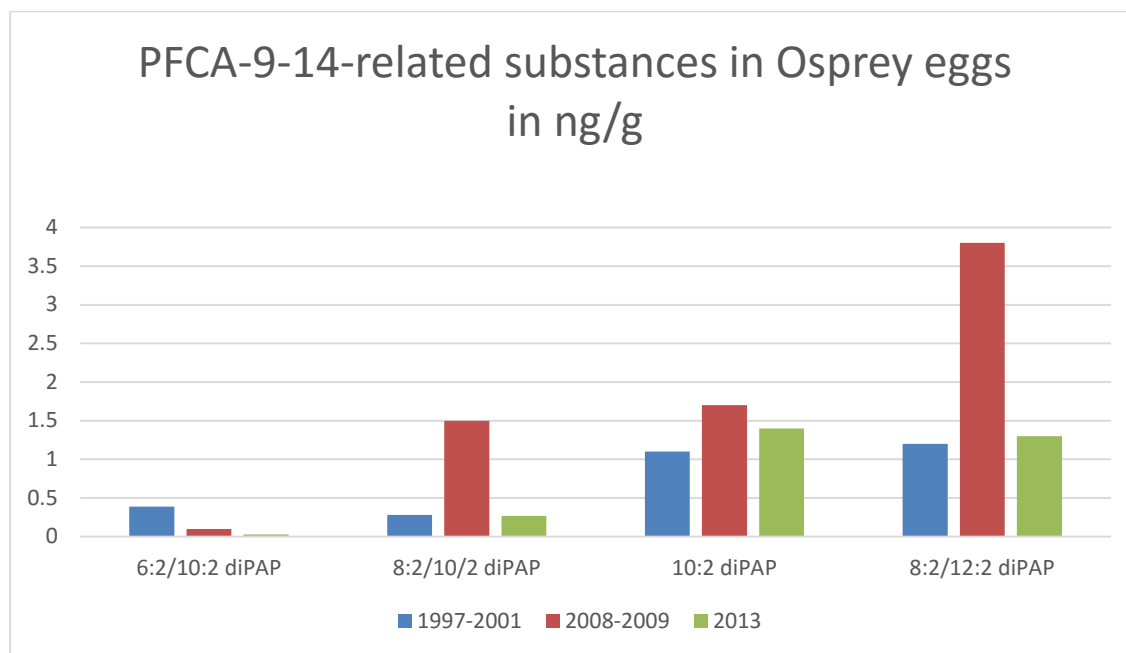
*Figure B.4- 14: Maximum values measured in osprey eggs (n=10) collected in Sweden. The substances were found in all samples (according (Eriksson et al., 2016))*

Conclusion:

In wildlife, the levels of C9-C14 PFCA have been found to increase in some species. Increasing temporal trends have been observed for C9-C14-PFCAs in migratory birds (Eriksson et al., 2016), marine fish and their predators (Faxneld et al., 2016) as well as in terrestrial mammals (Riget et al., 2013). Trend studies performed by the German Speciman Bank show that levels and trends of C9-C11 PFCAs vary even for one species, depending on the sampling site. In bream from the river Elbe C10-PFCA peaked in 2011, whereas in the river Rhine highest concentration were found in 2015 (the last sampling year).For deers in most sampling sites a decline of C9-PFCA and an increase of C10-PFCA until 2015 was shown.

In humans, C9-C14 PFCAs are detected in body fluids such as serum, cord blood and breast milk at similar levels, including remote locations such as Greenland (Gyllenhammar et al. 2016, Long et al., 2015, Manzano-Salgado et al. 2015, Motas Guzman et al. 2016). Temporal trend studies show that the concentrations of C9-C13 PFCAs have been increasing since the 1980s until approximately 2010 where the increase seem to level out (Axmon et al. 2014, Bjerregaard-Olesen et al, 2016, Gebbink et al. 2015, Gyllenhammar et al. 2015, Stubleski et al. 2016, Yeung et al. 2013).

## B.4.3. Bioaccumulation

C9-C14 PFCAs as well as the ammonium and sodium salts of C9-PFCA and C10-PFCA are listed as substances of very high concern on the REACH Candidate List. C11-C14 PFCAs has been assessed to fulfil the vB-criterion of REACH Annex XIII. C9-PFCA, C10-PFCA as well as their salts meet the B-criterion (vB not assessed). Details of the assessment can be found in the supporting documentation of the listing in the Candidate List (European Chemicals Agency, 2012b; European Chemicals Agency, 2012c; European Chemicals Agency, 2012d; European Chemicals Agency, 2012e; European Chemicals Agency, 2015c; European Chemicals Agency, 2016b).

# B.5. Human health hazard assessment

Below we present relevant human health hazard information of C9-C14 PFCA. The information presented is based on the endpoints leading to harmonised classification and labelling for C9-PFCA and 10-PFCA, but also taking into account other endpoints relevant in relation to the PBT- and vPvB-properties of C9-C14 PFCA.

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

C9- and C10-PFCA were identified as a Substances of Very High Concern because of their CMR and PBT properties by the ECHA Member State Committee on 30 November 2015 and 2 December 2016, respectively. C11-C14 PFCAs were identified as Substances of Very High Concern because of their vPvB properties by the ECHA Member State Committee on 13 December 2012.

In brief, studied PFCAs have shown to be readily absorbed (> 90%) in rodents following oral exposure (Kudo, 2015). Quantitative studies *in vivo* on C9-C14 PFCAs for other exposure routes, i.e. inhalation or dermal absorption, are lacking. However, toxicity studies on PFOA using these exposure routes demonstrate absorption based on the observed toxicity effects (Kennedy et al., 2004). No human PFASs absorption data is available, however biomonitoring data demonstrate the presence of C9-C14 PFCA in human blood and serum (for further information see section B.9.6).

Following absorption, PFAS including PFCA such as C9-PFCA, C10-PFCA and C12-PFCA, are distributed primarily to blood and blood rich-tissues such as the liver, kidneys and lungs (Dewitt, 2015). The distribution of PFASs to liver and serum is, at least partly, due to their high affinity to proteins. A large number of PFASs, including PFCAs such as PFOA and C10-PFCA have been shown to be highly bound to rat, human and bovine albumin in serum and intracellularly to liver fatty acid-bindning protein in the liver and α2u-globulins in the liver and kidney (Dewitt, 2015). A 1:1 ratio for human serum and plasma levels of a number of PFASs (including PFOA) was shown (Ehresman et al., 2007) and levels in these matrices can hence be considered comparable. Further, a 2:1 ratio for serum to whole blood was shown, equal to the volume displacement by the red blood cells in serum, thus whole blood levels of can be approximated to be the double of their corresponding serum levels.

In both humans and animals, PFASs are transferred to the fetus via the placenta and to the offspring via breast milk (Dewitt, 2015). Studies in humans have shown varying rates of placental and breast milk transfer between different C9-C14 PFCAs, with levels in fetal serum ranging from approximately 40% (C10-PFCA) to 180% (C13-PFCA) of that in maternal serum (Liu et al., 2011b). Levels of C9-C14 PFCAs in breast milk were in the range 3-4% of that in maternal serum (Liu et al., 2011b).

PFCAs are not metabolised in animals (Kudo, 2015). Studies on PFOA as well as PFSAs such as PFOS (C8-PFSA) and C10-PFSA in rats have shown that they are excreted untransformed, ie. Without forming any metabolites or conjugates. Thus, PFCAs are believed to represent metabolically inert and stable end-stage products. However, certain precursors have in rodents been shown to transform, to various extents, into e.g. their perfluorinated carboxylate "backbone structures", such as 8:2 FTOH that is metabolisd into e.g. PFOA and C9-PFCA (Henderson and Smith, 2007b).

The major route of excretion for PFCAs is renal elimination and to a smaller extent biliary and fecal excretion (Kudo, 2015). Elimination rates in rodents, monkeys and humans vary substantially between different homologues, animal species and gender. In general, the rate

of elimination from serum decreases with increasing carbon chain length, occur more rapidly in rats > mice > non-human primates > humans (Borg, 2013), Table B.5-1). Whereas the elimination half-lives are in the magnitude of hours and days for rodents and non-human primates, the half-lives are for humans in the order of years. Also, the elimination half-lives show pronounced gender differences within certain species (e.g., faster elimination in female rodents). The reason for the species and gender differences in elimination rates are believed to be due to active renal reabsorption via renal organic anion transporters which are expressed differentially between species and sex and for which PFASs, including PFCAs, has shown to be substrates.

*Table B.5-1: Serum elimination half-lives of C8-C11 PFCA in different species (including humans).*

| PFCA | Rat | | Mouse | | Monkey | | Human | |
|---|---|---|---|---|---|---|---|---|
| | M | F | M | F | M | F | M | F |
| C8-PFCA* | 5,6-13 days | 1,9-3,4 hours | 22 days | 16 days | 5,6-21 days | 2,7-33 days | 2,3-3,5 years | 2,3 years |
| C9-PFCA* | 30-47 days | 1,4-2,4 days | 34-69 days | 26-68 days | - | - | - | - |
| C10-PFCA* | 40 days | 59 days | - | - | - | - | 12 years | 4,5 years |
| C11-PFCA# | - | - | - | - | - | - | 12 years | 4,5 years |

* = Based on (Kudo, 2015), # = From (Liu et al., 2011b)

# B.5.2. Acute toxicity

This endpoint is not considered relevant for the human health risk assessment of C9-C14 PFCAs in the current dossier.

# B.5.3. Irritation

This endpoint is not considered relevant for the human health risk assessment of C9-C14 PFCAs in the current dossier.

# B.5.4. Corrosivity

This endpoint is not considered relevant for the human health risk assessment of C9-C14 PFCAs in the current dossier.

# B.5.5. Sensitisation

This endpoint is not considered relevant for the human health risk assessment of C9-C14 PFCAs in the current dossier.

# B.5.6. Repeated dosed toxicity

### B.5.6.1. Animal data

For PFASs in general, repeated-dose toxicity studies in rodents and monkeys show that liver is the main target organ (Borg and Håkansson, 2012). The hepatotoxicity is manifested as hepatocellular hypertrophy, increased liver weight, hepatocellular, vacuolation, pigmentation and necrosis, with the adversity being proportional with increasing dose. Other common toxic

effects observed following repeated dosing by PFASs are (Borg and Håkansson, 2012), (ATSDR, 2015):

- Decreased body weight.
- Effects on lipid metabolism: decreased serum cholesterol and serum triglycerides.
- Effects on thyroid hormone levels: decreased triiodothyronine (T3) and thyroxine (T4).
- Immunotoxicity (atrophy of thymus and spleen, suppressed antibody responses).
- Developmental toxicity (see Annex B.5.9).

## C9-PFCA

C9-PFCA has a harmonised classification as STOT RE 1 (H372) (liver, thymus, spleen).

In one study where Sprague Dawley rats were administered C9-PFCA via gavage for 14 days (0, 0,2, 1, 5 mg/kg/day) resulted in increases in serum glucose levels and decreases in high-density lipoprotein (HDL)-cholesterol levels (Fang et al., 2012a) and hepatocellular vacuolation at 5 mg/kg/day (Fang et al., 2012b).

An immunotoxicity study in BALB/c mice that were dosed with C9-PFCA via gavage for 14 days (0, 1, 3, and 5 mg/kg/day) found decreases in thymus and spleen weights at 3 mg/kg/day and alterations in splenic lymphocyte phenotypes at 1 mg/kg/day (Fang et al., 2008).

In a developmental toxicity study in 129S1/Svlmj mice, where dams were exposed via gavage to 0, 0.83, 1.1, 1.5 or 2 mg/kg/day C9-PFCA during GDs 1–18, increased liver weight was observed in the dams and in offspring on PND21 at the lowest dose, 0.83 mg/kg/day (Wolf et al., 2010).

In a developmental toxicity study in CD-1 mice, where dams were exposed via gavage to 0, 1, 3, 5 or 10 mg/kg/day C9-PFCA during GDs 1–17, increased liver weight was observed in dams and in offspring, persisting into adulthood, at the lowest dose 1 mg/kg/day (Das et al., 2015).

For more detailed information on the repeated-dose toxicity of C9-PFCA we refer to the proposal for harmonized classification and labelling of PFCA (Swedish Chemicals Agency, 2013).

## C10-PFCA

In a study by Harris and Birnbaum (Harris and Birnbaum, 1989) the developmental toxicity of C10-PFCA was investigated in C57BL/6N mice exposed via gavage at levels between 0 to 32 mg/kg/day during different windows of gestation. Increased liver weight was observed in the dams at 1.0 mg/kg/day.

In a study on wistar rats that were exposed to C10-PFCA via the diet at doses corresponding 0, 1.2, 2.4, 4.8, or 9.5 mg/kg/day for 7 days (Kawashima et al., 1995) increased absolute liver weight was observed at 2,4 mg/kg/day. At 9.5 mg/kg/day increased the number of lipid droplets containing amorphous material was observed, indicating marked toxicity to hepatocytes. C10-PFCA was considerably more potent than PFOA in causing increased liver weight.

For more detailed information on the repeated-dose toxicity of C10-PFCA we refer to the proposal for harmonized classification and labelling of C10-PFCA (Swedish Chemicals Agency", 2015c).

## C11-PFCA

A combined repeated dose and reproductive/developmental toxicity screening study (OECD guideline 422) where male and female rats were administered C11-PFCA via gavage at 0.1,

0.3, or 1.0 mg/kg/day was performed (Takahashi et al., 2014). Liver weight was increased in males at 0.3 mg/kg/day and above and in females at 1.0 mg/kg/day, and this change was observed also after a recovery period. In both sexes, centrilobular hypertrophy of hepatocytes was observed at 0.3 mg/kg/day and above and focal necrosis was observed at 1.0 mg/kg/day. In addition, at 1.0 mg/kg/day, body weight gain was decreased in both sexes and changes in various clinical blood parameters.

**C12-PFCA**

Dosing of male Sprague-Dawley rats with 0, 1, 5, or 10 mg/kg/day C12-PFCA via gavage for 14 days induced a decrease in body weights at 5 mg/kg/day and a 35% increase in total serum cholesterol at 10 mg/kg/day (Shi et al., 2007).

(Ding et al., 2009) and (Shi et al., 2009) used a similar experimental setup and exposed male rats to C12-PFCA via gavage for 110 days at the doses 0.02, 0.05, 0.2 or 0.5 mg/kg bw/day. Ding et al. (2009) reported hepatic steatosis at 0.02 mg/kg/day becoming more pronounced at higher doses. (Shi et al., 2009)reported significantly decreased serum testosterone levels at 0.05 mg/kg bw/day and significantly decreased body weights at 0.5 mg/kg bw/day.

A combined repeated dose and reproductive/developmental toxicity screening study (OECD guideline 422) where male and female rats were administered C12-PFCA by gavage at 0.1, 0.5, or 2.5 mg/kg/day was performed (Kato et al., 2015). Dosing at 0.5 and 2.5 mg/kg/day affected the liver, in which hypertrophy, necrosis, and inflammatory cholestasis were noted. Body weight gain was markedly inhibited in the 2.5 mg/kg/day group, and a decrease in hematopoiesis in the bone marrow and atrophic changes in the spleen, thymus, and adrenal gland were observed.

**C13-PFCA**

No relevant studies on the toxicity of C13-PFCA were found.

**C14-PFCA**

A combined repeated dose and reproductive/developmental toxicity screening study (OECD guideline 422) where male and female rats were administered C14-PFCA by gavage at 1, 3, or 10 mg/kg/day was performed (Hirata-Koizumi et al., 2015). At 3 and 10 mg/kg/day C14-PFCA caused hepatocellular hypertrophy and/or fatty changes in the liver and follicular cell hypertrophy in the thyroid.

### B.5.6.2. Human data

Not considered relevant for this dossier. C9-C14 PFCA are listed as SVHC substances under REACH due to their PBT/vPvB properties.

# B.5.7. Mutagenicity

This endpoint is not considered relevant for the human health risk assessment of C9-C14 PFCA in the current dossier.

# B.5.8. Carcinogenicity

There are few available studies on the carcinogenicity of C9-C14 PFCA. However, both C9-PFCA and C10-PFCA has harmonised classifications as Carc 2 based on read-across from PFOA. For more information we refer to the proposals for harmonized classification and

labelling of C9-PFCA (Swedish Chemicals Agency 2013) and C10-PFCA (Swedish Chemicals Agency 2015c).

# B.5.9. Toxicity for reproduction

## B.5.9.1. Animal data

A number of PFAAs have shown reproductive and developmental toxic properties in laboratory animals following exposure *in utero*. The toxicity is manifested as reduced fetal, perinatal and/or neonatal body weight and viability as well as reduced pup body-weight gain and litter loss in the dams (Borg, 2013). The most adverse of these toxic effects is a dose-dependent marked increase in neonatal mortality that has been observed for several PFAAs.

### C9-PFCA

C9-PFCA has a harmonised classification as Repr 1B (H360Df) and Lact (H362).

A developmental toxicity study was performed on 129S1/Svlmj mice where the dams were exposed by gavage to 0, 0.83, 1.1, 1.5 or 2 mg/kg/day C9-PFCA during GDs 1–18 (Wolf et al., 2010). A significant reduced survival was observed in the offspring at starting at 0,83 mg/kg/day.

In a developmental toxicity study in CD-1 mice, dams were exposed via gavage to 0, 1, 3, 5 or 10 mg/kg/day C9-PFCA during GDs 1–17 (Das et al., 2015). Dams given 10mg/kg/day C9-PFCA could not carry their pregnancy successfully and this dose group were not continued. At 5 mg/kg/day, most of the pups were born alive but 80% died during the first 10 days of life. In all dose-groups, neonates exposed to C9-PFCA exhibited dose-dependent decreases in body-weight and delays in eye opening and onset of puberty.

For more detailed information on the developmental/reproducive toxicity of C9-PFCA we refer to the proposal for harmonized classification and labelling of C9-PFCA (Swedish Chemicals Agency, 2013).

### C10-PFCA

C10-PFCA has a harmonised classification as Repr 1B (H360Df) and Lact (H362).

In a study by (Harris and Birnbaum, 1989) the developmental toxicity of C10-PFCA was investigated in C57BL/6N mice exposed via gavage at levels between 0 to 32 mg/kg/day during different windows of gestation. Offspring to dams exposed during GDs 6–15 showed significantly reduced body weights at 0.1 mg/kg bw/day.

For more detailed information on the developmental/reproductive toxicity of C10-PFCA we refer to the proposal for harmonized classification and labelling of C10-PFCA (Swedish Chemicals Agency ", 2015c).

### C11-PFCA

A combined repeated dose and reproductive/developmental toxicity screening study (OECD guideline 422) where male and female rats were administered C11-PFCA via gavage at 0.1, 0.3, or 1.0 mg/kg/day was performed (Takahashi et al., 2014). At 1,0 mg/kg/day birth weight was decreased in the pups and body weight gain at 4 days after birth was decreased.

### C12-PFCA

ANNEX XV RESTRICTION REPORT – C$_9$-C$_{14}$ PFCAs -including their salts and precursors-

A combined repeated dose and reproductive/developmental toxicity screening study (OECD guideline 422) where male and female rats were administered C12-PFCA via gavage at 0.1, 0.5, or 2.5 mg/kg/day was performed (Kato et al., 2015). Various histopathological changes, including decreased spermatid and spermatozoa counts, were observed in the male reproductive organs, while continuous diestrous was observed in the females of the 2.5 mg/kg/day group. Seven of twelve females receiving 2.5 mg/kg/day died during late pregnancy while four other females in this group did not deliver live pups.

**C13-PFCA**

No relevant studies on the toxicity of C13-PFCA were found.

**C14-PFCA**

A combined repeated dose and reproductive/developmental toxicity screening study (OECD guideline 422) where male and female rats were administered C14-PFCA by gavage at 1, 3, or 10 mg/kg/day was performed (Hirata-Koizumi et al., 2015). At 10 mg/kg/Day postnatal body weight gain in pups was decreased.

### B.5.9.2. Human data

Not considered relevant for this dossier. C9-C14 PFCA are listed as SVHC substances under REACH due to their PBT/vPvB properties.

# B.5.10. Other effects

No other effects are considered relevant for this dossier.

# B.5.11. Derivation of DNEL(s)/DMEL(s)

Derivation of DNELs and DMELs is not considered relevant for this dossier since the proposed restriction of C9-C14 PFCA is based on their PBT and vPvB-properties.

# B.6. Human health hazard assessment of physicochemical properties

Not relevant for this proposal.

# B.7. Environmental hazard assessment

Was not assessed, as C9-C14-PFCAs are PBT/vPvB-substances.

# B.8. PBT and vPvB assessment

# B.8.1. Assessment of PBT/vPvB Properties – Comparison with the Criteria of Annex XIII[1]

C9-C14 PFCAs are listed on the REACH Candidate List as substances of very high concern due to its PBT and vPvB-properties.

As C9-C14 PFCA related substances degrade to C9-C14 PFCAs in the environment (see chapter B.4.1.2) these substances need to be regarded as PBT/vPvB-substances as well (European Chemicals Agency, 2017a) (Regulation No 1907/2006 Annex XIII).

The following chapters are copied from the respective support documents for identification of the C9-C14 PFCAs as SVHCs.

**C9-PFCA** (European Chemicals Agency, 2015c)

A weight-of-evidence determination according to the provisions of Annex XIII of REACH is used to identify the substance as PBT. All available information (such as the results of standard tests, monitoring and modelling, information from the application of the category and analogue approach (grouping, read-across) and (Q)SAR results) is considered together in a weight-of-evidence approach.

C9-PFCA belongs to the chemical group of long-chained 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 other PFCAs with experimental and estimated data on C9-PFCA, it can be assumed that with increasing chain length water solubility decreases and the sorption potential increases. It can be stated with sufficient reliability that the behaviour of the PFCAs follows a regular pattern.

### Persistence

C9-PFCA is based on its stabile structure not expected to undergo abiotic degradation under relevant environmental conditions. A standard screening study on C9-PFCA supporting this understanding is available.

In general, the persistence of PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes the most stable organic compounds. It is not expected that the carboxylic group in PFCAs alters the persistence of these chemicals. The persistence of five PFCAs (C8-PFCA and C11-C14-PFCAs) (P and vP) was already confirmed by the Member State Committee.

Therefore, based on the information summarized above it is concluded that C9-PFCA is not degraded in the environment and thus fulfils the P- and vP- criteria in accordance with the criteria and provisions set out in Annex XIII of REACH.

### Bioaccumulation

There are no experimental BCF values available for C9-PFCA. The numeric criterion as suggested in REACH Annex XIII (sections 1.1.2 and 3.2.2(a)) for a bioaccumulative substance in aquatic species is not expected to be fulfilled for C9-PFCA based on read across. Due to its expected notable water solubility, C9-PFCA is, like the other PFCAs expected to quickly be excreted via gill permeation. Furthermore, C9-PFCA is present mainly in protein rich tissues like blood and liver. Hence, bioconcentration in gill breathing organisms and the accumulation in lipids is not the most relevant endpoint to consider. Field studies show that air-breathing organisms are more likely to bioaccumulate C9-PFCA and other PFCAs compared to water breathing organisms. Therefore, the numerical bioaccumulation (B) criterion defined in the REACH regulation Annex XIII (sections 1.1.2 and 3.2.2(a)) is not suitable to assess the bioaccumulation potential of C9-PFCA.

Annex XIII (section 3.2.2) defines information which shall be taken into account in the assessment and can be used to draw conclusions on the assessment even when the numerical criterion is not applicable. Such data are, for example, data on the bioaccumulation potential in terrestrial species, such as elevated levels in endangered species. C9-PFCA was found in

terrestrial species as well as in endangered species as shown for the polar bear and beluga whale. These findings indicate a bioaccumulation potential and are of high concern.

Furthermore, Annex XIII (section 3.2.2 (b)) requires to consider data from human body fluids or tissues and to take the toxicokinetic behavior of the substance assessed into account. For C9-PFCA gestational and lactational exposure in humans has been shown, which is of special concern as the foetus and newborn babies are highly vulnerable to exposure by toxic substances. On top of that, data from human body fluids clearly provide quantitative proof of the bioaccumulation of C9-PFCA: Elimination half-lives in humans are > 1 year. In addition, recent studies, taking into account relevant confounding factors, show that C9-PFCA blood concentrations in humans increase with increasing age.

Finally, Annex XIII (section 3.2.2 (c)) foresees that the potential for biomagnification in food chains of a substance is assessed. The available field data provide evidence that bioaccumulation and trophic magnification do occur in certain food webs in the environment. For C9-PFCA, field studies provide trophic magnification factors (TMFs) or biomagnification factors (BMFs) for C9-PFCA for aquatic and terrestrial food chains. When air breathing organisms are the top predators in these food chains biomagnification could be demonstrated by calculation of TMFs and BMFs > 1 in several food chains, for example for wolves and beluga whales.

The data summarized above is in high accordance with the bioaccumulation data on the other PFCAs. Altogether these show a regular pattern of bioaccumulation which depends on the chain-length of the perfluorinated alkyl chain.

*Conclusion*
1. C9-PFCA accumulates in humans
    a. C9-PFCA is present in human blood of the general population
    b. Elimination half-lives are > 1.7 years.
    c. Human elimination half-lives seem to be the longest amongst the available mammalian data, whereas the elimination half-lives in laboratory mammals vary highly depending on the study conditions.
    d. C9-PFCA levels increase with age after adjusting for relevant confounding factors.

2. There is evidence that C9-PFCA preferentially bioaccumulates in air-breathing mammals, including endangered species and humans
    a. BMFs range from 1.4 and 24 based on whole body values
    b. TMFs range from 2.9 to 9.88 referring to either whole body measurements or estimated whole body values.
    c. Protein corrected TMFs range between 2.9 to 6.19.

3. C9-PFCA does not seem to consistently accumulate in water breathing animals.
    a. No experimental BCFs are available for C9-PFCA. For the closest structural analogues BCFs range from 4.0 to 27 (C8-PFCA) and from 450 to 2700 (C10-PFCA)
    b. Whole body BAFs range from 0 to 3981
    c. Whole body BMFs range from 0.13 to 5.3 whereas most of the data are below 1
    d. Whole body TMFs range from 1 to 2.1 in aquatic piscivorous food webs

4. The bioaccumulation data on C9-PFCA in environmental species, in laboratory mammals and in humans is consistent with the data on other long-chain perfluorinated carboxylic acids, such as C8-PFCA.
    a. Recent models to explain the substantial bioaccumulation of PFCAs take into account the observed pattern of animal tissue distribution, the relationship between chain length and bioaccumulation and the species and gender-specific variation in elimination half-life.

To conclude, taken all available information together in a weight-of-evidence approach, the elimination half-lives from humans and other mammals show that C9-PFCA bioaccumulates. The available field data also indicate that bioaccumulation and trophic magnification occur in certain food webs in the environment. The data on C9-PFCA are in line with the expected regular pattern of fate properties of the already assessed C9-PFCA and C11-C14-PFCAs. Therefore, it is considered that the B criterion of REACH Annex XIII is fulfilled. Whether the vB criterion is fulfiled has not been assessed.

### Toxicity

C9-PFCA and its sodium and ammonium salts meet the criteria for classification as toxic for reproduction in accordance with Article 57 (c) of the REACH Regulation. As a consequence, the toxicity criterion of REACH Annex XIII is fulfilled.

### Summary and overall conclusions on the PBT and vPvB properties

In conclusion, C9-PFCA and its sodium and ammonium salts are identified as PBT substances according to Art. 57(d) of REACH by comparing all relevant and available information listed in Annex XIII of REACH with the criteria set out in the same Annex, in a weight-of-evidence determination.

### C10-PFCA (European Chemicals Agency, 2016b)

A weight-of-evidence determination according to the provisions of Annex XIII of REACH is used to identify the substance as PBT. All available information (such as the results of standard tests, monitoring and modelling, information from the application of the category approach (grouping, read-across) and (Q)SAR results) was considered together in a weight-of-evidence approach.

### Persistence

C10-PFCA is, based on its stable structure, not expected to undergo abiotic degradation under relevant environmental conditions.

In general, the persistence of C10-PFCA can be explained by the shielding effect of the fluorine atoms, blocking *e.g.* nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes the most stable organic compounds. It is not expected that the carboxylic group in PFCAs alters this persistence of these chemicals. The persistence of six PFCAs (C8-PFCA, C9-PFCA and C11-C14 PFCAs) (P and vP) was already confirmed by the Member State Committee.

Therefore, based on the knowledge of the stability of the C-F bond and the read-across approach with C8-PFCA, C9-PFCA and C11-C14 PFCAs it is concluded that C10-PFCA is expected to undergo extremely limited degradation in the environment and thus fulfils the P- and vP- criteria in accordance with the criteria and provisions set out in Annex XIII of REACH.

### Bioaccumulation

Due to its expected notable water solubility, C10-PFCA is, like the other PFCAs expected to be quickly excreted in fish via gill permeation. Hence, bioconcentration in gill-breathing organisms is not the most relevant endpoint to consider, as reflected by the differences between bioaccumulation data for gill- and air-breathing organisms. Field studies show that air-breathing organisms are more likely to bioaccumulate C10-PFCA and other PFCAs compared to gill-breathing organisms. Based on the BCF values for C10-PFCA it cannot be excluded that C10-PFCA is bioaccumulative in fish: BCF values range from 450 to 2700 for carcass, liver and blood. Conclusions on bioaccumulation should be based on whole body

values and carcass is seen as a good approximation for whole body. Based on the BCF of carcass C10-PFCA does not bioaccumulate in fish. However, as shown in this report, C10-PFCA does not accumulate in lipid but rather binds to protein and membrane phospholipids, therefore the carcass or whole-body BCF values are less relevant. Based on the BCF value in the blood of rainbow trout (2700±350), C10-PFCA can be considered bioaccumulative.

Annex XIII (section 3.2.2) defines information which shall be taken into account in the assessment and can be used to draw conclusions on the assessment even when the numerical criterion is not applicable. Such data are, for example, data on the bioaccumulation potential in terrestrial species, such as elevated levels in endangered species. C10-PFCA was found in terrestrial species as well as in endangered species as shown for the polar bear and the beluga whale. These findings indicate a bioaccumulation potential.

Furthermore, Annex XIII (section 3.2.2 (b)) requires to consider data from human body fluids or tissues and to take the toxicokinetic behaviour of the substance assessed into account. For C10-PFCA, gestational and lactational exposure in humans has been shown, which is of special concern as the foetus and newborn babies are highly vulnerable to exposure by xenobiotic substances. On top of that, data from human body fluids clearly provide quantitative proof of the bioaccumulation of C10-PFCA; elimination half-lives in humans are ≥ 4 years. In addition, recent studies, taking into account relevant confounding factors, show that C10-PFCA blood concentrations in humans increase with increasing age.

Finally, Annex XIII (section 3.2.2 (c)) foresees that the potential for biomagnification in food chains of a substance is assessed. The available field data provide evidence that bioaccumulation and trophic magnification do occur in certain food webs in the environment. For C10-PFCA, field studies provide trophic magnification factors (TMFs) or biomagnification factors (BMFs) in aquatic and terrestrial food chains. When air breathing organisms are the top predators in these food chains, biomagnification could be demonstrated by calculation of TMFs and BMFs to be > 1 in several food chains, for example for wolves, dolphins and beluga whales.

The data summarised above is in high accordance with the bioaccumulation data on the other PFCAs. Altogether these show a regular pattern of bioaccumulation which depends on the chain-length of the perfluorinated alkyl chain.

*Conclusion*:
1. C10-PFCA accumulates in humans.
    a. C10-PFCA is present in human blood of the general population. C10-PFCA has also been detected in human brain, lungs and kidney.
    b. Elimination half-lives are ≥ 4 years, which is longer than for C9-PFCA and C8-PFCA.
    c. C10-PFCA levels increase with age after adjusting for relevant confounding factors.

2. There is evidence that C10-PFCA preferentially bioaccumulates in air-breathing mammals, including endangered species and humans.
    a. BMFs range from 2.4 to 8.8 based on estimated whole body values in marine food web.
    b. TMFs range from 2.2 to 12.1 referring to either whole body measurements or estimated whole body values in marine wood web.

3. For part of the aquatic food chains investigated, C10-PFCA accumulates in water-breathing animals.
    a. BCFs range from 450 (carcass) to 2700 (in blood).
    b. whole body BAFs range from 714 to 7943.
    c. whole body BMFs range from 0.21 to 4.4.
    d. whole body TMFs range from 0.39 to 3.67 in aquatic piscivorous food webs.

4. The bioaccumulation data on C10-PFCA in environmental species, in laboratory mammals and in humans are consistent with the data on other long-chain perfluorinated carboxylic acids. Recent mechanistic bioconcentration models explain the substantial bioaccumulation of PFCAs by taking into account the observed pattern of animal tissue distribution, the relationship between chain length and bioaccumulation and the species and gender-specific variation in elimination half-life.

To conclude, taken all available information together in a weight-of-evidence approach, the elimination half-lives from humans and other mammals show that C10-PFCA bioaccumulates. The available field data also indicate that bioaccumulation and trophic magnification occur in certain food webs in the environment. The data on C10-PFCA are in line with the expected regular pattern of fate properties of the already assessed C8-PFCA (B), C9-PFCA (B) and C11-C14 PFCAs (vB). Therefore, it is considered that the B criterion of REACH Annex XIII is fulfilled. Whether the vB criterion is fulfilled has not been assessed.

### Toxicity

C10-PFCA and its sodium and ammonium salts meet the criteria for classification as toxic for reproduction in accordance with Article 57 (c) of the REACH Regulation. As a consequence, the toxicity criterion of REACH Annex XIII is fulfilled.

### Summary and overall conclusions on the PBT and vPvB properties

In conclusion, C10-PFCA and its sodium and ammonium salts are identified as PBT substances according to Art. 57(d) of REACH by comparing all relevant and available information listed in Annex XIII of REACH with the criteria set out in the same Annex, in a weight-of-evidence determination.

### C11-PFCA (European Chemicals Agency, 2012b)

A weight of evidence determination according to the provisions of Annex XIII of REACH is used to identify the substance as vPvB. All available information (such as results of standard tests, monitoring and modelling, information from the application of the category and analog approach (grouping, read-across) and (Q)SAR results) was considered together in a weight of evidence approach. The individual results have been considered in the assessment with differing weights depending on their nature, adequacy and relevance. The available results are assembled together in a single weight of evidence determination.

### Persistence

For C11-PFCA no experimental data on degradation are available. Therefore, data from chemically similar compounds should be considered in a read-across approach. The degradation potential of substances differing only in the number of carbons in the perfluorinated carbon chain has been analyzed in some studies which indicate that long-chain PFCAs are resistant to degradation in the environment.

PFCAs are synthetic compounds which contain a structural feature: a perfluorinated carbon chain combined with a carboxylic group. The perfluorinated carbon chain is a synthetic feature, there are no natural sources known. The chemical structure of these compounds differs only in the number of perfluorinated carbons in the carbon chain.

The stability of organic fluorine compounds has been described in detail by 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 the most stable organic compounds. These include

polarizability 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 (Siegemund et al., 2000).

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. The molecular reason for the persistence of highly fluorinated chemicals is the shielding effect of the substituted fluorine atoms described by Siegemund et al., 2000. Thus, using the described read across approach, we conclude that C13-PFCA is a very persistent synthetic compound which is resistant to abiotic and biotic degradation and fulfils both, the P and the vP criteria of Annex XIII.

*Abiotic degradation*
The data on the three CF2-groups C8-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days). The hydrolytic half-life of C8-PFCA at 25°C is greater than 92 years, with the most likely value of 235 years under relevant environmental conditions (3M. Co, 2001). No photodegradation of C8-PFCA has been observed in studies conducted under relevant environmental conditions. The estimated DT50 for indirect photolysis is 349 days.

*Biotic degradation*
Standard screening tests are available for C8,9,12,14-PFCAs. No biodegradation at all has been detected for C9,12,14-PFCAs within 28 days. For C8-PFCA test results differ from "no biodegratation" to 13% biodegradation of the ammonium salt. Thus, it can be concluded that C8,9,12,14-PFCAs are not readily biodegradable. For C8-PFCA a non-standard aerobic biodegradation simulation test, one non-standard anaerobic biodegradation simulation test and field monitoring data from contaminated sites provide evidence that no biodegradation in water, soil and sediment occurs.

*Conclusion*
C11-PFCA has no degradation studies available. Read across approach within C8-C14-PFCAs can be applied for the persistence assessment of these substances. C8-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups. As a result of comparing the experimental and estimated physico-chemical data of C8-PFCA (the analogue substance) with experimental and estimated data on C11-14-PFCAs it can be assumed that with increasing chain length water solubility decreases and the sorption potential increases. It can be with a sufficient reliability stated that the behaviour of these chemicals follow a regular pattern.

Due to both structural similarity and a regular pattern of physico-chemical properties, C8-14-PFCAs may be considered as a group or a category of substances for the purpose of the PBT/vPvB assessment and the read-across approach can be applied within this group.

In general, the persistence of C11-C14-PFCAs can be explained by the shielding effect of the fluorine atoms, blocking, e.g., nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the carboxylic group in PFCAs alters this persistence of these chemicals. This fact is confirmed by a hydrolysis study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,9,12,14-PFCAs showed no biodegradation within 28 days. Non-standard abiotic degradation tests with C8-PFCA could not detect any degradation products under environmentally relevant conditions. Furthermore, screening biodegradation studies on C8,9,12,14-PFCAs and one non-standard anaerobic biodegradation simulation test with C8-PFCA provide evidence of high persistence. Additionally, elements of non-standard higher tier aerobic biodegradation studies on C8-PFCA provide further support that no biodegradation in water, soil and sediment occurs.

Therefore, based on the information summarized above, it is concluded that C11-PFCA is not degraded in the environment and thus fulfils the P- and vP- criteria in accordance with the criteria and provisions set out in Annex XIII of REACH.

### Bioaccumulation

Bioaccumulative substances are defined in Annex XIII with a BCF >2000. If substances have a BCF >5000 they fulfil the criteria of being very bioaccumulative.

*Results from bioconcentration and bioaccumulation studies in aquatic species:*

The whole body BCF for C11-PFCA from the MITI flow-through study conducted with carp is in the range of 2300 – 3700 (National Institute of Technology and Evaluation, 2007). The study of Martin et al., propose that carcass BCFs closely approximate the whole-body BCF. This means the whole-body BCF would be approximately 2700 (mean value) C11-PFCA would therefore be bioaccumulative but not very bioaccumulative if referred to whole body according to Annex XIII of REACH.

However, if taking into account that PFCAs show hepatotoxic effects, focus could also be given to the higher accumulation potential in liver as bioaccumulation may be used as indicators for toxicity to organisms. Based on the findings there is a potential to reach critical levels that may elicit toxic effects over long-term exposures due to the high bioaccumulation potential to the liver.

BCF values of 5848-6326 (carcass) and 5246-5675 (liver) derived with two calculation methods from an experimental fish feeding study suggest that C11-PFCA is very bioaccumulative.

*Other information on the bioaccumulation potential and ability of the substance to biomagnify in the food chain:*

Available field based bioaccumulation data show BAF values for C11-PFCA well above the trigger-value of 5000 for various species from different studies.

Various available field-BMFs and even TMFs for C11-PFCA provide evidence on that biomagnification of the substance takes place in nature between different trophic levels of food chains and from the bottom to the top of food chains.

Comparing the different field-BMF and TMF values for C9-14-PFCAs within single studies revealed a trend between chain length and BMF and TMF values, showing that C11-PFCA has a higher biomagnification potential than the longer chained homologues. The potential to magnify in the food web declined from C11-PFCA to C14-PFCA indicating that trophic magnification is more pronounced for C11-PFCA than for the longer chained PFCAs. Hence, although C11-PFCA seems to have in laboratory studies a lower bioaccumulation potential than its longer chained homologues, based on field data it has a higher potential to transfer through the food web as demonstrated by high BMF, TMF and BAF values. This observation especially points to the need of expert judgement based on weight-of-evidence.

A human biomonitoring study indicates that C11-PFCA is eliminated from human serum at a slower rate compared to its longer chained homologues C12-14-PFCAs. These results further support that C11-PFCA shows a higher bioaccumulation potential compared to C12-14-PFCAs in certain studies.

*Conclusion on the bioaccumulation potential:*

Based on only the BCFs derived from flow-through tests, C11-PFCA clearly fulfils the B criterion but some uncertainty remains whether it fulfils the vB criterion. BCFs derived from BMFs of a fish feeding study are above 5000. Although these laboratory data indicate that the vB criterion may be fulfilled, further confirmation is sought from field data.

Bioaccumulation factors derived in field studies are clearly above the trigger of 5000 which can be considered analogous to a BCF > 5000. Furthermore, the various available field-BMFs

and TMFs for this substance provide evidence that biomagnification at high level takes place in nature. It is important to note that among C11-14-PFCAs, C11-PFCA based on field-BMFs and TMFs has the highest bioaccumulation potential indicating that trophic magnification is more pronounced for C11-PFCA than for the longer chained PFCAs. C12-14-PFCAs fulfill the vB criterion. Although for a large part of available information direct comparison with the vB criterion cannot be made, this information and especially the field data provide clear evidence on that the substance behaves in a way corresponding to bioaccumulation behaviour of substances which by direct comparison of the data to the vB criterion meet the criterion. Consequently, it is concluded that C11-PFCA fulfils both the B and the vB-criteria of REACH.

### *Toxicity*
Not relevant for the SVHC identification of the substance in accordance with Article 57 (e).

### *Summary and overall conclusions on the PBT, vPvB properties*
In conclusion, C11-PFCA is identified as a vPvB-substance according to Art. 57 (e) of REACH following the application of a weight of evidence determination using expert judgement by comparing all relevant and available information listed in Section 3 of Annex XIII of REACH with the criteria set out in Section 1 of the same Annex.

### **C12-PFCA** (European Chemicals Agency, 2012e)

A weight of evidence determination according to the provisions of Annex XIII of REACH is used to identify the substance as vPvB. All available information (such as results of standard tests, monitoring and modelling, information from the application of the category and analog approach (grouping, read-across) and (Q)SAR results) was considered together in a weight of evidence approach. The individual results have been considered in the assessment with differing weights depending on their nature, adequacy and relevance. The available results are assembled together in a single weight of evidence determination.

### *Persistence*

PFCAs are synthetic compounds which contain a structural feature: a perfluorinated carbon chain combined with a carboxylic group. The perfluorinated carbon chain is a synthetic feature, there are no natural sources known. The chemical structure of these compounds differs only in the number of perfluorinated carbons in the carbon chain.

The stability of organic fluorine compounds has been described in detail by 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 the most stable organic compounds. These include polarizability 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 (Siegemund et al., 2000).

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. The molecular reason for the persistence of highly fluorinated chemicals is the shielding effect of the substituted fluorine atoms described by Siegemund et al., 2000. Thus, using the described read across approach, we conclude that $C_{12}$-PFCA is a very persistent synthetic compound which is resistant to abiotic and biotic degradation and fulfils both, the P and the vP criteria of Annex XIII.

### *Abiotic degradation*

The data on C8-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days). The hydrolytic half-life of C8-PFCA at 25°C is greater than 92 years, with the most likely value of 235 years under relevant environmental conditions (3M. Co, 2001). No photodegradation of C8-PFCA has been observed in studies conducted under relevant environmental conditions. The estimated DT50 for indirect photolysis is 349 days.

*Biotic degradation*
A standard screening test is available for C12-PFCA. No biodegradation at all has been detected for within 28 days. For C8-PFCA test results differ from "no biodegratation" to 13% biodegradation of the ammonium salt. Thus, it can be concluded that C8,12-PFCAs are not readily biodegradable. For C8-PFCA a non-standard aerobic biodegradation simulation test, one non-standard anaerobic biodegradation simulation test and field monitoring data from contaminated sites provide evidence that no biodegradation in water, soil and sediment occurs.

*Conclusion*
C12-PFCA has no abiotic degradation studies available. Only one standard screening study is available (no biodegradation within 28 days).

Read across approach within C8-C14-PFCAs can be applied for the persistence assessment of these substances. C8-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups. As a result of comparing the experimental and estimated physico-chemical data of C8-PFCA (the analogue substance) with experimental and estimated data on C11-14-PFCAs it can be assumed that with increasing chain length water solubility decreases and the sorption potential increases. It can be with a sufficient reliability stated that the behaviour of these chemicals follow a regular pattern.

Due to both structural similarity and a regular pattern of physico-chemical properties, C8-14-PFCAs may be considered as a group or a category of substances for the purpose of the PBT/vPvB assessment and the read-across approach can be applied within this group.

In general, the persistence of C11-C14-PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the carboxylic group in PFCAs alters this persistence of these chemicals. This fact is confirmed by a hydrolysis study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,9,12,14-PFCAs showed no biodegradation within 28 days. Non-standard abiotic degradation tests with C8-PFCA could not detect any degradation products under environmentally relevant conditions. Furthermore, screening biodegradation studies on C8,9,12,14-PFCAs and one non-standard anaerobic biodegradation simulation test with C8-PFCA provide evidence of high persistence. Additionally, elements of non-standard higher tier aerobic biodegradation studies on C8-PFCA provide further support that no biodegradation in water, soil and sediment occurs.

Therefore, based on the information summarised above, it is concluded that C12-PFCA is not degraded in the environment and thus fulfils the P- and vP- criteria in accordance with the criteria and provisions set out in Annex XIII of REACH.

### Bioaccumulation

Regarding the bioaccumulation potential for C12-PFCA the available experimental BCF-values are above 5000. A number of field-BMFs and TMFs are available for C12-PFCA and they provide evidence that biomagnification of this substance takes place in nature between different trophic levels of food chains and from the bottom to the top of food chains. Due to the structural similarity and the regular pattern of physico-chemical properties within the group of C11-14-PFCAs, read across can be applied within the group. The available field

bioaccumulation data of C12-PFCA and the other substances of the group provide further support to assume that C12-PFCA biomagnifies in the food chain. Thus, it is concluded the B as well as the vB-criteria -are met in accordance with the criteria and provisions set out in Annex XIII of REACH.

### *Toxicity*

Not relevant for the SVHC identification of the substance in accordance with Article 57 (e).

### *Summary and overall conclusions on the PBT, vPvB properties*

C12-PFCA is not readily biodegradable. Further degradation studies are not available. Applying the read across approach, data from structurally similar compounds can be used to evaluate the degradation potential of the substance. C8-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups.

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. According to the read-across approach these chemicals follow a regular pattern as a result of structural similarity. Those substances may therefore be considered as a group or a category of substances and the read-across approach can be applied.

In general, the persistence of long-chain PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the substitution of a functional group – the carboxylic group in PFCAs– alters this persistence of these chemicals. This fact is confirmed by a study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,9,12,14-PFCA showed no biodegradation within 28 days. Non-standard tests with C8-PFCA could not detect any degradation products under environmentally relevant conditions. Moreover, a monitoring study showed that C8-PFCA remained in soil and groundwater, years after application of fire fighting foam which contained PFCAs.

Therefore, we conclude that C12-PFCA is not degraded in the environment and thus fulfils the P- and vP-criteria under REACH.

The available BCF-values of C12-PFCA are above 5000. Thus, the B as well as the vB-criteria according to Annex XIII of REACH are fulfilled.

In conclusion, C12-PFCAs is identified as a vPvB-substance according to Art. 57 (e) of REACH and by applying a weight of evidence determination using expert judgement by comparing all relevant and available information listed in Section 3 of Annex XIII of REACH with the criteria set out in Section 1 of the same Annex.

### **C13-PFCA** (European Chemicals Agency, 2012d)

A weight of evidence determination according to the provisions of Annex XIII of REACH is used to identify the substance as vPvB. All available information (such as results of standard tests monitoring and modelling, information from the application of the category and analog approach (grouping, read-across) and (Q)SAR results) was considered together in a weight of evidence approach. The individual results have been considered in the assessment with differing weights depending on their nature, adequacy and relevance. The available results are assembled together in a single weight of evidence determination.

*Persistence*

PFCAs are synthetic compounds which contain a structural feature: a perfluorinated carbon chain combined with a carboxylic group. The perfluorinated carbon chain is a synthetic feature, there are no natural sources known. The chemical structure of these compounds differs only in the number of perfluorinated carbons in the carbon chain.

The stability of organic fluorine compounds has been described in detail by 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 the most stable organic compounds. These include polarizability 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 (Siegemund et al., 2000).

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. The molecular reason for the persistence of highly fluorinated chemicals is the shielding effect of the substituted fluorine atoms described by Siegemund et al., 2000.

Thus, using the described read across approach, we conclude that C13-PFCA is a very persistent synthetic compound which is resistant to abiotic and biotic degradation and fulfils both, the P and the vP criteria of Annex XIII.

*Abiotic degradation*
The data on C8-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days). The hydrolytic half-life of C8-PFCA at 25°C is greater than 92 years, with the most likely value of 235 years under relevant environmental conditions (3M. Co, 2001). No photodegradation of C8-PFCA has been observed in studies conducted under relevant environmental conditions. The estimated DT50 for indirect photolysis is 349 days.

*Biotic degradation*
Standard screening tests are available for C8,9,12,14-PFCAs. No biodegradation at all has been detected for C9,12,14-PFCAs within 28 days. For C8-PFCA test results differ from "no biodegratation" to 13% biodegradation of the ammonium salt. Thus, it can be concluded that C8,9,12,14-PFCAs are not readily biodegradable. For C8-PFCA a non-standard aerobic biodegradation simulation test, one non-standard anaerobic biodegradation simulation test and field monitoring data from contaminated sites provide evidence that no biodegradation in water, soil and sediment occurs.

*Conclusion*
C13-PFCA has no degradation studies available.

Read across approach within C8-C14-PFCAs can be applied for the persistence assessment of these substances. C8-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups. As a result of comparing the experimental and estimated physico-chemical data of C8- PFCA (the analogue substance) with experimental and estimated data on C11-14-PFCAs it can be assumed that with increasing chain length water solubility decreases and the sorption potential increases. It can be with a sufficient reliability stated that the behaviour of these chemicals follow a regular pattern.

Due to both structural similarity and a regular pattern of physic-chemical properties, C8-14-PFCAs may be considered as a group or a category of substances for the purpose of the PBT/vPvB assessment and the read-across approach can be applied within this group.

In general, the persistence of C11-C14-PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the carboxylic group in PFCAs alters this persistence of these chemicals. This fact is confirmed by a hydrolysis study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,9,12,14-PFCAs showed no biodegradation within 28 days. Non-standard abiotic degradation tests with C8-PFCA could not detect any degradation products under environmentally relevant conditions. Furthermore, screening biodegradation studies on C8,9,12,14-PFCAs and one non-standard anaerobic biodegradation simulation test with C8-PFCA provide evidence of high persistence. Additionally, elements of non-standard higher tier aerobic biodegradation studies on C8-PFCA provide further support that no biodegradation in water, soil and sediment occurs.

Therefore, based on the information summarized above, it is concluded that C13-PFCA is not degraded in the environment and thus fulfils the P- and vP- criteria in accordance with the criteria and provisions set out in Annex XIII of REACH.

### Bioaccumulation

Regarding the bioaccumulation potential for C13-PFCA there are no available experimental BCFvalues. The BCFs of C12-PFCA and C14-PFCA from fish flow-through bioaccumulation tests are well above 5000. Due to the structural similarity and the regular pattern of physic-chemical properties within this group it can be with a high reliability assumed that also C13-PFCA has a BCF larger than 5000, too. A number of field-BMFs and TMFs are available for C13-PFCA and they provide evidence that biomagnification of this substance takes place in nature between different trophic levels of food chains and from the bottom to the top of food chains. Therefore, based on the information summarised above, it is concluded that C13-PFCA fulfils the B and the vB-criteria in Annex XIII of REACH.

### Toxicity

Not relevant for the SVHC identification of the substance in accordance with Article 57 (e).

### Summary and overall conclusions on the PBT, vPvB properties

Degradation studies on C13-PFCA are not available. Applying the read across approach, data from structurally similar compounds can be used to evaluate the degradation potential of the substance. C8,9-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups.

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. According to the read-across approach these chemicals follow a regular pattern as a result of structural similarity. Those substances may therefore be considered as a group or a category of substances and the read-across approach can be applied.

In general, the persistence of long-chain PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the substitution of a functional group – the carboxylic group in PFCAs– alters this persistence of these chemicals. This fact is confirmed by a study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,9,12,14-PFCA showed no biodegradation within 28 days. Non-standard tests with C8-PFCA could not detect any degradation products under environmentally relevant

conditions. Moreover, a monitoring study showed that C8-PFCA remained in soil and groundwater, years after application of fire fighting foam which contained PFCAs.

Therefore, we conclude that C13-PFCA is - like C8-PFCA - not degraded in the environment and thus fulfils the P- and vP-criteria under REACH.

For C13-PFCA, no BCF-value is available. The available BCF-values of C12,14-PFCAs are above 5000. Thus, the B as well as the vB-criteria according to Annex XIII of REACH are fulfilled. Due to the structural similarity to the other PFCAs it can be concluded that the BCF of C13-PFCA will be >5000, too. BMFs >1 were derived in one study indicating bioaccumulation, a fact confirming the bioaccumulative potential of the substance. Hence we conclude that C13-PFCA fulfils the B and the vB-criteria of REACH as well.

In conclusion, C13-PFCAs is identified as a vPvB-substance according to Art. 57 (e) of REACH and by applying a weight of evidence determination using expert judgement by comparing all relevant and available information listed in Section 3 of Annex XIII of REACH with the criteria set out in Section 1 of the same Annex.

**C14-PFCA** (European Chemicals Agency, 2012c)

A weight of evidence determination according to the provisions of Annex XIII of REACH is used to identify the substance as vPvB. All available information (such as results of standard tests, monitoring and modelling, information from the application of the category approach (grouping, read-across) and (Q)SAR results) was considered together in a weight of evidence approach. The individual results have been considered in the assessment with differing weights depending on their nature, adequacy and relevance. The available results are assembled together in a single weight of evidence determination.

*Persistence*

PFCAs are synthetic compounds which contain a structural feature: a perfluorinated carbon chain combined with a carboxylic group. The perfluorinated carbon chain is a synthetic feature, there are no natural sources known. The chemical structure of these compounds differs only in the number of perfluorinated carbons in the carbon chain.

The stability of organic fluorine compounds has been described in detail by 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 the most stable organic compounds. These include polarizability 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 (Siegemund et al., 2000).

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. The molecular reason for the persistence of highly fluorinated chemicals is the shielding effect of the substituted fluorine atoms described by Siegemund et al., 2000.

Thus, using the described read across approach, we conclude that C14-PFCA is a very persistent synthetic compound, which is resistant to abiotic and biotic degradation and fulfils both, the P and the vP criteria of Annex XIII.

*Abiotic degradation*

The data on C8-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days). The hydrolytic half-life of C8-PFCA at 25°C is greater than 92 years, with the most likely value of 235 years under relevant environmental conditions (3M. Co, 2001). No photodegradation of C8-PFCA has been observed in studies conducted under relevant environmental conditions. The estimated DT50 for indirect photolysis is 349 days.

*Biotic degradation*
A standard screening test is available for C14-PFCA. No biodegradation at all has been detected for within 28 days. For C8-PFCA test results differ from "no biodegratation" to 13% biodegradation of the ammonium salt. Thus, it can be concluded that C8,14-PFCAs are not readily biodegradable.

For C8-PFCA a non-standard aerobic biodegradation simulation test, one non-standard anaerobic biodegradation simulation test and field monitoring data from contaminated sites provide evidence that no biodegradation in water, soil and sediment occurs.

*Conclusion*
Heptacosafluorotetradecanoic acid (C14-PFCA) has no abiotic degradation studies available. Only one standard screening study is available (no biodegradation within 28 days).

Read across approach within C8-C14-PFCAs can be applied for the persistence assessment of these substances. C8-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups. As a result of comparing the experimental and estimated physico-chemical data of C8— PFCA (the analogue substance) with experimental and estimated data on C11-14-PFCAs it can be assumed that with increasing chain length water solubility decreases and the sorption potential increases. It can be with a sufficient reliability stated that the behaviour of these chemicals follow a regular pattern.

Due to both structural similarity and a regular pattern of physico-chemical properties, C8-14-PFCAs may be considered as a group or a category of substances for the purpose of the PBT/vPvB assessment and the read-across approach can be applied within this group.

In general, the persistence of C11-C14-PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the carboxylic group in PFCAs alters this persistence of these chemicals. This fact is confirmed by a hydrolysis study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,9,12,14-PFCAs showed no biodegradation within 28 days. Non-standard abiotic degradation tests with C8-PFCA could not detect any degradation products under environmentally relevant conditions. Furthermore, screening biodegradation studies on C8,9,12,14-PFCAs and one non-standard anaerobic biodegradation simulation test with C8-PFCA provide evidence of high persistence. Additionally, elements of non-standard higher tier aerobic biodegradation studies on C8-PFCA provide further support that no biodegradation in water, soil and sediment occurs.

Therefore, based on the information summarized above it is concluded that C14-PFCA is not degraded in the environment and thus fulfils the P- and vP- criteria in accordance with the criteria and provisions set out in Annex XIII of REACH.

**Bioaccumulation**

Regarding the bioaccumulation potential for C14-PFCA the available experimental BCF-values of C14-PFCA are above 5000. Furthermore, Table 13 of the supporting document ((European Chemicals Agency, 2012c) provides information on BCF, BMF and TMF of C9-14 PFCAs relevant to justify read across in the B assessment. Thus, the B as well as the vBcriteria -are met in accordance with the criteria and provisions set out in Annex XIII of REACH.

**Toxicity**

Not relevant for the SVHC identification of the substance in accordance with Article 57 (e).

***Summary and overall conclusions on the PBT, vPvB properties***

C14-PFCA is not readily biodegradable. Further degradation studies are not available. Applying the read across approach, data from structurally similar compounds can be used to evaluate the degradation potential of the substance. C8-14-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF2-groups.

Comparing the physico-chemical properties of C8-14-PFCAs it becomes obvious that with increasing chain length water solubility decreases and the sorption potential increases. This trend is based on the increasing number of CF2-groups in the molecular structure. According to the read-across approach these chemicals follow a regular pattern as a result of structural similarity. Those substances may therefore be considered as a group or a category of substances and the read-across approach can be applied.

In general, the persistence of long-chain PFCAs can be explained by the shielding effect of the fluorine atoms, blocking e.g. nucleophilic attacks to the carbon chain. High electronegativity, low polarizability and high bond energies make highly fluorinated alkanes to the most stable organic compounds. It is not expected that the substitution of a functional group – the carboxylic group in PFCAs– alters this persistence of these chemicals. This fact is confirmed by a study which obtained a DT50 of >92 years for C8-PFCA in water. Screening studies of C8,14-PFCA showed no biodegradation within 28 days. Non-standard tests with C8-PFCA could not detect any degradation products under environmentally relevant conditions. Moreover, a monitoring study showed that C8-PFCA remained in soil and groundwater, years after application of fire fighting foam which contained PFCAs.

Therefore, we conclude that C14-PFCA is not degraded in the environment and thus fulfils the P- and vP-criteria under REACH.

The available BCF-values of C14-PFCA is above 5000. Thus, the B as well as the vB-criteria according to Annex XIII of REACH are fulfilled.

In conclusion, C14-PFCAs is identified as a vPvB-substance according to Art. 57e) of REACH and by applying a weight of evidence determination using expert judgement by comparing all relevant and available information listed in Section 3 of Annex XIII of REACH with the criteria set out in Section 1 of the same Annex.

# B.8.2. Emission Characterisation

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

C9-C14 PFCAs are non-degradable as well in waste water treatment plants (WWTP) as in the natural environment. Consequently, 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 long-chain PFCAs is landfilling. In her PhD-thesis (Vierke, 2014a) investigated samples from WWTP as to the distribution of PFASs in the environment. Air-water concentration ratios were lower for long-chain PFCAs compared to short-chain PFCAs. So, an enrichment of C9-C14 PFCAs in water is likely. In a water-saturated sandy sediment system and at atmospheric particle-gas partitioning, long-chain PFCAs were retarded by sorption to the sediment. However, PFCAs could be easily mobilised again.

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).
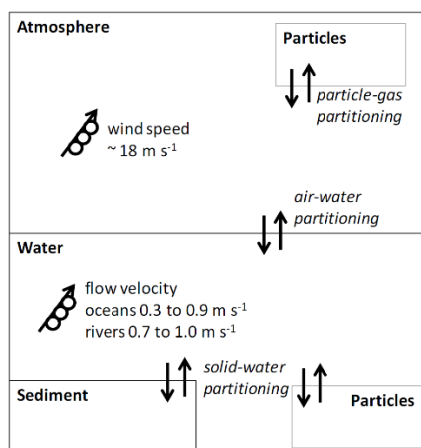


*Figure B.8- 1: Distribution of substances (equilibrium arrows) to mobile environmental media (circled arrows) ((Vierke, 2014b) based on Ballschmiter (1992) and multimedia models (Mackay, 2001; Scheringer, 2002)).*

Concluding, C9-C14 PFCAs could be found as well in sediments as in water and air. Water and air are highly mobile compartments. Hence, a long-range transport of these PFCAs is quite likely. On the other hand, soil and sediments serve as depot for the persistent PFCAs.

Numerous direct and indirect sources of C9-C14-PFCAs, their salts and related substances contribute to the overall environmental emission of C9-C14-PFCAs. As described in Annex A.2, C9-C14-PFCAs, their salts and related substances are used in many applications and were detected in various consumer articles 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 C9-14 PFCAs or their salts and during the life-cycle of articles that contain these substances as a constituent, impurity or residue. For example, fluoropolymer-based products such as PVDF contain C9-PFCA as residue when the substance has been used as processing aid.

Indirect sources refer to the formation of C9-14-PFCAs from their related substances (categorisation comparable to that of (Wang et al., 2014)).

Certain C9-C14-related substances, such as 10:2 FTOH, are volatile substances. They are released to air and wastewater during manufacture of the substances themselves, from side-chain fluorinated polymers and during use and disposal of consumer articles treated with C9-C14-PFCA-related substances. When emitted to the atmosphere, they can be degraded to C9-C14-PFCAs, and deposited on soil or surface waters. They are also washed out from the atmosphere via precipitation.

More details are provided on releases from specific uses:

Uses of C9-C14-related substances which are considered the most relevant regarding environmental exposure of C9-C14-PFCAs.

Although due to the large number of (unintentional) 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 releases are available on a global level based on a top-down approach. However, data gaps exist on the downstream user level. C9-14-PFCAs and related substances are used in various applications which are wide dispersive.

Therefore, a qualitative approach has been chosen for the description of emission sources and mainly worst case estimates of environmental releases 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

Releases of C9-C14 PFCAs, to the environment generally occur from their manufacture, use, and disposal; from being present as impurities in other PFCAs (such as PFOA) or from precursor substances that degrade abiotically or biotically in the environment (Buck et al., 2011).

### B.9.1.1 Human exposure

Human exposure to PFASs, including C9-C14 PFCAs, can occur via a large number of different exposure media including food and drinking water, house dust and ambient air (Vestergren et al., 2012). Vestergren et al. (2012) estimated the contribution of different exposure sources of C9-C14 PFCA, and for all homologues dietary intake was determined to be the major exposure route accounting for approximately 50-100%. For C14-PFCA ingestion of house dust was also a major route of exposure accounting for approximately 50%.

In addition to direct exposure to C9-C14 PFCA, humans are exposed to the wide range of precursors, present in e.g. consumer articles, and that can be metabolized to C9-C14 PFCAs after being absorbed into the human body (D'eon and Mabury, 2011b; Martin et al., 2010).

Exposure to C9-C14 PFCAs as well as their precursors that can degrade to these, makes up a very complex matrix of exposures to different substances via various exposure routes. Thus, serum concentrations of PFASs, including C9-C14 PFCAs, are commonly used as measure of human exposure to these. Blood/serum is a suitable matrix to analyze based on the relatively long half-lives of many PFASs, including C9-C14 PFCAs in humans, spanning from months to years. One advantage of using blood/serum concentrations is also that these represent an integrated measure of exposure for PFCAs, irrespective of the source, e.g. precursor molecules that can be metabolized into the respective PFCA(s). Another advantage of using serum concentrations is that it enables easy comparisons to internal dose levels in animal studies and facilitates kinetic extrapolations from animals to humans. Similarly, fetuses are exposed to PFCAs via placental transfer during pregnancy (Kim et al., 2011) and breast milk is the main source of PFASs for infants (Haug et al., 2011), through which their intake may equal the dietary intake in adults (Thomsen et al., 2010).

## B.9.1.2 Environmental exposure

### B.9.1.2.1 Global historical emissions of C9-C14 PFCAs and their salts and related substances

Globally, the manufacturing of C8-based fluorochemicals, the intentional manufacturing of C9-C14 PFCAs and the uses of their salts (e.g. APFN) in fluoropolymer manufacture (e.g. polyvinylidenefluorinde PVDF) have been identified as the main direct emission sources. These direct emission sources have been significantly reduced in the USA, Europe and Japan, due to a voluntary agreement between the US EPA and eight of the largest global fluorochemical manufacturers to phase out long-chain PFCAs and related substances by the end of 2015 (US EPA 2010/15 PFOA Stewardship Program). However, it is important to note, that the manufacture of fluoropolymers is shifting to countries such as Russia and China, where it is assumed that a large share of fluoropolymers is still produced using long-chain PFCAs, such as the ammonium salt of APFN. The global fluoropolymer market is continuously growing (5-6% per year globally).

The global annual production of ammonium perfluorononanoate (the ammonium salt of C9-PFCA; APFN) was estimated between 15 and 75 tonnes per year in 2004. Long-chain PFCAs and their ammonium salts were marketed e.g. in the product Surflon S-111 (CAS 72968-3-88). It was commonly used as a polymerization aid for the production of fluoropolymers. C9-PFCA is the dominant chemical compound at 74% by weight, followed by C11-PFCA with 20%, and C13-PFCA with 5% in this product (Prevedouros et al., 2006). This product was imported in quantities below 5 t/a between 2004 and 2008 into the EU (van der Putte et al., 2010).

Wang and co-workers estimated use rates of APFN during the period from 2011 to 2015 in the range from 17 to 107 t/a worldwide[5]. The main use of APFN is manufacturing of polyvinylidene fluoride (PVDF) (see Annex A.2 for further details). The authors considered that companies committed to the US EPA Stewardship Program will have ceased the manufacturing of APFN and thus manufacturing volumes will decline (Wang et al., 2014), see table below.

*Table B.9- 1: Estimated global manufacturing volumes and emissions of APFN, the ammonium salt of C9-PFCA.*

| Time period | Globally manufactured APFN (estimates) [t] | Global APFN Emissions [t] (APFN manufacture) | Global APFN Emissions [t] (PVDF-manufacture with APFN) | Reference |
|---|---|---|---|---|
| 1975-2004 | 800-2300 | 70-200 | 400-1400 | (Prevedouros et al., 2006) |
| 1951-2002 | | 20-180 | 270-1270 | (Wang et al., 2014) |
| 2004 | 15-75 | | | Posner et al., 2009 |
| 2003-2005 | 11-99 | 0-50 | 30-220 | (Wang et al., 2014) |

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[5] Wang et al. (2014) have estimated total global annual and cumulative emissions of C4-C14 PFCAs from 1951-2030. Changes in industrial practices that have occurred over time have been considered, e.g. there has been a shift towards shorter-chain substances, triggered by political efforts as the US EPA stewardship program. Projected emissions in 2016-2030 are based on the assumption that long-chain PFCAs and their precursors will not be longer produced in country group I (Japan, Western Europe and the US), but may be still contained in products in these regions due to import. For producers in country group II (Russia, China, India and Poland) only qualitative but no quantitative data on emission reductions was available. Therefore, for this group of countries Wang et al. set up a lower scenario (producers cease production and use of long-chain PFCAs and their precursors in line with global transition trends) and a higher scenario (emissions scenario in 2015 assumed to remain constant until 2030).

| | | | | |
|---|---|---|---|---|
| 2006-2010 | 13-105 | 0 | 0 | |
| 2011-2015 | 17-107 | 0 | 0 | |

Wang and co-workers (2014) estimated the global emissions of APFN from PVDF production. Emission factors of 5-10 wt% were assumed for APFN manufacturing sites based on APFN production. For the period from 2006 to 2015, the authors reduced the emission factors by 80% that is the average of annual emission reductions reported by one producer to the US-EPA Stewardship Program. Wang and co-workers suggest that in 2015 a reduction of 98% was achieved, because of the phase out of long-chain PFCAs as the results of the US EPA Stewardship Program. Companies committed to this program reduced emissions of APFN from manufacturing sites by 95% by 2010 in comparison to the baseline year 1999-2000.

According to Prevedouros (2006) 100 to 200 ppm of APFN are estimated to remain in PVDF dispersion products. Wang et al estimated that 60% of APFN are thermally decomposed during processing and the other 40% were emitted most likely to air. For the period from 2003 – 2015 the authors assumed an extra reduction factor of 80%. The authors state that there is no recent information available on the actual reduction of APFN residual levels in PFDV dispersion products.

According to Wang et al. (2014), the majority of the C9-, C11- and C13-PFCA were emitted from PFOA and C9-PFCA-based products in 1951-2015 as direct sources. The C10-PFCA was mainly released as impurity in fluorotelomer-based products and to a smaller part from C9-PFCA-based products. C12- and C14-PFCA were mainly emitted from C9-PFCA-based products in 1951 – 2002. From 2003-2015, C12- and C14–PFCA mainly occurred as degradation product from fluorotelomer based products (indirect source).

Examples for C9-C14 PFCA related substances are fluorotelomer-based products including various polymeric and non-polymeric species in numerous industrial and consumer applications. Only non-polymeric species readily degrade into PFCAs in the environment. Fluorotelomer-based products also contain PFCA impurities that can be directly released during the life-cycle of fluorotelomer-based products. Fluorotelomer-based products manufactured prior to 2015 are a mixture of major 8:2-based species and their lower and higher homologues, which may degrade into different PFCA homologues, whereas the products manufactured after 2015 are principally 6:2 based species with a purity of >99 % (Wang et al., 2014).

The estimated global annual emission fluxes for some C9-C14 based fluorotelomer alcohols are listed in the following table.

*Table B.9- 2: Estimated global annual emission flux of certain C9-C14 PFCA related substances (Wang et al., 2014)*

| Chemical | Year | Area | Estimated global annual flux (t/a) |
|---|---|---|---|
| 10:2 FTOH | 2010 | Globe | 12.8 -231 |
| 10:2 FTOH | 2004 | North America | 80 (median) |
| 10:2 FTOH | 2007 | North America | 2.5 (median) |
| 10:2 FTOH | 2007 | Switzerland | 67-535 |
| 10:2 FTOH | 2010 | Zurich | 17-37 |
| 12:2 FTOH | 2004 | Globe | 2.9 |
| 14:2 FTOH | 2004 | Globe | 0.6 |

After being manufactured, most of the fluorotelomer-based products are transported off-site to downstream users, where they are used for specific applicactions or further processed.

ANNEX XV RESTRICTION REPORT – C$_9$-C$_{14}$ PFCAs -including their salts and precursors-

It was reported by Wang et al., 2014 that 80% of the fluorotelomers are used in polymers and 20% in non-polymeric applications. Based on data of the Telomere Research Program (2002), polymeric uses of 10:2-, 12:2- and 14:2-Fluorotelomers were estimated to be at around 90 % and about 10% non-polymeric uses were estimated (in Wang et al., 2014).

The following table lists the estimated global cumulative emissions of individual PFCA-homologues from all quantified sources.

*Table B.9- 3: Estimated global cumulative emissions of C9-C14 PFCA homologues from quantified sources in tonnes (Wang et al., 2014)[6]*

| Substance | 1951-2002 [t] | | 2003-2015 [t] | | 2016-2030 [t] | | Total [t] |
|---|---|---|---|---|---|---|---|
| | Western countries | Russia, China, India, Poland | Western countries | Russia, China, India, Poland | Western countries | Russia, China, India, Poland | |
| C9-PFCA | 222 | 1371 | 28 | 469 | 0 | 62 | 250 – 1901 |
| C10-PFCA | 3 | 109 | 4 | 93 | 1 | 20 | 8-222 |
| C11-PFCA | 59 | 471 | 7 | 173 | 0 | 45 | 67-689 |
| C12-PFCA | 0 | 40 | 0 | 20 | 0 | 3 | 0-63 |
| C13-PFCA | 15 | 109 | 2 | 35 | 0 | 3 | 17-147 |
| C14-PFCA | 0 | 16 | 0 | 2 | 0 | 1 | 0-19 |
| **SUM** | **299** | **2116** | **41** | **792** | **1** | **134** | **324-3041** |

Thus, estimated total global cumulative emissions of C9-C14 PFCAs from 1951 to 2030 are in the range from 342 to 3041 t (according to Wang et al., 2014). From 2016 to 2030 estimated global cumulative emissions are in the range from 1 to 134 t (according to Wang et al., 2014). The authors discuss that the estimates levels of PFCA impurities are underestimated in their dataset.

*Conclusion*:

The available data on global manufacturing volumes and emissions are rare. However it can be concluded that on a global scale, manufacturing of C9-C14 PFCAs, their salts and related substances is decreasing. Thus, decreasing emissions into the environment can be expected. However, in Wang's estimations only the degradation of non-polymeric species is taken into account. Side-chain fluorinated polymers, however, will degrade in the environment at a very slow rate. Thus it needs to be considered that long-term emissions of those polymers will occur.

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[6] Wang et al. (2014) have estimated total global annual and cumulative emissions of C4-C14 PFCAs from 1951-2030. Changes in industrial practices that have occurred over time have been considered, e.g. there has been a shift towards shorter-chain substances, triggered by political efforts as the US EPA stewardship program. Projected emissions in 2016-2030 are based on the assumption that long-chain PFCAs and their precursors will not be longer produced in country group I (Japan, Western Europe and the US), but may be still contained in products in these regions due to import. For producers in country group II (Russia, China, India and Poland) only qualitative but no quantitative data on emission reductions was available. Therefore, for this group of countries Wang et al. set up a lower scenario (producers cease production and use of long-chain PFCAs and their precursors in line with global transition trends) and a higher scenario (emissions scenario in 2015 assumed to remain constant until 2030).

## B.9.1.2.2 Emissions via wastewater treatment plantsin Europe

As reported in Annex A.2, C9-C14 PFCAs, their salts and related substances occur as impurity in a huge amount of consumer articles and mixtures such as textiles, cosmetics and cleaning agents, that contain other per- and polyfluorinated substances. Articles and mixtures purchased some years ago may contain perfluorinated substances in higher levels of C9-C14 PFCAs and related substances than those available today. The reason is that C8-based fluorochemicals were used which contained higher concentrations of C9-C14 PFCAs and related substances compared to the use of short chain alternatives or even fluorine free articles and mixtures. Due to their long period of use, especially textiles may contribute to C9-C14 contamination from former uses of different perfluorinated compounds. Articles and mixtures containing more or less C9-C14 PFCA impurities are found in almost every household in the EU. This results in a wide dispersive release of these substances into air and into waste water e.g. laundry. It is impossible to gather all single release points, however WWTPs are a major source of the released C9-C14 PFCAs, their salts and related substances. C9-C14-PFCAs will not degrade in the WWTPs and therefore they will reach the effluent water or accumulate in sewage sludge. Moreover, C9-C14 PFCA related substances degrade in WWTPs to the corresponding perfluorinated acids (C9-C14 PFCAs).

The load of PFCAs as well as in the influent, the effluent as within the sludge of several WWTPs has been investigated in the last years by different authors worldwide. Depending on the shares of the water qualities to be treated, the technical equipment in the WWTPs, the treatment stages and further factors, the concentration of PFCAs vary extremely from below the detection limit up to several µg per kg dw sludge or effluent water. The load of C9-C14 PFCAs that will be released into the European environment via WWTPs until 2022 has been roughly estimated in this dossier mainly based on the publications from (Ahrens et al., 2009a; Gomez-Canela et al., 2012; Guo et al., 2010; Heidler and Halden, 2008; Olofsson et al., 2013; Ulrich et al., 2016). The values were averaged and interrelated to the European default WWTPs capacity. In the EU a municipal sewage treatment capacity of about 775 million resident equivalents is available (Neumann, 2013). That is equal to 77,500 default WWTP according to the Technical Guidance Document on Risk Assessment Part II (10,000 inhabitant equivalents; capacity per day 2000m³). An average daily sludge production of 0.74 t dw sludge in a default WWTP (0.037% of the WWTP treatment capacity) was then derived from this data. The averaged data from these publications also indicate a concentration of the long-chain PFCAs in the sludge. The measured concentrations of C9-C14 PFCAs in the sludge reach a range of µg per kg dw, whereas the concentrations in effluent water are a magnitude lower; in the range of ng per L (kg). In average only 0.125 % of C9, 0.027 % of C10, 0.008% of C11 could be found per Litre effluent water compared to the concentration in one kg sludge. The concentrations of C12-C14 PFCAs in the effluent water mainly were below the detection limits. With this ratio, the release of C9-C14 PFCA in the sludge and in the effluent water was calculated further. The longer the chain length of a perfluorinated acid, the more it will be adsorbed to soil and particles (see Annex B.4.2.1) Both the PFCA load in the sludge and in the aqueous phase was summarised as total annual emissions from a default WWTP (see Figure B.9- 1).
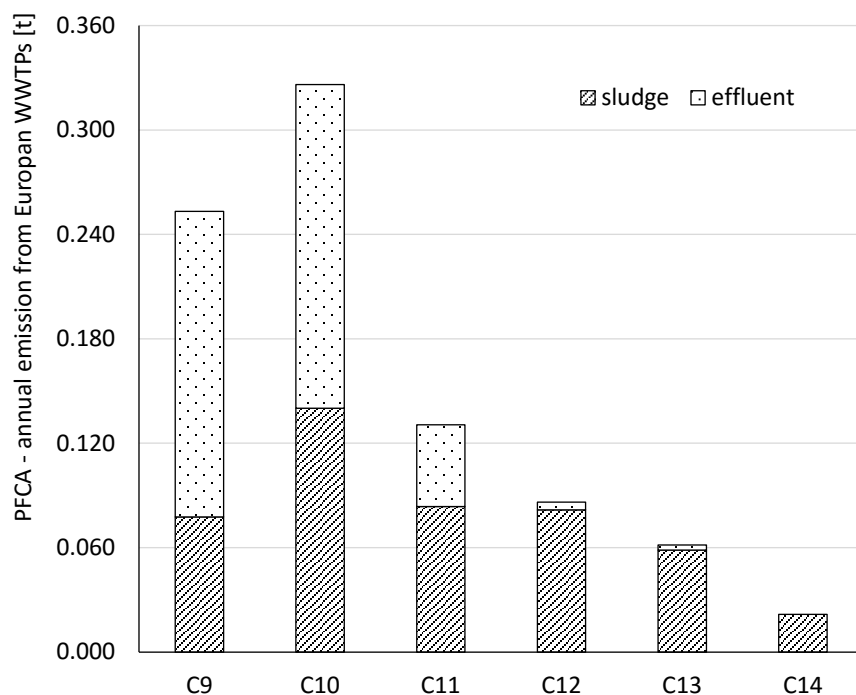
*Figure B.9- 1: Annual Emission of C9-C14 PFCAs via WWTP sludge and effluent water in 2009/2010 [t/a]*

The annual numbers were calculated using the averaged concentrations of C9-C14 PFCAs given by different authors for effluent water and sludge. These values were interrelated to the annual European default WWTPs capacity.

Although, the long-chain PFCAs adsorb to particles, the release of C9-C14 PFCAs via WWTP effluent water is not negligible (Figure B.9-4). According to the used data, 69% of C9-PFCA and 57% of C10 PFCA were released via effluent water from European WWTPs. The reason is due to the enormous amount of effluent water compared to the small amount of sludge. Several factors may influence the sorption and desorption of C9-C14 PFCAs in a WWTP. Such processes are equilibrium processes that are time and capacity dependent. On the one hand, the transit time through the WWTP obviously may be too short for a total adsorption of the PFCAs. On the other hand the concentration of PFCAs in water is much lower, so a partial desorption also could be taken into consideration. Further, the change in pH, in oxidation potential and many other factors influence the sorption equilibrium. For the environmental exposure this means that the C9-C14 PFCAs are deposited in the sediments of rivers and lakes into which the WWTPs drain. The transit time as well as the concentration gradients are different in surface waters compared than in a WWTP.

Another fact became evident when evaluating the data in several publications. The amount of C9-C14 PFCAs leaving a WWTP (effluent) is higher than the amount entering the WWTP via the influent. The averaged data for C9 and C10 from Heidler and Halden and Guo et al. demonstrate this gap (Figure B.9- 2) (Guo et al., 2010; Heidler and Halden, 2008). The concentration of the long-chain PFCAs in sludge from the water phase is one aspect in emerging this gap. More important is the degradation of precursor compounds to the non-degradable PFCAs (see Annex B. 4.1.2).
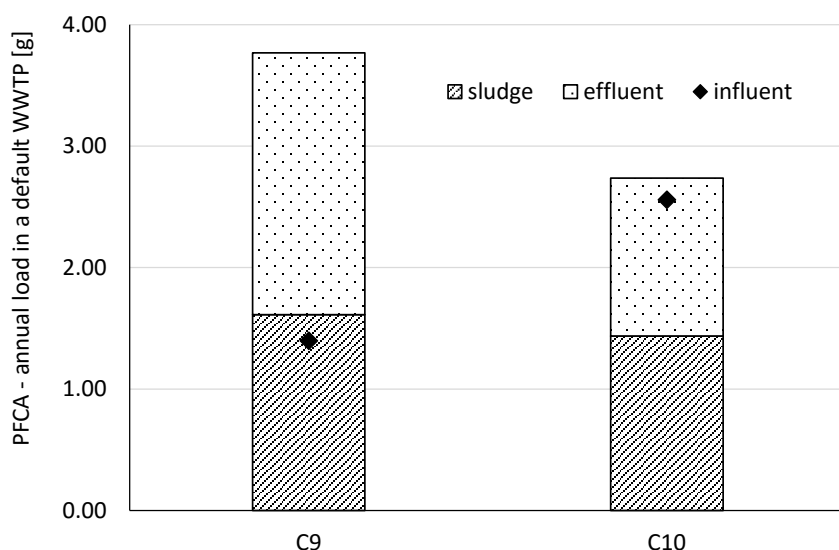
*Figure B.9- 2: The gap in the annual load of C9-PFCA and C10-PFCA between influent and effluent (effluent water and sludge) in one default WWTP [g/a] based on the data from Guo et al., 2010 and Heidler & Halden, 2008*

Because of regulatory pressure and the step-wise phase out of long-chain PFAS, especially PFOA and PFOS were substituted in consumer articles and mixtures in the last years. Hence, also the content of C9-C14 PFCAs is noticeable decreasing in consumer articles and mixtures and as a consequence also in the WWTP effluent and sludge. Ulrich et al. 2016 investigated 4,981 sludge samples from 1,165 different Bavarian WWTPs on PFCAs between 2008 and 2013. The measured concentrations of C9-C14 PFCAs belong to the upper range of concentrations that were found in the publications. Unfortunately, this study only concideres the concentration of C9-C14 PFCAs in the sludge. Data for the effluent water are lacking. Therefore the average content of PFCAs in the effluent water was estimated with the percental sludge/water distribution calculated above. Finally, the total release of C9-C14 PFCAs via total WWTP effluent (sludge and effluent water) in Europe was calculated. From these data the emission of long-chain PFCAs in the total WWTP effluent (sludge and effluent water) until 2022 was deduced by extrapolation taking the curve-fitting equitation with the highest r²-value (see Figure B.9- 3 – Figure B.9- 5). This estimation describes a realistic worst case scenario for the next years. Finally, the cumulative release of C9-C14 PFCAs in Europe via WWTP, which represents the emission from various wide dispersive (consumer-) uses, was calculated.
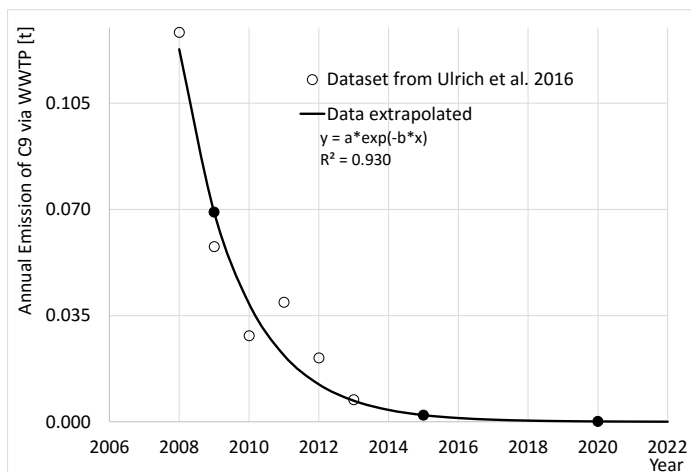
*Figure B.9- 3: Total release of C9-PFCA via WWTP effluent (sluge and effluent water) in Europe, deduced values on the basis of the data from Ulrich et al. 2016 using a calculated sludge/effluent water distribution quotient for each PFCA; black dots show the calculated emissions in 2009, 2015 and 2020*
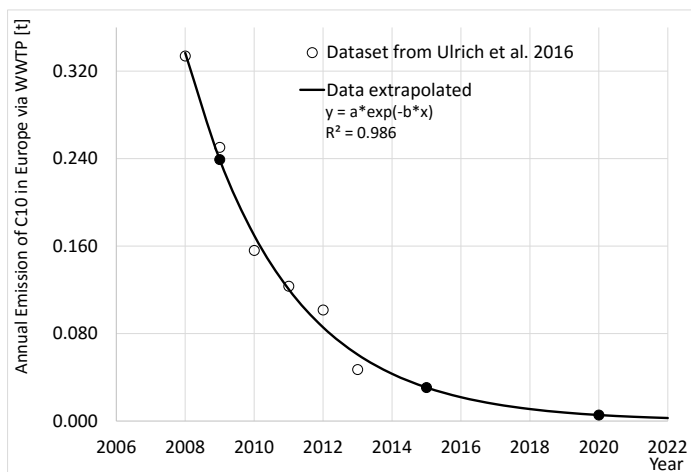


*Figure B.9- 4: Total release of C10-PFCA via WWTP effluent (sluge and effluent water) in Europe, deduced values on the basis of the data from Ulrich et al. 2016 using a calculated sludge/effluent water distribution quotient for each PFCA; black dots show the calculated emissions in 2009, 2015 and 2020*
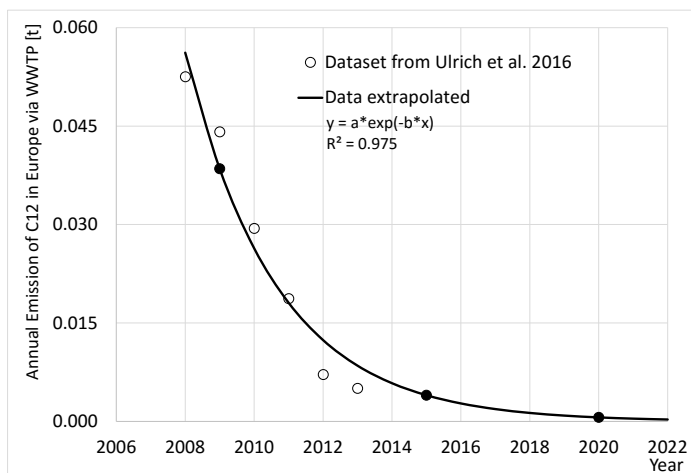


*Figure B.9- 5: Total release of C12-PFCA via WWTP effluent (sluge and effluent water) in Europe, deduced values on the basis of the data from Ulrich et al. 2016 using a calculated sludge/effluent water distribution quotient for each PFCA; black dots show the calculated emissions in 2009, 2015 and 2020*

There will be a distinct decrease in C9-C14 PFCAs emission in the next years, due to the substitution of perfluorinated substances in consumer articles and by the step by step removal of older articles that still contain higher concentrations of C9-C14 PFCAs as impurity It could be assumed, that about 0.005 t of C9-PFCA, about 0.099 t of C10-PFCA and 0.012 t of C12-PFCA are emitted cumulatively into the European environment via WWTP effluents (effluent water and sludge) between 2015 and 2022.

Via sludge 1.15 kg of C9-PFCA, 57.56 kg C10-PFCA and 12.05 kg C12-PFCA are estimated to be emitted in Europe between 2015 and 2022. Composting of organic waste and sludge represents an important and well established part of waste management in Europe. Composting and digestion of organic residues and application of compost to soils follow the principle of sustainability. Between 50% and 100% of accruing sludge from WWTPs is composted or directly used in European agriculture. Thus we assume that about 35 -70 kg of C9, 10, 12-PFCA could be directly emitted to the soil until 2022.

A wide spread release of the C9-C14 PFCAs, their salts and their related substances into the environment has to be considered despite there are no intentional uses of long-chain PFCAs announced by European industries (see Annex A.2). Wang et al., 2016 estimates a total global cumulative release of C9-C14 between 1-134 t until 2033. Based on the assuming calculations made above and the expecting emissions from wide spread use of articles and mixtures that unintentionally contain C9-C14 PFCAs and related substances, 116 kg of C9-C14 PFCAs will be emitted to the European environment via WWTPs until 2022. Evaluating the data, the degradation of precursors may still be underestimated. Moreover, C9-C14 PFCA related substances can be released additionally to the atmosphere from WWTPs. Thus, the releases of C9-C14 PFCAs from WWTPs may even be higher in Europe.

### B.9.1.2.4 Releases from unintentional use of C9-C14 PFCAs and related substances in firefighting foams

Table A.2-4 gives an average of 36 µg C9-C14 PFCAs/kg firefihting foam concentrate. For professional firefighting an annual demand of fluoro-surfactant containing firefighting foam concentrate of about 11 000 t is estimated in Europe (personal communication Blunk, University of Cologne 2017). Taking the average C9-C14 PFCA content of 36 µg per kg foam concentrate from the Swedish Chemicals Agency study, in Europe **400 kg** of C9-C14 PFCAs are released to the environment annually by using fluorosurfactants in firefighting foams. Assuming a constant use of those foams from 2015 and, having in mind that PFCAs are not degradable, **3 t** of C9-C14 PFCAs will be emitted cumulatively until 2022 in Europe.

In Germany about 2,000 t of foam concentrate is demanded for professional firefighting per year. That results to an estimated annual release of 72 kg C9-C14 PFCAs (calculating with the values from the Swedish Chemicals Agency study). So, **600 kg** of these substances will be emitted in Germany cumulatively between 2015 and 2022. That are about 18% of the European Release by professional firefighting. The release into the environment can be reduced by collecting, recycling or disposal of the extinguishing water. The joint stocks of such firefighting foams of the German armed forces, of larger airports, of refineries, municipal fire departments, chemical industrial fire departments was 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.

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 this data. At their operations fluorinated foams mainly were used as surface-active agent in a

concentration of 0.1%. At each operation 1,150 kg average ready to use foam was used. Calculating with the value of 36 µg C9-C14 PFCAs per kg foam concentrate measured by Swedish Chemicals Agency, about 41 µg C9-C14 PFCAs are released locally to the environment at each firefighting operation. Foams with perflourinated substances are deployed at about 54 operations per year by a volunteer fire brigade. In Germany exist about 24,000 volunteer fire brigades. This results in a direct emission of about 186 kg C9-C14 PFCAs in Germany per year. Assuming roughly the same ratio between German and European use of firefighting foams, an European release of C9-C14 PFCAs by volunteer fire brigades of **2 t** cumulatively could be derived between 2015 and 2022.

Different from professional firefighting, often it is not possible to collect and to recycle the extinguishing water. So, it can be concluded that the estimated amount of C9-C14 PFCAs will directly enter the environment.

It has to be mentioned that the use of PFASs in the AFFF by volunteer fire brigades already has been reduced within in the last years from 3 or 1% to 0.1% foam solutions.

### B.9.1.2.5 Releases from unintentional use of C9-C14 PFCAs and related substances in textiles

Studies have simulated evaporation and washing to assess releases from jackets, including freshly impregnated textiles. 10:2-FTOH was found in all air samples in concentrations from 2.74 - 110 µg/m² after 5 days (Gremmel et al., 2016; Knepper et al., 2014).

Two separate washing experiments were in the studies conducted using four different jacket pieces at once each time in order to trace additional releases of PFASs into washing water. Washing experiments revealed releases of 131, 119, 35, and 77% for C9-, C10-, C11- and C14-PFCA, respectively. C12- and C13-PFCA were not detected in the washing water.

Internal standards were applied, when summing up releases from the first and second wash cycle. Surprisingly some releases showed results above 100%. It could not be concluded whether C9- and C10-PFCA originate from residues in fluoropolymer manufacture or from the degradation of C9-C14-PFCA-related substances.

Moreover, the release of volatile PFASs from the wearing of outdoor jackets was simulated based on the ratio between concentrations measured by solvent extraction of jackets and concentrations measured in the air (µg/m2). It has been shown that 27.2 - 60.5% 10:2 FTOH were emitted.

It was shown that DWR jackets contribute as one particular source among many others to the overall release of C9-14-PFCA and C9-14-PFCA -related substances (Gremmel et al., 2016; Knepper et al., 2014).

Environmental release of C9-C12-PFCA from washing of textiles has also been shown for professional applications. Clara et al. tested two laundry and cleaning sites and found the four substances in the waste water of only one of the facilities (Clara et al., 2008). In the facility for yarn production, the highest emission levels were observed with concentrations of 320 ng/l (C9-PFCA), 96 ng/l (C10-PFCA), 70 ng/l (C11-PFCA), and 42 ng/l (C12-PFCA).

## B.9.2. Combined human exposure assessment

Exposure to C9-C14 PFCAs and their precursors makes up a very complex exposure matrix. Thus, blood/serum concentrations of C9-C14 PFCAs are a better measure of exposure to C9-C14 PFCAs since that represents an integrated measure of exposure to these substances, irrespective of the source and specific precursor compound. In addition, levels of C9-C14

PFCAs in breast milk represent an integrated measure of exposure for infants and toddlers. This is possibole due to their long or presumed long half-life in humans.

Human biomonitoring studies in European populations on serum and breast milk levels of C9-C14 PFCAs with samples collected between 2007 – 2017 have been used for the human exposure assessment in this dossier. The populations included consists of populations also in remote locations such as Greenland (Antignac et al., 2013; Axmon et al., 2014; Bjerregaard-Olesen et al., 2016; Gebbink et al., 2015; Gyllenhammar et al., 2015; Karrman et al., 2010; Manzano-Salgado et al., 2015; Motas Guzman et al., 2016; Stubleski et al., 2016; Yeung et al., 2013).

## C9-PFCA

In total 29 human biomonitoring studies investigating C9-PFCA in human serum were found (Appendix I). Overall, the serum concentrations of C9-PFCA were the highest of the C9-C14 PFCA, ranging from high pg/ml to low ng/ml (most samples) to high pg/ml in human serum. The detection frequency were high in the studies, often 100%. Temporal trends in human serum show that the levels of C9-PFCA have been increasing between 1980 – 2010 and that the levels seem to level out or slightly decrease after that.

In total 9 human biomonitoring studies investigating C9-PFCA in human breast milk were found (Appendix I). The concentrations of C9-PFCA in human breast milk samples ranged from < LOD to low pg/ml breast milk. The detection frequency in the studies were low, between 0-10%. One study investigating temporal trends of C9-PFCA in human breast milk in primiparous women in two Swedish cities was found (Nyberg et al. 2017). The result showed that C9-PFCA was increasing from 1972 to approximately 2010 and that the levels seem to level out or slightly decrease after that.

## C10-PFCA

In total 25 human biomonitoring studies investigating C10-PFCA in human serum were found (Appendix I). The serum concentrations of C10-PFCA were ranging from low ng/ml to high pg/ml (most samples) to low ng/ml in human serum. The detection frequencies were high in the studies, often >90%. Temporal trends in human serum show that the levels of C10-PFCA have been increasing between 1980 – 2010 and that the levels seem to level out or slightly decrease after that.

In total 9 human biomonitoring studies investigating C10-PFCA in human breast milk were found (Appendix I). The concentrations of PFDNA in human breast milk samples ranged from < LOD to low pg/ml breast milk. The detection frequencies in the studies were low, between 0-10%. One study investigating temporal trends of C10-PFCA in human breast milk in primiparous women in two Swedish cities was found (Nyberg et al. 2017). The result showed that C10-PFCA was increasing from 1972 to approximately 2010 and that the levels seem to level out or slightly decrease after that.

## C11-PFCA

In total 19 human biomonitoring studies investigating C11-PFCA in human serum were found (Appendix I). The serum concentrations of C11-PFCA were ranging from low ng/ml to high pg/ml (most samples) to low ng/ml in human serum. The detection frequencies were moderate in the studies, often >75%. Temporal trends in human serum show that the levels of C11-PFCA have been increasing between 1980 – 2010 and that the levels seem to level out or slightly decrease after that.

In total 7 human biomonitoring studies investigating C11-PFCA in human breast milk were found (Appendix I). The concentrations of C11-PFCA in human breast milk samples ranged

from < LOD to low pg/ml breast milk. The detection frequency in the studies were low, between 0-10%. One study investigating temporal trends of C11-PFCA in human breast milk in primiparous women in two Swedish cities was found (Nyberg et al. 2017). The result showed that C11-PFCA was increasing from 1972 to approximately 2010 and that the levels seem to level out or slightly decrease after that.

## C12-PFCA

In total 10 human biomonitoring studies investigating C12-PFCA in human serum were found (Appendix I). The serum concentrations of C12-PFCA were in the pg/ml range in human serum. The detection frequencies were fairly low in the studies, often 30-80%. Temporal trends in human serum show that the levels of C12-PFCA have been increasing between 1980 – 2010 and that the levels seem to level out or slightly decrease after that..

In total 5 human biomonitoring studies investigating C12-PFCA in human breast milk were found (Appendix I). The concentrations of C12-PFCA in human breast milk samples ranged from < LOD to low pg/ml breast milk. The detection frequencies in the studies were very low, between 0-3%. One study investigating temporal trends of C12-PFCA in human breast milk in primiparous women in two Swedish cities was found (Nyberg et al. 2017). The result showed that C12-PFCA was increasing from 2000 to approximately 2010 and that the levels seem to level out or slightly decrease after that.

## C13-PFCA

In total 8 human biomonitoring studies investigating C13-PFCA in human serum were found (Appendix I). The serum concentrations of C13-PFCA were in the pg/ml range in human serum. The detection frequencies were fairly low in the studies, often 30-80%. Temporal trends in human serum show that the levels of C13-PFCA have been increasing between 1980 – 2010 and that the levels seem to level out or slightly decrease after that.

In total 2 human biomonitoring studies investigating C13-PFCA in human breast milk were found (Appendix I). The concentrations of C13-PFCA in human breast milk samples ranged from < LOD to low pg/ml breast milk. The detection frequency in the studies were low, between 0-10%. No studies investigating temporal trends of C13-PFCA in human breast milk were found. One study investigating temporal trends of C13-PFCA in human breast milk in primiparous women in two Swedish cities was found (Nyberg et al. 2017). The result showed that C13-PFCA was increasing from 1972 to approximately 2010 and that the levels seem to level out or slightly decrease after that.

## C14-PFCA

In total 6 human biomonitoring studies investigating C14-PFCA in human serum were found (Appendix I). The serum concentrations of C14-PFCA were in the pg/ml range in human serum. The detection frequencies were low in the studies, 0-36%. No temporal trend studies on C14-PFCA were found.

One human biomonitoring study investigating temporal trends of C12-PFCA in human breast milk in primiparous women in two Swedish cities was found (Nyberg et al. 2017)(Appendix I). The concentrations of C14-PFCA in human breast milk samples ranged from < LOD to low pg/ml breast milk. The detection frequencies in the study was very low, between 0-3%. The result showed that C14-PFCA has increased since around 2007.

**Summary**

The human biomonitoring studies show that C9-C14 PFCA have been detected in various human body fluids such as serum and breast milk (Gyllenhammar et al., 2015; Manzano-Salgado et al., 2015; Motas Guzman et al., 2016). Overall, the concentrations of C9-PFCA, C10-PFCA and C11-PFCA in serum are in the similar range of high pg/ml to low ng/ml to whereas the levels of C12-PFCA, C13-PFCA and C14-PFCA in serum were in the pg/ml range (for details see Appendix I). Temporal trend studies show that the concentrations of C9-C13 PFCA in serum have been increasing since the 1980s until approximately 2010 where the increase seem to level out or slightly decrease (Axmon et al., 2014; Bjerregaard-Olesen et al., 2016; Gebbink et al., 2015; Gyllenhammar et al., 2015; Stubleski et al., 2016; Yeung et al., 2013). The concentrations of C14-PFCA were too close to or below LOD for reliable temporal trend analyses (Gebbink et al. 2015, Yeung et al. 2013). The concentrations of C9-C14 PFCA in breast milk were lower, ranging from < LOD to low pg/ml (Antignac et al., 2013; Karrman et al., 2010). One temporal trend study (Nyberg et al. 2017) show increasing concentrations of C9-C14 PFCA in breast milk that seem to levels out or decrease from approximately 2010.

For a complete summary of the human biomonitoring data see Appendix I.

# B.10. Risk characterisation

Due to the established PBT/vPvB properties of C9-C14 PFCA, risk characterisation for these substances are not considered for this dossier.

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

Based on the PBT- or vPvB- properties of the C9-C14 PFCAs and their related substances a union-wide restriction is needed to minimize the release of C9-C14 PFCAs and their related substances to the environment and reduce human exposure to a minimum. These considerations are described below.

C9-C14 PFCAs are PBT or vPvB substances. This persistence implies that the substances persist in the environment and may have irreversible adverse effects on the environment and human health in the long run. In order to prevent these long-term effects, the release of these substances have to be stopped. C9-C14 PFCA related substances might degrade to the corresponding perfluorinated carboxylic acids and they need to be regarded as PBT/vPvB-substances as well. Furthermore, C9-C14 PFCAs and related substances have the potential for long-range environmental transport which makes release of these substances a transboundary pollution problem. Consequently, they are found in the environment on a global scale, also in remote areas (Annex B.4.2.4. and Annex B.4.2.5.).

According to REACH regulation Article 60 (3) the risk to the environment cannot be adequately controlled for PBT or vPvB substances. No safe concentrations, thus no threshold (PNEC), can be determined for PBT and vPvB substances.

A large variety of emission sources contributes to the exposure of humans to C9-C14 PFCAs (Annex B.9.). Human biomonitoring shows that the whole EU population is exposed to C9-C14 PFCAs.

Temporal trend studies show that the concentrations of C9-C13 PFCA have been increasing since the 1980s until approximately 2010 where the increase seem to level out or slightly decrease. In the environment for some species raising environmental concentrations were recently reported (Annex B.4.2.5).

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 C9-C14 PFCAs for direct human exposure. Relevant articles such as furniture or textile and leather care articles, cosmetics are placed on the market and used in all EU Member States. A considerable share of articles containing C9-C14 PFCAs or related substances is imported from outside the EU.

No current intentional use in the EU could be found during the stakeholder consultation. C9-C14-PFCAs, their salts and related substances occur as unintended by-product during the manufacturing of per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms. There were indications that imported articles may still contain the substances.

The data from the Swedish Product Register show a sharp decline of the uses of C9-C14 PFCAs and their related substances in Sweden in the recent years. It can be assumed that the same trend is valid for the rest of the EU.

Stakeholder explained that the decline of C9-C14 PFCAs, their salts and related substances was triggered by the US-EPA 2010/2015 Stewardship Program and the Canadian restriction on long-chain PFCAs and indirectly also by the Norwegian ban of PFOA in textiles and the EU-restriction on PFOA.

Since it is possible that companies not bound to the voluntary US-EPA Stewardship Program may still use long-chain PFCAs including PFOA, imported goods may still contain these substances. Moreover, it is possible that after the enforcement of the PFOA restriction, C9-C14 PFCAs may be used as second best option for certain uses.

Therefore, any national regulatory action will not adequately manage the risks of C9-C14 PFCAs and related substances. Risk management measures need to be taken on a Union-wide basis. This need is acknowledged by the fact that C9-C14 are on the Candidate List for being considered as SVHC which should be substituted wherever possible.

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 (considering the PBT/vPvB properties) 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 C$_9$-C$_{14}$ PFCAs, their 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

## D.1

The Baseline scenario set out the basis for the Business As Usual scenario (BAU), which would occur even if the restriction dossier on C9-C14 PFCA was not implemented. A number of voluntary and non-voluntary actions to reduce PFAS in general are either under implementation or will be implemented in the near future. These actions, for example the PFOA restriction in the EU and the American and Canadian policy measures to reduce PFAS (US EPA Stewardship Program) are described in section D1.1, below. There is also a consumer demand for more environmental friendly products, in for example the outdoor industry, which is driving a phasing out of PFAS in general. These actions and trends (which also can have an effect on the phasing out of C9-C14 PFCAs) will occur without the restriction proposed in this report and are therefore part of the business as usual- scenario.

The general trend for the future in production and manufacture of C9-C14 PFCAs and their related substances show a somewhat different trend depending on the type of application. One clear trend is a substitution process towards shorter chain length, where C4 or C6 chemistry is used, which cannot transform into C9-C14 (OECD, 2013). A substitution process towards fluorine free alternatives is also ongoing (see Annex E.2). These trends are supported by both data from the Swedish product registry and stakeholder consultation.

The PFOA restriction is an important restriction also for the reduction of C9-C14 PFCAs, since it will come into place before the implementation time of this restriction. In for example impregnation of textiles, paper production and paint production chemical compounds containing both C8 and C9-C14 are used.  The restriction on PFOA, PFOA salts and PFOA-related substances was submitted by Norway and Germany in 2014 and will be binding except for derogations in 2020. In the exposure assessment chapter (1.1.5.3.) it is estimated that emissions of C9-C14, which are connected to the usage of C8 will decrease from 12.3 t/a to 1.4 t/a once the PFOA restriction becomes binding in 2020. But these numbers are uncertain.

There are two possible scenarios:

1)  PFOA and its related substances are used intentionally and C9-C14 PFCAs and related substances are present as part of a mixture (complements) or as unintentionally by-products (impurities)
2)  C9-C14 PFCAs, their salts and related substances are substitutes for PFOA, its salts and related substances.

In scenario 1) where PFOA is used together with  C9-C14 PFCAs (unintentionally or intentionally), the PFOA restriction will directly affect the use of C9-C14 PFCAs, their salts and related substances as well. Scenario 2) occurs when C9-C14 PFCAs their salts and related substances are used as C8- substitutes once the PFOA restrictions becomes binding. However, to date there are no indications that case 2) would actually occur , but we address this as a possible uncertainty factor since the market is not yet in equilibrium since the PFOA restriction is not fully implemented until 2020

## D. 1.1. International activities

USA

US EPA has initiated the 2010/15 PFOA Stewardship Program with eight major companies (including some European companies) which target PFOA, precursor chemicals and higher homologue chemicals. The industry committed voluntarily to reduce global facility emissions

and product content on a global basis by 95 percent no later than 2010, and to work toward eliminating emissions and product content of these chemicals by 2015. The latest report for 2013 and 2014, released in January 2015, shows that the companies were on track to reach the program's goal (US EPA, 2015).

On January 15, 2015, US EPA proposed a Significant New Use Rule (SNUR) under the Toxic Substances Control Act to require manufacturers (including importers) of some long-chain PFAS chemicals, including as part of articles, and processors of these chemicals to notify EPA at least 90 days before starting or resuming new uses of these chemicals in any article. This notification would allow EPA the opportunity to evaluate the new use and, if necessary, take action to prohibit or limit the activity. The SNUR is effective from July 15, 2016 (US EPA, 2015).

CANADA

The government of Canada prohibits manufacture, use, sale, offer for sale, import and export of the substances (C8-PFCA, as well as long-chain (C9-C20) perfluorocarboxylic acids (PFCAs) and their salts and precursors) and articles containing these substances.

In June 2006, the Government of Canada published a Notice of Action Plan for the assessment and management of perfluorocarboxylic acids and their precursors. The Action Plan included measures to prevent the introduction of new substances into Canada that would contribute to the level of PFCAs (perfluorocarboxylic acids) in the environment, and to seek action from industry to address sources of PFCAs already in Canadian commerce. To this end, a voluntary Environmental Performance Agreement was signed on March 30, 2010. Signatories to the Performance Agreement agreed to reduce the amount of PFOA and long-chain perfluorocarboxylic acids in perfluorinated chemicals in Canadian commerce by 95% by December 31, 2010, and to virtually eliminate them by December 31, 2015. Furthermore, in October 2016, the *Regulations Amending the Prohibition of Certain Toxic Substances Regulations, 2012,* were published in Canada. As of December 23, 2016, these amendments prohibit PFOA, its salts and precursors and articles containing them, unless present in manufactured items. Furthermore, the amendments provide time-limited exemptions for photo media coatings, water based inks and ongoing permitted uses for aqueous film-forming foams used in firefighting applications.

Norway

Long-chain PFCAs, including C14-C10 PFCAs were included on Norway's priority list of substances in 2014 (http://www.environment.no/List-of-Priority-Substances/). Release of substances included into the list should be eliminated by 2020.

Existing EU-legislation

To our knowledge there are yet no EU legislation that specifically regulates C9-C14-PFCAs and their related substances.

# D 1.2 Use of C9-C14 PFCA-related substances in specific applications, an example from Sweden

As mentioned above a substitution process towards fluorine free alternatives is ongoing (see Annex E.2). This substitution process is also supported by data from the Swedish Product Register. The potential importance of the PFOA restriction for the reduction of C9-C14 PFCAs is also supported by this data from the Swedish Product Register. This data concerns small volumes, which do not require REACH registration. In part it is made up of imports (but it is hard to determine to what degree, since it is not known to what degree imports (to Sweden) from another EU country in turn has been imported from a non-EU country), either of articles

or compounds used in other articles. Therefore this data complements the rest of the data collection efforts since they give an overview of the development of imports of articles containing C9-C14 PFCA (see Annex A.2.1)

These time trend examples from Sweden (see annex A.2.1) show that a substitution process or phasing out has taken place for the use of C9-C14 PFCA-related substances in several important application areas. Based on the data information apprehended during the data collection process for this dossier (see Appendix G and Annex A.2 for details) it is assumed that a similar substitution process has taken place or is under way in the rest of EU. This substitution process may be both policy driven and demand driven. The PFOA restriction, other EU – and international regulation as well as national Swedish policy measures can in combination with an increase in demand for fluorine free products by consumers, be the explanation of the downward trend which has been observed. However one interesting observation is made when C8 chemistry (PFOA and its related substances) is included in the analysis. Over all time series and for all years and all applications it seems as if all entries contain C8 chemistry.

Thus, if PFOA is intentionally used and C9-C14 PFCAs occur as unintended by-product the PFOA restriction will directly affect the use of C9-C14 PFCA as well.

It is assumed to be most probable that C8 chemistry is the essential part in these C9-C14 PFCA related substances and that these substances have already been phased out in part due to the upcoming PFOA restriction. After 2020 when the PFOA restriction becomes binding, further phasing out is anticipated. Still the use of PFOA and related substances will be ongoing for certain exempted uses. Thus, release of C9-C14 PFCA to the environment from exempted PFOA sources will still be ongoing.

Once the PFOA restriction becomes binding a substitution process towards a second best C9-C14 PFCA solution might occur. Therefore this restriction on C9-C14 PFCA is very important in closing the substitution window for C9-C14 PFCAs.


# D 1.3 PVDF-fluoropolymers

Regarding fluoropolymers and especially polyvinylidence fluoride (PVDF) 41000 t/a is produced worldwide (in thermoplastics) in the year 2015 (Kunststoffe International 10/2016) It has been reported that PVDF contains 100-200 ppm C9-PFCA (Prevedouros et al., 2006).

However we assume that a large share of the PVDF is produced with short-chain PFCAs or completely without PFCAs today. Arkema, the producer of Kynar, claims to be world market leader for PVDF with a market share of more than 40 percent and to produce without any fluorosurfactants. Other large producers like Solvay and Dyneon are members of the PFOA Stewardship Program and therefore might produce without long-chain PFCAs.

Stakeholders reported, that C9-PFCA is not used within the EU for manufacturing PVDF. This indicates that the trend for C9-PFCA in thermoplastics can be expected to decrease even if the production of thermoplastics show an increasing trend. The time trend for the use of PVDF indicates an increasing trend of 3% according to one study and of 5.1% according to another study (ReportLinker, 2016).

For use in semiconductors, wire & cable insulation and artificial membrane in biomedical science an increase in the use of PVDF from 1234 t/a to 1952 t/a is predicted by 2020. This indicates an increase in C9 of 143.6 kg/a by 2020 ceteris paribus if this restriction dossier is

not implemented. There are several possible error sources in these numbers. Both double accounting and emissions not being accounted for is possible (Market Research Store, 2016).

In sum, we do not have numbers on the European use of PVDF as a share of the world use, and how much PVDF is imported that contains C9-PFCA. It is therefore difficult to assess if the trend for C9-PFCA in imported thermoplastics is expected to increase or decrease, without the implementation of this restriction.


## D 1.4 Current use of C9-C14 PFCA and their precursors in the EU according to registrations to ECHA

During the stakeholder consultation the REACH registrations containing C9-C14 PFCAs, their salts and related substances were set inactive. The last production and use date for this user was in December 2015. Stockpiles at downstream user sites could still be in use. However, precise information was not received. Regarding the use of C9-C14 PFCAs in transported intermediates, one such use has been reported. This reported use concerned a 20 % C10 PFCA and 7, 5 % C12 PFCA, use in a C8 PFOA transport intermediate. The use of C9-C14 PFCAs in transport intermediates are however exempted from this restriction (see the summary of this report).

According to our assessment there is no active user of C9-C14 PFCAs their salts and related substances in the EU, but one active use in imports (semiconductors) (see chapter A-2 and appendix G).

There are indications that C9-C14 PFCAs, their salts and their related substances could be present in imported goods and articles. One such example is the use of PVDF for thermoplastics, described above, and one application towards semiconductors has been reported in the stakeholder consultation process. Therefore imports of articles containing C9-C14 PFCAs and their related substances is a potential concern. Articles can moreover contain C9-C14 PFCAs without the importers knowledge. Any import of articles with C9-C14 PFCAs which do occur will continue in a similar fashion if this proposed restriction is not implemented.

Stocks of C9-C14 PFCAs might also be a concern for future releases into the environment. Landfills and articles already on the market are a potential source of future C9-C14 PFCAs releases. These stock sources will to some part not be affected by this restriction because already placed on the market before the restriction entries into force (i.e. second hand articles) are excluded from the scope of the restriction proposal.


## D 1.5 BAU a short summary

In summary, the business as usual (BAU) scenario shows that unintentional use and production of C9-C14 PFCAs has been decreased in the EU, due to the shift from using C8 (PFOA) based substances to shorter chain per- and polyfluorinated substances and fluorine free alternatives. Data from the Swedish Product Register indicate that a substitution process is also under way in the EU for imported articles to a large extend. This decreasing trend is triggered by the US-EPA stewardship program, the Canadian regulation for long-chain PFASs as well as the Norwegian restriction on PFOA in consumer articles and the EU-restriction on PFOA its salts and related substances. However, there are indications that C9-C14-PFCAs, their salts and related substances may be used outside the EU, e.g. in Asia. Thus, imported goods may still contain the substances. Without the restriction these uses are expected to continue. Further, the C9-C14 PFCA related substances have been included into the proposal

for listing PFOA as a POP under the Stockholm convention. A decision is expected in 2019. The outcome of this decision cannot be foreseen today.

Moreover, it is possible that with the enforcement of the PFOA-restriction in the EU it may be possible that C9-C14 PFCAs their salts and related substances may be used as alternatives for certain uses, although there is no indication to date. Therefore, it may be possible that uses of C9-C14 PFCAs their salts and related substances may increase after 2020, without this restriction.

# Annex E: Impact Assessment

## E.1. Risk Management Options

## E.1.1. Proposed option for restriction (phase out over 18 months with excemptions)

The proposed restriction is defined as a ban on the use of C9-C14 PFCAs, their salts and related substances. This includes a restriction on the manufacturing, placing on the market and use of C9-C14 PFCAs, their salts and their related substances in the EU and the import of C9-C14 PFCAs, their salts and their related substances in articles to the EU.

C9-C14 PFCAs, their salts and related substances are manufactured as unintended fraction during the manufacturing of per- and polyfluorinated substances containing a carbon chain of less than nine carbon atoms. Thus, the use of PFOA its salts and related substances involves the unintentional use of C9-C14 PFCAs, their salts and related substances. The restriction of PFOA will enter into force in 2020. Therefore, it seems reasonable to propose a short transitional period of 18 month after entry into force. This would also avoid any substitution towards C9-C14 PFCAs once the PFOA restriction becomes binding.

Moreover, also the use of the so called C6 technology contains impurities of C9-C14 PFCAs, their salts and related substances. Thus, manufacturers of C6 technology requested a derogation for manufacturing short-chain per- and polyfluorinated substances and for transported isolated intermediates.

The restriction proposal also includes recycled material and articles made from recycled materials. In this dossier, we have demonstrated aconcern resulting from the exposure of humans and the environment to C9-C14 PFCAs, its salts and related substances. This means there is also a concern if recycled materials contain these substances. In addition, it is not only a problem with the recycled material itself. There may also be a release during its life cycle and the article itself will generate a waste.

This is in line with the Commission's regulation (EU) 2017/1000 on PFOA. As the Commission states in its detailed explanation for PFOA, 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. This, in our opinion, would also be the case for articles containing C9-C14 PFCAs, its salts and related substances. In addition (as the Commission also states for PFOA), substances with POP properties like C9-C14 PFCAs, its salts and related substances, in line with the objectives of Regulation (EC) No 850/2004, should not be recycled.

Articles placed on the market before the proposed restriction entries into force (i.e. second hand articles) are excluded from the scope. There are primarily two reasons for this:

1. The second hand market is difficult to control, in many cases this involves one single article donated or sold by one consumer to e.g. a non-profit organisation, which in turn is purchased by another consumer. It would not be practical to revoke single articles from the market.
2. To use e.g. a jacket as long as possible before it turns into waste is a sustainable management of resources.

Based on the information provided by industry, it is concluded the following thresholds are feasible for mixtures and articles placed on the market:

- 25 ppb for the sum of C9-C14 PFCAs and their salts
- 260 ppb for the sum of C9-C14 PFCA related substances

# E.1.2. Discarded restriction options (phase out over 18 months with no exemptions)

The disregarded restriction option is defined as a ban on the use of C9-C14 PFCAs, their salts and their related substances without any derogations. This implies a restriction on both manufacturing, placing on the market and use of C9-C14 PFCAs, their salts and their related substances in the EU. This includes the import of C9-C14 PFCAs, their salts and their related substances in articles to the EU. The difference between the discarded restriction option and the proposed restriction option (see above) is that the discarded restriction option lacks a time derogation for second hand (articles placed on the market before the entry into force of the restriction). See point 1 & 2 in section E.1.1. above.

This option will phase out the manufacturing, placing on the market and use of C9-C14 PFCAs, its salts, and related substances 18 months after entry into force. The phase out will cover C9-C14 PFCAs, its salts, and related substances on its own, in mixtures and articles above a content of the proposed set of thresholds. It is important that the restriction covers imported articles and imported mixtures in order to effectively reduce human and environmental exposure with C9-C14 PFCAs, its salts, and related substances. The restriction will complement the decreasing trend in the use of C9-C14 PFCAs, its salts, and related substances triggered by the US-EPA PFOA Stewardship Program (see D.1.1), the Canadian restriction on long-chain PFCAS, the Norwegian ban of PFOA in consumer articles and the EU-restriction of PFOA, its salts and related substances.

As shown in Annex B.2.4., C9-C14 PFCAs, its salts, and related substances can be found in many articles. Fluorine free alternatives are already available on the market and widely used in several branches (see chapter E.2). This option is considered as discarded since it would be very difficult to enforce the restriction on articles already placed on the market, and that this would not be proportionate.

# E.1.3. Other Union-wide risk management options than restriction

There is a potential need for managing the stock of C9-C14 PFCAs in for example landfills and other parts of the techno sphere. This is however outside the scope of this restriction (and REACH), but if such EU-wide regulatory measures where considered, it would be a complement to this restriction and not dual control.

# E.2. Alternatives

# E.2.1. Description of the use and function of the restricted substance(s)

C9-C14 PFCAs and their salts can be used as emulsifying agents for manufacturing fluoropolymers (Annex B.2.). C9-C14 PFCAs can be used for manufacturing side chain fluorinated polymers. Those polymers provide water, grease and oil repellence to treated articles, such as textiles. Some other functions are listed below.

- Wetting agents

- Levelling agents

- Impregnation

- Water and oil repellents

- Surface treatment

- Dispersants in paints

- Cleaning agents

- Anti-foaming agents

# E.2.2. Identification of potential alternative substances and techniques fulfilling the function

For most uses of C9-C14-PFCAs and related substances alternatives exist. These alternatives are often short-chain per- and polyfluorinated substances. For some uses fluorine-free alternatives are also available.

### E.2.3. Risk reduction, technical and economic feasibility, and availability of alternatives

### E.2.3.1. Assessment of fluorotelomer-based short-chain chemistry

As the fluorotelomer-based short-chain chemistry give evidence for concern (see following chapters xx) this alternative should only be used if no other alternative (e.g. fluorine-free alternatives, with potentially less environmental impact ) is available.

E.2.3.1.1. Availability of fluorotelomer-based short-chain chemistry

Short-chain fluorotelomers are available and are already being used by industry. For fluorotelomer-based products (e.g. fluorotelomer-based surfactants or polymers), which are based on n: 2 FTOH (n≥8), the shorter-chain 6:2 FTOH (CAS: 647-42-7; EC: 211-477-1) is used as an alternative.

E.2.3.1.2. Human health risks related to fluorotelomer-based short-chain chemistry

Short-chain PFASs exhibit similar effects as long-chain PFASs in laboratory animals. Common observed effects include liver toxicity, effects on lipid metabolism, haematological effects and reproductive/developmental toxicity ((Borg and Håkansson, 2012)). However, effects levels are commonly higher for short-chain PFASs. This is likely due to their shorter serum elimination half-lives in rodents as compared to long-chain PFASs though their intrinsic potencies may be similar (Gomis Ferreira et al., 2017). In addition, measured serum levels

of short-chain PFASs are generally lower than for long-chain PFASs (Berg et al., 2014; Glynn et al., 2012; Schroter-Kermani et al., 2013; Yeung et al., 2013). Altogether, the higher effect levels (NOAEL/LOAEL) of short-chain PFASs together with lower human internal exposure levels results in lower health risks for short-chain PFASs, when assessed individually. However, based on their similar biological properties as long-chain PFASs, short-chain PFASs has been assumed to act additiative with long-chain PFASs resulting in cumulative limit values for e.g. drinking water in Sweden (Glynn and Sand, 2014) and Denmark (Miljöstyrelsen, 2015).

### E.2.3.1.3. Environment risks related to alternative fluorotelomer-based short-chain chemistry

As shown in chapter B4.1.2.1 6:2 FTOH and other short-chain fluorotelomer derivate will be transformed to PFCAs containing three to five full fluorinated carbon atoms. These PFCAs are structurally very similar to the long-chain PFCAs and differ only in the number of fluorinated carbon atoms. Based on the high energy of the carbon-fluorine bond (Siegemund et al., 2000), it can be assumed that short-chain PFCAs are extremely persistent similar to the persistence of long-chain PFCAs and cannot be degraded under biotic or abiotic conditions.

It is expected that the bioaccumulation potential of PFCAs with less than seven fluorinated carbon atoms is lower compared to the long-chain PFCAs. Nevertheless, there is evidence that short-chain PFCAs are very mobile and have the potential to reach water bodies, which are of special concern regarding human exposure (e.g. groundwater and raw water for drinking water treatment) (Eschauzier et al., 2013; Gellrich et al., 2012). Due to the low adsorption potential short-chain PFCAs can only hardly be removed from the environment (Zhang et al., 2013a).

Elimination half-lives of short-chain PFAAs are non-negligible: Depending on the species, they range from a couple of hours to several days in some mammals (Chengelis et al., 2009; Gannon et al., 2011; Numata et al., 2014) including humans (Nilsson et al., 2010; Russell et al., 2013). These elimination half-lives are short in comparison with some long-chain homologues, but still of concern, as short-chain PFAAs will still remain for some time in organisms. Some short-chain PFAAs have considerable protein binding potentials (Bischel et al., 2011).

Short-chain PFCAs are known to enrich in plants due to their high water solubility and low adsorption potential, especially in the edible part of the plants (Felizeter et al., 2014; Wen et al., 2014).

The available data of short-chain PFCAs (see Table E.2- 1) indicate low toxicity to aquatic organisms (except fish toxicity of C5-PFCA). 6:2 FTOH is moderate toxic to aquatic organisms and has a notified classification as Aquatic Chronic 2.

*Table E.2- 1: Aquatic toxicity data of 6:2 FTOH and their main degradation product C4-C6-PFCAs*

| Substance | Endpoint | Result [mg/L] | Reference |
|---|---|---|---|
| 6:2 FTOH | 96h $LC_{50}$ (fish)<br>48h $LC_{50}$ (daphnia)<br>72h $ErC_{50}$ (algae) | 4.84<br>7.84<br>4.52 | Registration dossier |
| | 21d NOEC (daphnia) | 2.16 | |
| 5:3 acid | 48h $LC_{50}$ (daphnia)<br>72h $ErC_{50}$ (algae)<br>Fish not detected | >103<br>53.3 | (Hoke et al., 2012) |
| | 90d NOEC (fish)<br>21d NOEC (daphnia) | 9.14<br>1.25 | No published data |
| C4-PFCA | 48h $LC_{50}$ (daphnia)<br>48h $EC_{50}$ (daphnia) | > 100<br>5251 | (Hoke et al., 2012) |

| | Fish and algae not detected | | |
|---|---|---|---|
| C5-PFCA | 96h LC$_{50}$ (fish) <br> 48h LC$_{50}$ (daphnia) <br> 72h ErC$_{50}$ (algae) | 32 <br> >112 <br> 99.2 | (Hoke et al., 2012) |
| C6-PFCA | 96h LC$_{50}$ (fish) <br> 48h LC$_{50}$ (daphnia) <br> 72h ErC$_{50}$ (algae) <br> 48h EC$_{50}$ (daphnia) | > 99.2 <br> > 96.5 <br> > 100 <br> 1048 | (Hoke et al., 2012) <br><br><br> (Barmentlo et al., 2015) |
| | 90d NOEC (fish) <br> 21d EC10 (daphnia) | 10 <br> 737 (offspring) <br> 797 (population growth rate) | No published data <br> (Barmentlo et al., 2015) |

### E.2.2.1.4. Technical and economic feasibility of fluorotelomer-based short-chain chemistry

Many companies are already using fluorotelomer-based short-chain chemistry to manufacture fluorotelomer based product. This is an indication for the technical and economic feasibility of these alternatives. However, in general ≤ C6-based fluorotelomer chemistry is more expensive, i.e. higher volumes must be applied to achieve the same technical performance and costs of ≤ C6-based fluorotelomer products are higher. According to some stakeholders the quality/performance of C6 based products is still not as good as long-chain based products, e.g. with regard to oil repellence.

## E.2.3.2. Assessment of fluorine-free alternatives

### E.2.3.2.1. Availability of fluorine-free alternatives

Fluorine-free alternatives are available for certain uses, especially for textiles and fire-fighting foams.

As highly fluorinated substances have a number of desirable functions it is difficult to find fluorine-free alternatives that can match all of these functions. Nevertheless, in Table XX some fluorine-free alternatives are listed.

*Table E.2- 2: Fluorine-free alternatives (European Chemicals Agency, 2015a; Swedish Chemicals Agency, 2015b; UNEP, 2012; UNEP, 2015)*

| Alternative | Uses |
|---|---|
| Propylated aromatics (naphthalenes/biphenyls) | Water-repellent agents for rust prevention systems, marine paints,resins, printing inks and coatings in electrical applications. |
| Fatty alcohol polyglycol ether sulfonates | Levelling and wetting agents |
| Sulfosuccinates | Levelling and wetting agents <br> Wetting agents and dispersants in paints and the surface treatment <br> industry |
| Surface-active hydrocarbons, silicone chemicals and digital techniques | Photographic industry |
| Siloxane and silicone polymers | Impregnation of textiles, leather and carpets or surface treatment |

| | Wetting agents in the paint and ink industries |
|---|---|
| | Cleaning agents, polish and car wax |
| | Anti-foaming agents |
| Stearamidomethyl pyridine chloride | Impregnation of all-weather textiles, leather and carpets |
| Polypropylene glycol ether, amines, sulfates | Levelling and wetting agents |
| | Decorative chrome plating, etc. |
| Paraffins and waxes | Textiles and leather |
| Fatty-acid modified melamine resins | Textiles and leather |
| Fatty-acid modified polyurethane | Textiles and leather |
| Mixtures of silicones and stearamidomethyl pyridine chloride, sometimes together with carbamide (urea) and melamine resins. | Textiles and leather |
| Dendrimers | Textiles and leather |
| Reverse osmosis membrane (alternative to PTFE membrane) | Textiles and leather |
| Woven fabrics | Textiles |
| High density paper which prevents the passage of grease through it (mechanical process, without using any persistent chemical) | Paper- and food-packaging |
| Protein-based or detergent-based fire-fighting foams | Fire-fighting foam |
| Silicone-based surfactants (often used in combination with fluorosurfactants) | Fire-fighting foam |
| Hydrocarbon-based surfactants (often used in combination with fluorosurfactants) | Fire-fighting foam |
| Ceramic coating based on silicon | Cookware |
| Wetting agents in paints and inks: e.g. sulfosuccinates, silicone polymers; Water repelling agents for rust protection: e.g. Aliphatic alcohols (sulfosuccinate and fatty alcohol ethoxylates) | Coating of architectural materials (fabric, metals, stone, tiles etc.), additives in paints and coatings |
| Phosphate esters | Aviation hydraulic fluids |
| Hyperbranched hydrophobic polymers and specifically adjusted comb polymers as active components. Glycols are added as solvents and cationic surfactants in small amounts act as emulsifiers | Textile, leather, coating |
| Sulfosuccinates, for example the sodium salt of di-(2-ethylhexyl) sulfosuccinate dissolved in ethanol and water | Surfactants for the impregnation of textile fabrics, leather, carpets, rugs and upholstery and similar articles |

As no intentional use of C9-C14 PFCAs and related substances is known, these alternatives would not be described further in this report. More information is available e.g. in reports of the Swedish Chemicals Agency (Swedish Chemicals Agency, 2015b) and UNEP (UNEP, 2012; UNEP, 2015).

## E.2.3.2.2. Availability of fluorine-free alternatives for the textiles sector

During the stakeholder consultation textile manufacturers were consulted (the full report from the stakeholder consultation with the textile sector is available in Annex G). They do not use C9-C14 PFCAs intentionally, and have never done so in the EU, according to the stakeholders. They did however forward their knowledge on the ongoing substitution process from C6 (and C8) to fluorine free. We include this information as an illustrative example, but it has no bearing on our restriction case, since there are no intentionally usage of C9-C14 in textile industry (and since C6 chemistry is still allowed).

The quality of fluorine free DWR jackets is lower. Durability cannot be achieved to the same extent with alternative PFC-free systems, which provide initial water repellence but are less robust.

A manufacturer of outdoor cloths reported that DWR-textiles will be PFASs free by 2020. Already now, PFASs-free DWR-textiles are available.

Another manufacturer of outdoor cloths reported that 20% of the DW- textiles still contain C6-chemistry, but 80 % are fluorine free. For footwear and backpacks the phase out of fluorinated chemicals is slower, because of lower production volumes of fabric and leather. Thus, producing small volumes of PFASs-free material in parallel production lines is not attractive for suppliers which are usually situated outside the EU.

One stakeholder reported that some suppliers refused to apply PFASs-free laminate, because of a missing glue-effect that is provided by PFASs.

A retailer stated that currently 80% of own brands are PFASs free in the spring/summer collection 2017 and more than 90% in the autumn/winter collection. The stakeholder is aiming for 100% PFASs-free of own brands by 2018.

Stakeholders representing work wear and impregnation/professional laundries stated that to date fluorine free alternatives do not meet the requirements (water and oil repellence, chemical resistance), thus, C6-based chemistries are used.

**Substitution cost from C6 chemistry to fluorine free**

As an example the substitution costs, which arise in moving from a C6 chemistry based DWR, to fluorine free DWR is introduced. This is the only substitution costs, which was reported for fluorine free alternatives in the stakeholder consultation. This is however not the correct substitution costs when moving from C9-C14 to fluorine free, which is not available since we have no user of C9-C14 PFCAs. It is still included as an illustrative and best available example. It is here very important to notice that C6 chemistry is still an allowed alternative and this substitution cost only arise for those actors who voluntary moves to fluorine free. The rising consumer demand for fluorine free products and the environmental conscious of the outdoor industry might make this an interesting alternative for some producers despite somewhat higher costs.

Costs of fluorine free options are higher for several reasons. The amount of chemicals/additives used is higher. PFASs-free material has a higher water demand in production, because machines have to be rinsed between batches to avoid cross-contamination. The costs for this are allocated to the PFASs-free material. Also different curing temperatures and/or durations are needed. Some suppliers double the curing time for the PFASs-free material and some need to apply an extra pre-wash on the fabric. PFASs-free material shows a wider variety, with silicone based, wax, hydrocarbon and ester as basis.

Currently, the rise is 0,33-0,42 EUR (based on 1USD=0,8351 EUR, 2017-09-22) per yard of fabric, or 0,04-0,33 EUR for a backpack; for clothing, the increase is 5-20 US Cent per yard. Roughly estimated the production costs are 2.3 – 3.5 % higher for fluorine free products.

One company switched production of PFOA-based DWR coating to PFAS-free alternatives in 2011. It led to increased prices for the fabric, in 2011, about 0,06-0,18 EUR (based on 1 USD=0,8356 EUR)) were added for the fabric by the supplier, depending on the quality. Today, the cost for fluorine-free fabric is 0,03 EUR/m higher, the difference evened out. There are no differences in prices for chemicals.

Another stakeholder reported that cost rise for PFASs-free DWR, due to smaller volumes, the increase is estimated to be around 0,17-0,33 EUR/yard.

One manufacturer for shoes evaluated for which purposes per-and polyfluorinated substances are necessary and for which kind of shoes they were not important. The manufacturer shifted its whole production line and separated waterproof styles and styles where water repellence is not needed (e.g. for sandals). Now PFASs are only used for those shoes that need to meet highest demands (e.g. special work wear), whereas other articles such as sandals do not need treatment at all. PFASs-free alternatives are used for those shoes that need to be water proof. The company reported that altogether the shift in the production will not induce extra costs. Articles that do not need any impregnation are now able to be made at a lower price, whereas those where fluorine-free alternatives are used, higher prices arise. Thus, the costs for using fluorine- free alternatives are levelled out (chemical watch webinar "Lessons for Safer Chemicals in Products – PFAS", March 14, 2017).

### E.2.3.2.3. Availability of fluorine-free alternatives for the sector of firefighting foams

Fires are classified according to the burning material. Class A fires denote fires with combustible materials consisting of solid substances and Class B fires denote flammable liquid fires. In contrast to class A firefighting foams, Class B firefighting foams normally contain fluorotelomer-based surfactants. Class B firefighting foams are especially used for hydrocarbon fuel fires occurring in military, industrial, aviation, and municipal applications.

Fluorinated firefighting foams can also be used in firefighting trainings, in households and public buildings (where mostly fires of class A or B should be extinguished using portable extinguishers and trolley units). Environmental emissions are expected from open uses and from improper waste disposal (the agent has to be exchanged every 2-8 years).

As fluorine free alternatives, the following surfactants can be used in firefighting foams:

(i) Silicone-based surfactants, often used in combination with fluorosurfactants.

(ii) Hydrocarbon-based surfactants, often used in combination with fluorosurfactants.

(iii) Synthetic detergent foams, often used for forestry and high-expansion applications and for training; new products with glycols.

(iv) Protein-based foams, which are less effective for flammable liquid fuel fires and are mainly used for training but also have some marine uses.

Regarding efficiency, fluorine-free foams can require more foam and more time for fighting fire compared to foams containing PFASs. According to industry this is due to the poorer film-forming capacity. Furthermore, industry partially reported problems with viscosity, burn-back resistance and compatibility across different brands that might emerge. Fluorine-free foams can, however, be effectively applied in any class B fires except large tank fires. Certain fluorine free alternatives are also solvent free, offering better characteristics when discharged to the environment.

Swedavia AB owns and operates ten commercial airports in Sweden which cover about 90 percent of the domestic traffic and 80 percent of the international traffic. The company has used a fluorine-free fire-fighting foam for several years at the company's airports, for example at Stockholm Arlanda Airport.

The institute for fire and disaster control Heyrothsberge in Germany tested six fluorine free alcohol resistant firefighting foams and one PFAS containing foam for their ability to extinguish fires of five different polar liquids. The authors conclude that there are fluorine free foams available which show a similar performance compared with PFAS containing foams (Keutel and Koch, 2016).

# E.3. Restriction scenario (s)

# E.4.  Socio Economic Analysis (SEA)

The SEA rests on the baseline scenario described in Annex D of the restriction report. This SEA concern the restriction scenario of C9-C14 PFCAs and their related substances. The restriction covers the production, use and placing on the market of these substances as well as the import of C9-C14 PFCAs and their related substances in articles. It also covers recycled material, but issues a derogation on articles already placed on the market (i.e. second hand articles)

C9-C14 PFCAs are vPvB or PBT substances. Quantification of impacts for PBT and vPvB-substances is not possible. Instead a cost-effectiveness analysis based on emission reduction of PBT or vPvB substance and the compliance costs could be included in the assessment. The emission reduction is here seen as a proxy for the benefits (in terms of reduced risk) which can be compared to the cost per unit reduction. If possible the cost per unit of reduction can be compared to a suitable benchmark to assess the net benefit to society. In our case no current use of C9-C14 PFCA has been identified (except one case in imports). Therefore the preferable approach with a cost effectiveness analysis as the foundation where reduction of emission releases is used as a proxy for benefits in the form of risk reduction has not been possible. Since no usage of C9-C14 PFCAs and their related substances have been identified within the EU, and only one case of use in imports (semiconductors) limited economic consequences could be identified.

Nevertheless, this restriction is very important in the dossier submitter's point of view. The restriction is needed in order to prevent possible future uses which might occur when the PFOA restriction becomes binding in the EU. The vPvB or PBT properties of C9-C14 PFCAs are also an argument for this restriction. There is also a possibility that these substances are still present in imported articles, but this is regarded as an area of uncertainty since this has not been indicated in the stakeholder consultation (except one case). Unintended use in the form of impurities in production of short-chain PFCAs are also an issue.  Levels of C9-C14 PFCA have been observed in human blood and serum and levels have been seen to increase in e.g. migrating birds. In Axmon et al. 2014, Bjerregaard-Olesen et al, 2016, Gebbink et al. 2015, Gyllenhammar et al. 2015, Stubleski et al. 2016, Yeung et al. 2013, the levels of C9-C13 have been seen to increase until 2010 where the increase is seen to level out. (See chapter B.4.2.5. for details)These time trends occurs despite a decrease in the flow into the environment of C9-C14 PFCAs from industry and articles. This might be due to the very persistent and bioaccumulation properties of these vPvB and PBT substances. This leads to an increase or level out (in most cases) of the stocks in the environment despite a decrease of the flow of C9-C14 PFCAs into the environment. Over time even small flows can create large stocks when the substances are very persistent.  A restriction is therefore motivated despite small and decreasing flows into the environment.

Another benefit of this restriction on C9-C14 PFCAs and their related substances is that it may pave the way for the global restriction process on i) PFOA[7] and ii) all long-chain PFASs under the Stockholm Convention. Regarding a listing process under the Stockholm Convention this restriction in addition to the restriction on PFOA would enable the European Union and its members to set exemplary agendas for i) PFOA[1] and ii) all long-chain PFAS.

The impacts of the restrictions will be analysed with regards to its impact on the users of C9-C14 PFCAs, as well as the impact on the rest of society. Data limitations, due to the fact that only one user of C9-C14, with imported  semiconductors as application was identified (for a complete overview of the data collections efforts, which have been made, see Annex G) excludes some of the standard quantitative methods, and in most cases a qualitative approach has been taken. The user, with imported semiconductor as application have asked for a time derogation until 2023. This request has appeared very late in the process and more information have been demanded by the dossier submitters in order to assess the derogation request.

# E.4.1. Economic impacts

Since only one application towards semiconductors (imported) was reported there are also few economic consequences which have been identified. For this user more information is needed in order to assess if a time derogation is motivated. Regarding the use of PVDF-fluoropolymers for thermoplastics (see Annex A.2.2. for details) industry contacts indicated that within the EU C9-C14 PFCAs and their salts are not used anymore for PVDF manufacturing. It is however possible that some part of the industry, most certain located outside the EU can experience cost increases when transition is made to C9-C14-PFCA free production process.

C9-C14-PFCAs are manufactured unintentionally in the EU as unintended side fraction during the manufacturing of per- and polyfluorinated chemicals containing a carbon chain of less than nine carbon atoms , e.g. based on a C6- perfluorinated carbon chain. During the manufacturing of C8-based substances, the amount of C9-C14 PFCAs as impurities is higher compared with the levels in the C6-based substances. In the EU, North America and Japan, the manufacturing and use of C8-based substances has been reduced drastically during the last decade. This transition is still ongoing in other countries, such as China and Russia. There is also a possibility of intended use in imported goods, which has not yet been identified. Thus, imported articles may contain higher fractions of C9-C14 PFCAs compared with articles manufactured and treated with short chain technology (such as the C6-based chemistries) in the EU.

 Costs might occur for importers, downstream users and consumers if these articles can no longer be imported. Unless additional information is provided in the public consultation  these costs are assumed to be negligible.

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[7] PFOA has been proposed as a POP under the Stockholm Convention by the EU COM in 2015. During the POPRC 12 Meeting in 2016, C9-C20 PFCA related substances were included into this restriction proposal because they can also degrade to a small degree to PFOA.
http://chm.pops.int/Default.aspx?tabid=5171w

## E.4.1.1. Administrative costs

Some companies in the outdoor textile industry have indicated that they intend to send some of their products to independent laboratories for testing once a restriction is implemented. This is done to test the occurrence of C9-C14 PFCAs through unintended use. This will induce some costs for the companies (241 EUR is estimated for a C9-C14 PFCA test, according to Eurofins (mail contact, 2017-09-13). Part of these testing costs can most probably be shared with the testing needed to comply with the PFOA restriction. The cost for a PFOA test is estimated to be 168 EUR, and the cost for a test package for both PFOA and C9-C14 PFCAs cost 320 EUR according to Eurofins (mail contact; 2017-09-13). According to these numbers administrative costs due to testing could be 89 EUR less for a company who comply with both the PFOA restriction and the C9-C14 PFCA restriction at once. Even though it has not been implied in the data collection process by any other stakeholder it cannot be ruled out that similar testing costs might be incurred on other type of companies.

## E.4.1.2. Substitute cost

No costs of substitution have been identified since no use of C9-C14 PFCA have been identified in the EU. Unless anything else is reported further along in the stake holder consultation process, we assume that there are no substitution costs in the EU.

### E.4.1.3. Comparison with other similar PBT & vPvB, PFAS cases

In cases with other similar PBT and vPvB substances, where concentrations have reached the recommended guidance level, for example PFAS in drinking water in Sweden (from firefighting foam), it has been proven (Swedish Chemicals Agency, 2016), to be a cost effective measure to regulate these substances in beforehand rather than paying for the abatement and substitution cost afterwards. This follows from the large replacement costs for a contaminated water source, which makes the cost of regulation in beforehand much smaller than replacing the water source afterwards. We argue (for a similar hypothetical case)that it would be cost effective to regulate the use of C9-C14 PFCA and their related substances in beforehand as well rather than abating or replacing a water source if, if recommended guidance levels where to be exceeded.

## E.4.1.4. Enforcement Cost

Average enforcement costs have been identified in connection to the restriction on lead compounds in PVC (ECHA, 2016) for EU28 member state agencies to ensure compliance with EU regulation. In this report ECHA assessed the administrative cost of member states to comply with restrictions to be approximately EUR 55 600 per year. This number should only be seen as an indications of the magnitude of the enforcement costs, since a variation in costs is observed for different restrictions. It is in general believed that the enforcement costs of this restriction will be lower than on average since some of these costs can be shared with the enforcement costs associated with the PFOA restriction. An inspection and the following testing for the occurrence of both PFOA and C9-C14 PFCA in articles at the same time is cheaper than doing two separate inspections and testing procedures. Thus, part of the costs described above can already be attributed to the enforcement of the PFOA-restriction.

### E.4.1.5. Competition

It is anticipated that this restriction will have no effect at all on competition, since all companies on the common market are affected in the same way.

## E.4.2. Human health and environmental impacts

### E.4.2.1. Human health impacts

The potential harm to humans from C9-C14 PFCA follows from the PBT or vPvB properties of these substances.

There are in general two main exposure pathways for C9-C14 PFCAs to humans. Intake via food and drinking water and through exposure to house dust. No human absorption data is available but monitoring data demonstrate the presence of C9-C14 PFCAs in human blood and serum (see Appendix I). Some of these detected C9-C14 PFCA levels in human blood and serum have also been seen to increase or level out despite a decreasing time trend for the use of C9-C14 PFCAs in manufacture and production. Increasing time trends have also been observed in human breast milk. One explanation for this may be their persistent and bio accumulating properties. (see annex B.5.)

Due to their PBT and vPvB properties it is urgent to minimize the use of C9-C14 PFCAs. At date only indications of serious human health risks are documented, but since these substances persist and accumulate in humans and wildlife they may be all but impossible to remove if serious health concerns should be documented in the future. (see annex B.5.)

No monetary valuation of human health impacts has been possible since clear cause and effect relationship between C9-C14 PFCAs levels and different health impacts have not been concluded.

### E.4.2.2. Impacts to the environment

Several studies indicate an increasing time trend for C9-C14 PFCAs in the environment, from 1980 until 2010, when the increase seem to level out (see Annex B.4.2.5 for details). Increasing levels have been seen in both migratory birds, marine fish and their predators as well as in terrestrial mammals. (Axmon et al. 2014, Bjerregaard-Olesen et al, 2016, Gebbink et al. 2015, Gyllenhammar et al. 2015, Stubleski et al. 2016, Yeung et al. 2013) This indicates that C9-C14 PFCAs are spread worldwide over several types of ecosystems and that increasing or non-decreasing trends are observed at different levels of these ecosystems. At the same time flow into the environment from imported articles as well as from production and manufacturing of C9-C14 PFCAs has been seen to decrease for most application, at least at an EU-level. (see annex B.4.)

The discrepancy between the observed levels in nature (and humans) and the flow into the environment from production and manufacture application can be explained by the persistent and bio accumulating properties of C9-C14 PFCAs. The stock of the substance in the environment and in human blood and serum levels might therefore increase or level out despite a decrease of the flow of C9-C14 PFCAs into the environment. These PBT and vPvB – properties of C9-C14 PFCAs (described in detail in Annex B.8) make it important to decrease the emissions into the environment even further by the implementation of this restriction. There might also be stockpiles of C9-C14 PFCAs in for example landfills, which will continue to be a source of release of C9-C14 PFCAs despite the implementation of this restriction.

A monetary valuation of the potential decrease of C9-C14 PFCAs due to the implementation of this dossier is not possible. Standard procedure for PBT and vPvB substances is to use the reduced volumes as a proxy for the value of the reduction in terms of risk reduction. In this case no clear definition of the volumes of C9-C14 PFCAs, which might be reduced has been possible. Therefore no clear volume reduction is available to base the valuation on.

## E.4.3. Potential risk reduction capacity

The risk reduction capacity of a restriction for vPvB and PBT substances is in the standard case measured by the volume (ton per year) of the substance which is reduced by the restriction. In this case only one intentionally user (imported semiconductors) was reported by consulted stakeholders and they have not reported their use with any certainty, but indicate that only kilograms are used. It is therefore not possible to make a complete quantitative assessment of the risk reduction capacity of the restriction. Based on a qualitative assessment we do however argue that this restriction has an important risk reducing capacity in reducing the uncertain volumes which could be contained in imported goods. It is also considered important to reduce the uncertainty connected to any second best substitution which might occur once the PFOA restriction becomes binding. In an attempt to quantify the volumes for this second part connected to substitution from C8 (PFOA and its related substances) to C9-C14 (PFCAs and their related substances) we conducted a scenario analysis to create a case scenario. Based on textiles (post 2015, central estimate values) it is argued (in Annex F.3) that a possible scenario would be if 5 % of the C8 users substituted to C9-C14 instead of C6 or fluorine free alternatives. This results in a 75 ton/year risk reduction potential. Based on the same assumptions of a 5 % substitution scenario case from C8 to C9-C14 for the total (post 2015, central estimate) C8 tonnage gives a 95 ton/year C9-C14 PFCAs risk reduction potential for this restriction.

This might seem as fairly small volumes for the potential risk reduction capacity (and the calculated numbers do not include all uncertain volumes, which can potentially be included in imported articles). Nevertheless since C9-C14-PFCAs do not break down in the environment at all, even small emissions of these pollutants might create large stocks in the environment over time.

## E.4.4. Other impacts, practicability and monitorability

### E.4.4.1. Social impacts

The social impacts of the restriction on C9-C14 PFCAs and their related substances are assumed to be negligible. This follows from the fact that only one intentionally use of C9-C14 PFCAs was identified, for imports of semiconductors. For this user further information is needed in order to assess their demand for a time derogation. As is discussed in previous chapters importers of articles containing PFCAs can potentially be affected even though only one importers have been identified in the data collection process.

### E.4.4.2. Wider economic impacts

The wider economic impact are considered to be of a moderate magnitude. There might be impacts on article prices, and article quality if import of C9-C14 PFCAs in articles are identified in the public consultation. This might affect article quality, consumer prices and the importing companies. There are however only one indication that C9-C14 PFCAs are used in imported articles to an extent. It is nevertheless assumed that the risk of C9-C14 PFCA being included in imported articles without the knowledge of the importer is present. It can also be the case that C9-C14 PFCAs are included in articles but that importers have missed to report this in the public consultation process, we therefore regard this as an area of uncertainty. We cannot however assess the magnitude of this uncertainty and awaits further information through the public consultation.

It is assumed that the proposed restriction on C9-C14 PFCAs at an aggregated level will have a small but positive effect on the competeveness of EU-companies who have already substituted to PFAS- free substitutes, or short-chain alternatives, if imports using C9-C14

PFCAs turn out to be important. Since no EU companies are using C9-C14 PFCAs none will lose competiveness on export markets, compared to the BAU case. It can be assumed that the substitution by industry to shorter chain length or fluorine free alternatives is both policy and demand driven. Both the PFOA restriction, consumer demand, anticipation of a future long-chain restriction on PFCAs as well as American and Canadian policy measures might be behind this phasing out process in the EU (and few users to begin with).

This voluntary and policy driven substitution process without a time limit is less costly Ceteris Paribus. There might however be (small) quality and cost advantages for non-EU companies which may intentionally still use C9-C14 PFCAs and related substances in imports to the EU. The implementation of this restriction will equalise these potential cost and quality differences on the European market since imported articles are covered as well. But the voluntary phase-out indicates that the (net) benefit of phasing out are larger than these (potential) costs for the EU-industry. However if imports using C9-C14 PFCAs are relevant, a small but positive effect on EU competiveness will be created by the restriction, (even though it is important to state that no binding restriction hinders anyone from using C9-C14 PFCAs today).

### E.4.4.3. Distributional impacts

It is anticipated that the restriction will only have minor distributional effects. This follow from the fact that no active user of C9-C14 PFCA has been identified within the EU and only one active user have been identified for imports to the EU

### E.4.4.4. Practicality and monitorability

We argue that this restriction fulfils demand for both practicality and monitorability. Frameworks and other regulation put in place to comply with the PFOA dossier will to some extent be useful in the implementation of this restriction as well. On average we argue that the practicality and monitorability issues will be in parity with those arising in the implementation of the PFOA restriction.

#### E.4.4.4.1. Enforceability

Although there are no standard analytical methods to measure the content of C9-C14 PFCAs, their salts and related substances in articles and mixtures yet available, those methods are being developed already for the restriction of PFOA and related substances. The same methods can be applied for testing C9-C14 PFCAs and related substances.

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. Nevertheless, the establishment of an EU standard method could make the routine implementation of these tests easier, but it would also imply expenditure of time and money. At the same time the efforts for the development of such a standardized method are minimized due to the fact that there is already a standardized method (under development) for the very similar restriction of PFOS.

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 long chain perfluorinated and polyfluorinated substances in textile products that include long chain per- and polyfluorinated compounds from C7 – C14.

Articles and mixtures to be targeted by sampling for enforcement are listed in Annex A.2.4.

## E.4.4.4.2. Implementability and manageability

The proposed restriction is considered to represent an implementable option for the actors involved within the timeframe of 18 months. As described in Annex E.2. it appears that the necessary technology, techniques and alternatives are available and economically feasible. The RMO is in line with the US-EPA Stewardship Program. Thus, many industry actors are already preparing for using different substances and technologies from 2015 on.

## E.4.4.4.3 Monitorability

There are numerous analytical methods reported in the scientific literature to measure C9-C14 PFCAs and some related substances in almost all environmental media, e.g. water, air, biota, and in humans.

Furthermore, at least in Germany, there is a norm (DIN 38407-42) for analysing C9-C14 PFCAs (and other 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 unfiltered 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 C9-C14 PFCA-related substances without knowing every single substance is the conversion of these substances to the corresponding acids and subsequent analysis of C9-C14 PFCAs, for example in water samples. Oxidation can be performed with hydroxyl radicals (Houtz and Sedlak, 2012). These 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 C9-C14 PFCAs are persistent substances, which 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 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 emissions of C9-C14 PFCAs and related substances in the environment should result in decreasing C9-C14 PFCAs concentrations in such a trend monitoring. It might be sufficient to measure C9-C14 PFCAs in such a trend monitoring, because C9-C14 PFCAs related substance will be degraded to C9-C14 PFCAs 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 C9-C14 PFCAs from environmental sinks, like sediment, might bias time trend in some cases.

## E.4.4.5. Proportionality (comparison of options)

We argue that this restriction is proportionate. It has small costs (and benefits) due to the fact that only one user of C9-C14 PFCAs have been identified, (in imported semiconductors). It nevertheless has risk reducing properties which we argue outweighs the cost to society associated with the implementation of this restriction (see section E.4.3.).  It is thus anticipated that the cost-benefit ratio is either unaffected, or slightly improved.

## E.4.4.6. Comparison of Restriction Options

Only one main restriction option is analysed. This follows from the fact that only one user (imports of semiconductors) of C9-C14 PFCAs are identified. If new information is presented in the public hearing, this can be changed.

## E.4.4.7. Comparison of costs and benefits

Since we have only identified one user of C9-C14 PFCAs in the EU, for imported semiconductors there are also few costs and benefits to compare. This company still need to provide additional information in order for us to assess their request for a time derogation. We have argued that enforcement costs are lower than on average since part of these costs can be shared with the enforcement costs connected with the implementation of the PFOA restriction. The average enforcement cost of EUR 55 600 year for member states is here seen as a high estimation of these costs. Costs might also occur if C9-C14 PFCAs are included in imported articles to a large extent. We have however only been able to verify one use of C9-C14 in imports, but see this as a potential uncertainty. The benefits from the risk reducing capacity (described in section E.4.3.) of this proposed restriction are not quantifiable, but we argue that they exceed the moderate enforcement costs described above. Thus the benefit-cost ratio is either unchanged or slightly improved.

## Annex F. Assumptions, uncertainties and sensitivities

There are uncertainties and assumptions which might affect the results of this SEA. These are of different character and can potentially affect the results in different directions.

## F.1. Data collection and uses

The data collection process is an area of potential concern. No active user was identified in the EU, but one active user with regard to imports to the EU have been identified (semiconductors). Two main scenarios are possible. The first possibility is that additional users exists, but this has been missed in the data collection process. The second possibility is that no other active user exist and that this is the reason for the lack of identified users.

For the data collection process a questionnaire has been sent out to 69 chemical companies, downstream users and to relevant industrial interest organisations. For the industrial organisations it is not known how many companies they contacted through their network, but it is believed that all relevant stakeholders have been contacted either directly through the questionnaire or through the Call for Evidence process by ECHA, or through the deep interviews conducted in the data collection process. It is therefore assumed that all possible actions which with regard to proportionally can be made have been made. The combined efforts in this data collection process have however not yielded any indication of an active user, or manufacturer, of C9-C14 PFCAs and their related substances within the EU. Only one importer of articles with C9-C14 PFCAs and their related substances have  been found (semiconductors). As is described in Annex A.1.1 the REACH registrations which was found for C9-C14 PFCAs related substances, was after the deep interviews found to be inactive and the registrant had already substituted to fluorine free substitutes. For a detailed description of the data collection process, see Appendix G. Based on this data collection process we assume that the second possibility, that there are no other active user in the EU is correct. This is however something that might change if new information is made available in the final stage of the public consultation process.

## F.2. Imports

The data from the Swedish Product Register, discussed in the BAU scenario is in part made up of imports. It is however hard to verify if imports to Sweden from another EU country in turn have been imported from outside the EU by that EU country.  As seen in chapter A.2. this data shows a downward trend and indicates a total phase out for several applications. Most applications which show a positive use in 2015 also contain C8 PFOA. It is believed that most of these uses will be affected and disappear once the PFOA restriction becomes binding. It has however not been possible to verify this with certainty. It has neither been possible to verify how well this data from the Swedish Product Register represents the trend for the rest of EU.  Import is thus still regarded as a potential area of concern and uncertainty.   We believe that it is correct to await the public consultation to verify (or falsify) if the assumption about uses patterns and the economic consequences due to C9-C14 PFCAs in imported articles being negligible is correct. So far only one importer of articles containing C9-C14 PFCAs have been identified (semiconductors).

## F.3.Substitution after the C8-PFOA restriction becomes binding

The restriction on PFOA, PFOA-related substances and its salts will become binding in 2020 with the exception of certain derogations. C8 chemistry represents the preferred choice of chain length for almost all fluorinated applications due to its superior properties with regard to quality and cost. Large part of the industry has already substituted away from C8 towards

C6 or fluorine free substitutes. It is believed that the vast majority (if not all) of the remaining companies using C8 chemistry will substitute to C6 or fluorine-free alternatives. The market is however not in an equilibrium yet with regard to the substitution process away from C8 chemistry. There is therefore a small but positive possibility that some of the users of C8 chemistry will end up substituting in part to C9-C14.

An example of this is the small but positive C9-C14 PFCA related use, which has been identified through the Swedish Product Register (too small volumes to be registered in REACH). It is in the SEA assumed that these volumes in large are by-products and complements to the use of C8-chemistry. If this assumption is correct these small volumes will be phased out once the PFOA restriction becomes binding. We do however believe that there is a small but positive probability that C9-C14 PFCAs can become second best substitutes to C8 PFOA, for these volumes and that a substitution process could take place once the PFOA restriction becomes binding. It is however not possible to say with any certainty how large this substitution can become (if any).

It is nonetheless possible to exemplify what kind of volumes this substitution might lead to, by doing a scenario analysis using the data from the PFOA dossier. This is here done using textiles as an example. This is a simplified example where we assume that a possible scenario for the substitution from C8 chemistry to C9-C14 occurs when five percent of the C8 textile users choose to substitute to C9-C14 (the remaining 95 percent are assumed to substitute to C6 chemistry or to fluorine free alternatives). Since we do not have a reference point in C9-C14 substitution costs it is however not possible to quantify the magnitude of the cost that could occur if it is not possible to substitute from C8 to C9-C14 due to this restriction on C9-C14 . It is however possible to illustrate with the worst substitution cost case from the PFOA dossier. If textile industry are (economic) rational they will only substitute from C8 to C9-C14 (rather than C6 chemistry or fluorinate free) if the benefit from that substitution is positive. Thus the cost of substitution for not being able to substitute from C8 to C9-C14 is always less than the worst case of substitution cost from the PFOA dossier (under the assumption of rationality). The worst case of cost in EUR per kilo of substitution for textile for C8 to C6 chemistry or fluorinate free is EUR 35/kg. Thus we can argue that the cost of not being able to substitute to C9-C14 from C8 is always less than 35 EUR/kg if the industry act rational. In table F.3.1 below the volumes are exemplified if five percent of the C8 textile industry (post 2015 central estimate values) chooses to substitute to C9-C14. A similar argument can be made for all other uses of C8. Included in this table is therefore also an example with the total (post 2015, central estimate) volumes for C8 and the corresponding volumes for a five percent s substitution scenario towards C9-C14 for all PFOA usage. It should be noted that the five percent scenario has been chosen, based on what the writer of this restriction think is plausible. However other types of substitution patterns might be realised in reality. The only aspect that would change with other assumed percentage for substitution is the volumes affected.

*Table F.3- 1 – Substitution scenario*

|  | C8 volumes for, central estimate ton/year (post 2015). | Worst case scenario, 5% of C8 volumes substitutes to C9-C14, ton/year (post 2015). |
|---|---|---|
| Textile treatments in the EU | 300 | 15 |
| Imports of textile | 1500 | 75 |
| Total C8 tonnage | 1900 | 95 |

It is at the moment not possible to assess if second best substitution from C8 to C9-C14 might occur once the C8 restriction becomes binding. It can however be argued in a similar way, as is done in the example above for textiles that substitution to C9-C14 for other application areas will always be more cost effective than the worst case of substitution cost from the

PFOA dossier. This holds if the industry are acting (economic) rational and only substitutes if there is a net benefit to be made from that substitution. The cost measured in EUR/kg will however differ depending on the application area. For a total overview of all of these cost measures we refer to the PFOA restriction dossier.

# F.4.Environmental and health effects

There are some uncertainties with regard to the effects on the environment and human health. One such uncertainty is the cause and effect between C9-C14 PFCA levels and different health impacts. But as described in appendix E.4.2.1 and E4.2.2. these uncertainties together with the very persistent properties of C9-C14 PFCA are also a strong reason for the implementation of a restriction on C9-C14 PFCA.

# Annex G: Stakeholder information

Several consultations has been realised for gathering information on e.g. uses and alternatives. Besides consultations on national- and EU-level also international stakeholders were consulted.

*Table G- 1: Stakeholder consultations on C9-C14 PFCAs, their salts, and related substances*

| Consultation | Date | Remark |
|---|---|---|
| RMOA-consultation | May-July 2016 | Mail to importers, manufactures and downstream users of C9-C14 PFCAs, their salts, and related substances as well as concerned industry associations for circulation among their members<br>Link to consultation was available on DE-CA website (http://www.reach-clp-biozid-helpdesk.de/de/REACH/SVHC-Roadmap/DE_RMOA-Liste/DE_Stoffliste.html) |
| Expert meeting | 24 March 2017 | Meeting with stakeholders, that have responded during the RMOA-consultation |
| Stakeholder consultation by Ökopol and Swerea on behalf of UBA | November 2016-February 2017 | Invitation to survey sent  to importers, manufactures and downstream users of C9-C14 PFCAs, their salts, and related substances as well as concerned industry associations for circulation among their members<br>Promotion e.g. on UBA-REACH-website and ECHA Weekly 07 December 2016 with link to consultation website:<br>http://www.oekopol.de/themen/chemikalienpolitik/umfragen/pfca/ |
| Targeted interviews with stakeholders | March/ April 2017 | |
| Mail exchange with National Industrial Chemicals Notification and Assessment Scheme, Australia | March 2017 | |
| Conference call with certain international | 12 April 2017 | Participants of the PFAS Science and Policy Group: international scientists and regulators |

| stakeholders dealing with PFASs | | |
|---|---|---|
| Meeting with registrant | 5 May 2017 | |
| Telefone conference with one stakeholder | 11. August 2017 | |

**RMOA-consultation**

Questions:

1. Information on institute/organization/person
2. Are you manufacturer, importer and/or downstream user of the substance or its precursors/salts?
3. Which amounts of the substance or its precursors/salts do you manufacture/use per year?
4. Please describe your use/s of the substance or its precursors/salts. If possible, specify the amounts of the substance or its precursors/salts per use. Which additional uses are known to you?

**Consulted stakeholders (Ökopol)**

1. Survey

The feedback on the survey was very poor. Even though the survey has been announced via direct contact of companies and multiplication associations, ECHA as an official call for information, the REACH/CLP helpdesk in Germany, UBA reach-info website, only five responses have been filed.

2. Targeted interviews

Following the survey a targeted interview process was initiated. The focus was given to sectors that were assumed to use fluorinated compounds to a higher degree, but also other sectors were screened for potential relevance. The process was started with already available information from former consultations, internet searches and assessment of databases.

Core questions to be discussed with the stakeholders were:

- Use of C9-14 PFCAs and related substance

- Tonnage of used substance (if directly used)

- Content of substance in other substances (impurities in other substances)

      - Content

      - Amount and application of contaminated substance

- Alternatives for C9-14 PFCAs

- Economic effect of restriction (cost for substitution, loss of business/applications etc.

The main field of the interviews covered:

- Manufacture of substances themselves or similar fluorochemicals (Ökopol)

- Manufacture of fluoropolymers, especially PVDF manufacturers (Ökopol)

- Manufacture of fluorinated polymers

  - Textile water repellents (Swerea/Ökopol)

  - Paper treatment/food contact impregnation (Swerea/Ökopol)

- Furniture (Swerea)

- Direct uses of C-9-14 PFCAs and related substances

  - Fire fighting foams (Ökopol)

  - Paints and varnishes (Ökopol)

  - Cosmetics (Ökopol)

Overall 69 companies and other organisations were identified that could potentially contribute with information. Not with all of them interviews could be arranged and some provided further input in written form. Sometime no contact could be established but some information could be directly retrieved from websites or publically available documents in the internet[8]. For the fire fighting foam sector the association declared that respective substances are not in use in nor have been. So no interviews were planned as follow up. Altogether 30 companies provided information.

Neither the literature study or the survey nor the interviews indicated, that C9-C14 PFCAs and related substances are used intentionally in any sector in the EU. Also most applications that can contain these PFCAs as unintended impurities seem to be of very low relevance, as the restriction of PFOA already is a strong driver to purify such products from C8 compounds and as a side effect also remove the longer chain compounds of relevance. In other areas where a shift towards PFCAs containing a carbon chain of less than 9 carbon atoms was implemented or fluorine was completely substituted the process have been initiated to remove PFOA, also. This mean that cost for the purification of raw materials for products and/or substitution costs should not be allocated to a restriction of C9-14 PFCAs. There was no case described that mentioned substances of the current restriction proposal as a driver of such an activity. This is also true for the only direct application of one substance the C9 PFCA. All contacted market actors described this as a historical use and substitution has rather been performed in the frame of the US EPA stewardship programme. But similar to the situation for PFOA large shares of the world production of PVDF are already free of C9 and therefore a restriction could contribute to tackle potential imports that have not undergone substitution. It can be expected that market effects on the users of the PVDF are rather limited.

Other direct uses could not be identified. From a chemical and economical perspective this seems reasonable. When market actors want a very effective substance the use of C8 chemistry leads to the best results in regard to the amount of substance to be used. Use of longer chain lengths would lead to following consequences:

- Decrease of intended effect $\Rightarrow$ as a result to overcome this effect more of the chemical would be used to compensate this (the same would be true for short chain PFCAs)

- Chemical production process needs more elongation cycles[9] + purification of unintended C8 products $\Rightarrow$ This would increase the consumption of building bloc and energy, therefore a substitution by C6 or C4 would be much more process efficient

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[8] There might be some additional companies that delivered data after this reporting phase mid of May.

[9] Telomerisation undergoes chain elongations of $C_2$

In conclusion one can say there is no incentive for users to apply C9-14 PFCAs as the use of PFOA led to the optimal technical result. To use the substances as substitutes would not be economically as performance of C6 or C4 will be similar with less production efforts.
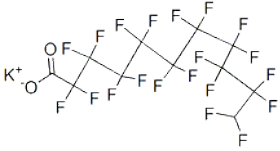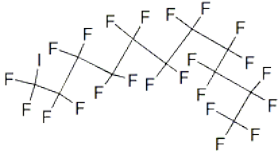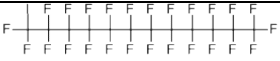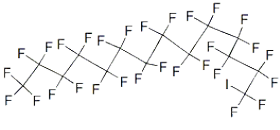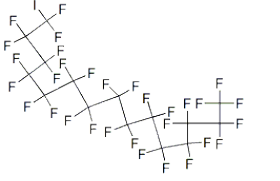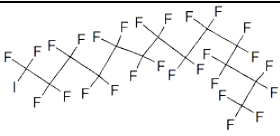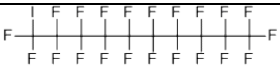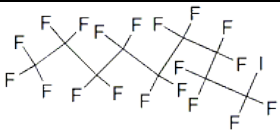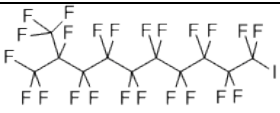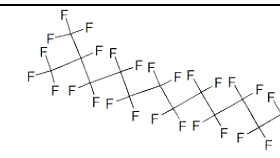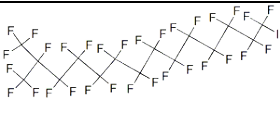
There are strong indications that in many fields the restriction of PFOA also leads to a significant reduction of other compounds that originate for the chain length distribution of the telomerisation process. So it can be expected that emissions of C10, C12 and C14 from products that contain fluorinated substances based on telomerisation products have decreased during the last years.

Overall it has to be concluded that no arguments could be found that would not legitimate the introduction of a restriction neither on the technical level nor based on socio-economic effects.

# APPENDICES:

# Appendix B.1: Examples of C9-C14 PFCA related substances
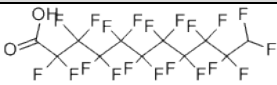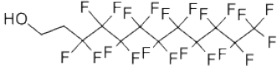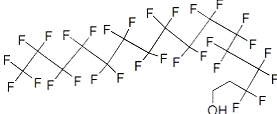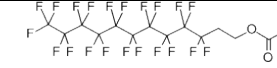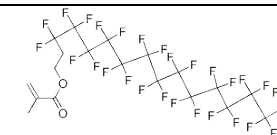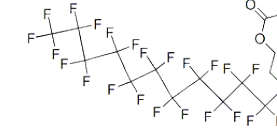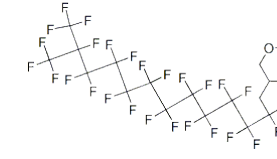
| Substance name | CAS-No. | Chemical structures |
|---|---|---|
| Fatty acids, C7-13, perfluoro (TSCA, NDSL, EINECS) | 68333-92-6 | |
| Fatty acids, C7-19, perfluoro (EINECS) | 91032-01-8 | |
| Dodecanoyl fluoride, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,12,12, 12- docosafluoro-11-(trifluoromethyl)- (TSCA) | 15811-52-6 |  |
| Dodecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,12,12, 12-docosafluoro- 11-(trifluoromethyl)- (TSCA) | 16486-96-7 |  |
| Tetradecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12, 12,13, 14,14,14-hexacosafluoro-13-(trifluoromethyl)- (TSCA) | 18024-09-4 |  |
| Dodecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,12,12, 12-docosafluoro- 11-(trifluoromethyl)-, compd. With ethanamine (1:1) (TSCA, NDSL) | 68015-87-2 | |
| Tetradecanoyl fluoride, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11, 12,12,13,14,14,14-hexacosafluoro-13- (trifluoromethyl)- (TSCA, NDSL) | 68025-62-7 |  |
| ammonium nonadecafluorodecanoate (EINECS) | 3108-42-7 |  |
| Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10- octadecafluoro-9- (trifluoromethyl)-, ammonium salt (TSCA, NDSL) | 3658-63-7 |  |
| ammonium tricosafluorododecanoate (EINECS) | 3793-74-6 |  |
| Fatty acids, C7-13, perfluoro, ammonium salts (TSCA) | 72968-38-8 | |

| | | |
|---|---|---|
| Undecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-eicosafluoro-, potassium salt (TSCA, NDSL) | 307-71-1 |  |
| **Perfluorinated halides** | | |
| Undecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-tricosafluoro-11-iodo- (ENCS) | 307-50-6 |  |
| Dodecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-pentacosafluoro-12-iodo- (TSCA, NDSL, ENCS) | 307-60-8 |  |
| Tetradecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-nonacosafluoro-14-iodo- (TSCA, NDSL, ENCS) | 307-63-1 |  |
| Pentadecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13, 14,14,15,15-hentriacontafluoro-15-iodo- (ENCS) | 335-79-5 |  |
| Tridecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-heptacosafluoro-13-iodo- (ENCS) | 376-04-5 |  |
| Decane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heneicosafluoro-10-iodo- (TSCA, NDSL, ENCS) | 423-62-1 |  |
| Nonane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-nonadecafluoro-9-iodo- (TSCA,NDSL, ENCS) | 558-97-4 |  |
| Decane, 1,1,1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-eicosafluoro-10-iodo-2-(trifluoromethyl)- (TSCA, NDSL) | 677-93-0 |  |
| Dodecane, 1,1,1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-tetracosafluoro-12-iodo-2-(trifluoromethyl)- (TSCA, NDSL) | 3248-61-1 |  |
| Tetradecane, 1,1,1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-octacosafluoro-14-iodo-2-(trifluoromethyl)- (TSCA, NDSL) | 3248-63-3 |  |
| Alkyl iodides, C6-18, perfluoro (EINECS) | 90622-71-2 | |

| | | |
|---|---|---|
| iodures d'alkyles en C6-18, perfluoro (French) (EINECS) | | |
| Polyfluorinated phosphonic and phosphinic acids | | |
| Phosphonic acid, perfluoro-C6-12-alkyl derivs. (TSCA, DSL, EINECS) | 68412-68-0 | |
| Phosphinic acid, bis(perfluoro-C6-12-alkyl) derivs. (TSCA, DSL, EINECS) | 68412-69-1 | |
| Phosphinic acid, bis(perfluoro-C6-12-alkyl) derivs., 200etrieved salts (EINECS) | 93062-53-4 | |
| Polyfluorinated carboxylic acids | | |
| Undecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11- eicosafluoro- (TSCA, NDSL, ENCS) | 1765-48-6 |  |
| Fluorotelomer alcohols | | |
| 1-Dodecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12-heneicosafluoro- (TSCA, DSL, AICS) | 865-86-1 |  |
| 1-Hexadecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14, 15,15,16,16,16-nonacosafluoro- (TSCA, DSL) | 60699-51-6 |  |
| 1-Tetradecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,14-pentacosafluoro- (TSCA, DSL, AICS) | 39239-77-5 |  |
| Polyfluorinated acrylates and methacrylates | | |
| 2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12- heneicosafluorododecyl ester (TSCA, DSL, ENCS, AICS) | 2144-54-9 |  |
| 2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13, 14,14,15,15,16,16,16-nonacosafluorohexadecyl ester (TSCA, DSL, ENCS) | 4980-53-4 |  |
| 2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13, 14,14,14-pentacosafluorotetradecyl ester (TSCA, DSL, ENCS) | 6014-75-1 |  |
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,15,15,15-tetracosafluoro-2- 200etrieve-14-(trifluoromethyl)pentadecyl acrylate (EINECS) | 16083-87-7 |  |

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| 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,14,14,14-tetracosafluoro-13-(trifluoromethyl)tetradecyl acrylate (EINECS) | 52956-82-8 | |
| 2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12-heneicosafluorododecyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,10-heptadecafluorodecyl 2-methyl-2-propenoate, methyl 2-methyl-2-propenoate,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,1 1,11,12,12,13,13,14,14,14-pentacosafluorotetradecyl 2-methyl-2-propenoate and 3,3,4,4,5,5,6,6, 7,7,8,8,8-tridecafluorooctyl 2-methyl-2-propenoate (TSCA, NDSL) | 65104-45-2 | |
| 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,12,12,12-icosafluoro-11-(trifluoromethyl) dodecyl methacrylate (EINECS) | 74256-14-7 | |
| 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,14,14,14-tetracosafluoro-13-(trifluoromethyl)tetradecyl methacrylate (EINECS) | 74256-15-8 | |
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,1 3,14,15,15,15-tetracosafluoro-2-201etrieve-14-(trifluoromethyl)pentadecyl acrylate (EINECS) | 16083-87-7 | |
| Polyfluorinated phosphates | | |
| | 1895-26-7 | |
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,13,13,1 3-icosafluoro-2-hydroxy-12-(trifluoromethyl)tridecyl dihydrogen phosphate (EINECS) | 63295-27-2 | |
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,1 3,14,15,15,15-tetracosafluoro-2-201etrieve-14-(trifluoromethyl)pentadecyl dihydrogen phosphate (EINECS) | 63295-28-3 | |

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|---|---|---|
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-2-hydroxytridecyl dihydrogen phosphate (EINECS) | 94158-70-0 |  |
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15-pentacosafluoro-2-hydroxypentadecyl dihydrogen phosphate (EINECS) | 94200-42-7 |  |
| 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-nonacosafluoro-2-hydroxyheptadecyl dihydrogen phosphate (EINECS) | 94200-43-8 |  |
| diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-2-hydroxytridecyl phosphate (EINECS) | 94200-46-1 |  |
| diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15-pentacosafluoro-2-hydroxypentadecyl phosphate (EINECS) | 94200-47-2 |  |
| diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,17-nonacosafluoro-2-hydroxyheptadecyl phosphate (EINECS) | 94200-48-3 |  |
| diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,13,13,13-icosafluoro-2-202etrieve-12-(trifluoromethyl)tridecyl phosphate (EINECS) | 94200-50-7 |  |
| diammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,15,15,15-tetracosafluoro-2-hydroxy-14-(trifluoromethyl)pentadecyl phosphate (EINECS) | 94200-51-8 |  |
| 1,1'-[oxybis[(1-methylethylene)oxy]]bis[4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15-pentacosafluoropentadecan-2-ol] (EINECS) | 93776-00-2 |  |
| Polyfluorinated iodides | | |
| Dodecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heneicosafluoro-12-iodo- (TSCA, NDSL) | 2043-54-1 |  |

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| Tetradecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11, 11,12,12- pentacosafluoro-14-iodo- (TSCA, NDSL) | 30046-31-2 |  |
| Hexadecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11, 11,12,12,13,13,14, 14-nonacosafluoro-16-iodo- (TSCA, NDSL) | 65510-55-6 |  |
| Undecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9- nonadecafluoro-11-iodo- (TSCA, NDSL) | 65510-56-7 |  |
| Alkyl iodides, C4-20, γ-ω-perfluoro (TSCA, NDSL, EINECS) | 68188-12-5 | |
| Alkyl iodides, C10-12, γ-ω-perfluoro (TSCA, NDSL) | 68390-33-0 | |
| others | | |
| bis(2- hydroxyethyl)methyl(4,4,5,5,6,6,7,7,8,8,9,9,10 ,10,11,11,12,12,13,13, 14,14,15,15,15-pentacosafluoro-2- hydroxypentadecyl)ammonium iodide (EINECS) | 93776-16-0 |  |
| [4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13, 13,13-henicosafluoro-2- hydroxytridecan-1-yl][bis(2- hydroxyethyl)]methylammonium iodide (EINECS) | 93776-17-1 |  |
| bis(2- hydroxyethyl)methyl[4,4,5,5,6,6,7,7,8,8,9,9,10 ,10,11,11,12,12,13,13,14, 15,15,15-tetracosafluoro-2-hydroxy-14- (trifluoromethyl)pentadecyl] ammonium iodide (EINECS) | 94159-76-9 |  |
| 1-[[3-(dimethylamino)propyl]amino]- 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,15- pentacosafluoropentadecan-2-ol (EINECS) | 94159-79-2 |  |
| 1-[[3-(dimethylamino)propyl]amino]- 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,13-henicosafluorotridecan-2-ol (EINECS) | 94159-80-5 |  |
| 1-[[3-(dimethylamino)propyl]amino]- 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,15,15,15-tetracosafluoro-14- (trifluoromethyl)pentadecan-2-ol (EINECS) | 94159-82-7 |  |
| 1-[[3-(dimethylamino)propyl]amino]- 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11, 12,13,13,13-icosafluoro-12- (trifluoromethyl)tridecan-1-ol (EINECS) | 94159-83-8 |  |

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| (2-carboxylatoethyl)(dimethyl)[3-[(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13, 14,14,15,15,15-pentacosafluoro-2-hydroxypentadecyl)amino]propyl] ammonium (English, French) (EINECS) | 93776-12-6 | |
| (2-carboxylatoethyl)[3-[(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-2-hydroxytridecyl)amino]propyl]dimethylammonium (English, French) (EINECS) | 93776-13-7 | |
| (2-carboxylatoethyl)(dimethyl)[[[4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13, 14,15,15,15-tetracosafluoro-2-hydroxy-14-(trifluoromethyl)pentadecyl] amino] propyl]mmonium (EINECS) | 93776-15-9 | |
| 1-[[3-(dimethylamino)propyl]amino]-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,15-pentacosafluoropentadecan-2-ol (EINECS) | 94159-79-2 |  |
| 1-[[3-(dimethylamino)propyl]amino]-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,13-henicosafluorotridecan-2-ol (EINECS) | 94159-80-5 |  |
| 1-[[3-(dimethylamino)propyl]amino]-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,15,15,15-tetracosafluoro-14-(trifluoromethyl)pentadecan-2-ol (EINECS) | 94159-82-7 |  |
| 1-[[3-(dimethylamino)propyl]amino]-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12, 13,13,13-icosafluoro-12-(trifluoromethyl)tridecan-1-ol (EINECS) | 94159-83-8 |  |
| 2-Propenoic acid, γ-ω-perfluoro-C8-14-alkyl esters (DSL, EINECS, AICS) | 85631-54-5 | |
| 2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluorododecyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-propenoate, hexadecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, octadecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11, 12,12,13,13,14,14,14-pentacosafluorotetradecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-propenoate (DSL, AICS) | 115592-83-1 | |
| 2-Propenoic acid, 2-methyl-, C10-16-alkyl esters, polymers with 2-hydroxyethyl methacrylate, Me methacrylate and γ-ω perfluoro-C8-14-alkyl acrylate (DSL) | 129783-45-5 | |

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| 2-Propenoic acid, dodecyl ester, polymers with Bu (1-oxo-2-propenyl)carbamate and γ-ω-perfluoro-C8-14-alkyl acrylate (DSL) | 144031-01-6 | |
| Amides, C7-19, α-ω-perfluoro-*N,N*-bis(hydroxyethyl) (EINECS) | 90622-99-4 | |
| 1-(carboxylatomethyl)-1-(2-hydroxyethyl)-4-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro-1-oxodecyl)piperazinium (English, French) (EINECS) | 71356-38-2 | |
| 2-Propenoic acid, perfluoro-C8-16-alkyl esters (EINECS) <br> acide propene-2 oique, esters de perfluoro-alkyles en C8-16 (French) (EINECS) <br> 2-Propensaure, Perfluor-C8-16-alkylester (German) (EINECS) <br> acido 2-propenoico, perfluoro-C8-16-alquil 205etrie (Spanish) (EINECS) | 85681-64-7 | |
| 2-Propenoic acid, 2-methyl-, C10-16-alkyl esters, polymers with 2-hydroxyethyl methacrylate, Me methacrylate and perfluoro-C8-14-alkyl acrylate (DSL) | 125328-29-2 | |
| 2*H*-Pyran, 2,2,3,3,4,4,5,5,6-nonafluorotetrahydro-6-(nonadecafluorononyl)-(TSCA, NDSL) <br> Perfluoro[6-nonyl(tetrahydro-2*H*-pyrane)] (French) (NDSL) | 68155-54-4 |  |

# Appendix B.2: Monitoring and Trends

| Substance | Compartment | Location | Sampling year | Mean concentrations/range | References |
|---|---|---|---|---|---|
| C9-PFCA | household dust | Czech Republic<br>Canada<br>USA | 2013 | 3 ng/g<br>19.4 ng/g<br>10.9 ng/g | Karásková et al., 2016 |
| | household dust | Greece, Athens<br>Spain,Catalonia<br>Sweden, Örebro, Växjö | 2013–2014<br>2009<br>2013–2014 | <0.96 ng/g–17.7 ng/g<br><0.96 ng/g–42.6 ng/g<br><0.96 ng/g–8.54 ng/g | Eriksson et al., 2015 |
| | household dust | Norway, Oslo | 2008 | 3.90–92 ng/g | Haug et al., 2011 |
| | household dust | Norway, Tromsø | 2007/2008 | 3.3–26.7 ng/g | Huber et al., 2011 |
| | household dust | Belgium, Flanders | 2008 | – | D'Hollander et al., 2010 |
| | indoor dust | Korea | 2009 | 1.5 ng/g | Tian et al., 2016 |
| | sediment | Baltic Sea | 2013-2014 | 0.178 ng/g | Gebbink et al., 2014 |
| | sediment | China | 2010-2012 | 0.01 – 0.12 ng/g | Lam et al., 2014 |
| | sediment | U.S. military installations | 2014 | 1.1 ng/g | Anderson et al., 2016 |
| | sediment | China, Liao River<br>China, Taihu Lake | 2009 | 0.02 ng/g<br>0.06 ng/g | Yang et al., 2011 |
| | sediment | German Bight (North Sea)<br>Baltic Sea | 2004-2009<br>2004-2010 | Median, 0.055 ng/g<br>Median, 0.121 ng/g | Theobald et al., 2011 |
| | dissolved phase surface water | France, lake and river water | 2012 | <0.4-30 | Munoz et al., 2015 |
| | sediment | Czech aquatic ecosystem | 2010 | 0.547 ng/g | Hloušková et al., 2013 |
| | surface soil | U.S. military installations | 2014 | 1.3 ng/g | Anderson et al., 2016 |
| | 206etrieved206 soil | U.S. military installations | 2014 | 1.5 ng/g | Anderson et al., 2016 |
| | sewage sludge | Germany, Bavarian | 2008<br>2009<br>2010<br>2011<br>2012<br>2013 | 1.4 ng/g-11 ng/g<br>0.63 ng/g-10 ng/g<br>0.31 ng/g-10 ng/g<br>0.43 ng/g-10 ng/g<br>0.23 ng/g – 10 ng/g<br>0.08 ng/g-10 ng/g | Ulrich et al., 2016 |
| | water | Baltic Sea | 2013-2014 | 0.1 ng/L | Gebbink et al., 2014 |
| | water | China | 2010-2012 | 0.08 – 2.32 ng/L | Lam et al., 2014 |
| | water | Ontario, Welland River, downstream of Hamilton Intern. Airport (several sampling points) | 2007-2010 | 0.9 – 17.3 ng/L | Solla et al., 2011 |
| | sediment | France, lake and river sediment | 2012 | <0.04-0.97 | Munoz et al., 2015 SciTotEnv |
| | water | China, Liao River<br>China, Taihu Lake | 2009 | ND<br>ND | Yang et al., 2011<br>- |
| | surface water | U.S. military installations | 2014 | 0.096 ng/g | Anderson et al., 2016 |
| | groundwater | U.S. military installations | 2014 | 0.105 ng/g | Anderson et al., 2016 |

| | groundwater | French | 2011 | 17.8 ng/L | Lopez et al., 2014 |
|---|---|---|---|---|---|
| | groundwater(sample OW1-f1) | Netherlands | 2011 | >LOQ – 0.1 ng/L | Eschauzier et al., 2013 |
| | deep-sea | Cap de Creus Canyon( CC300-1) | 2011–12 | <LOQ – 0.38 ng/L | Sanchez-Vidal et al., 2015 |
| **Biota** | zooplankton, Baltic Sea herring (Clupea harengus membras), Baltic Sea sprat (Sprattus sprattus), Baltic Sea guillemot (Uria aalge), egg, Baltic Sea | 2013-2014 | <0.05 ng/g<br><br>0.55 ng/g<br><br>0.23 ng/g<br><br>3.9 ng/g | Gebbink et al., 2014 |
| **Biota** | albatross (Phoebastria nigripes), liver, Midway Atoll albatross (Phoebastria nigripes), muscle, Midway Atoll albatross (Phoebastria nigripes), adipose tissue, Midway Atoll | 2011 | 3.42 ng/g<br><br><br>0.81 ng/g<br><br><br>0.24 ng/g | Chu et al., 2015 |
| **Biota** | several fish species, Australia | 2015 | <0.1 ng/g | Taylor et al., 2016 |
| **Biota** | Phytoplankton, Korean<br>Micro-zooplankton, Korean<br>Meso-zooplankton, Korean Crucian carp (Carassius auratus), blood, Korean Crucian carp (Carassius auratus), liver, Korean Mandarin fish (Siniperca scherzeri), blood, Korean Mandarin fish (Siniperca scherzeri), liver, Korean | 2010-2012 | 0.43 ng/g<br><br>0.2 ng/g<br><br>0.25 ng/g<br><br>1.46 ng/g<br><br>0.07 ng/g<br><br>0.21 ng/g<br><br>ND | Lam et al., 2014 |
| **Biota** | European Honey samples | 2006-2012 | ND – 0.253 | Surma et al., 2016 |
| **Biota** | Minke whales (Balaenoptera acutorostrata) (immature males), liver, Korean Long-beaked dolphins (Delphinus capensis) (mature males), liver, Korean | 2006 | 1.9  - 2.1 ng/g<br><br><br><br>7.1 – 9.4 ng/g | Moon et al., 2010 |
| **Biota** | snapping turtles (Chelydra plasma, Canada amphipod(Gammarus or Hyalella), Ontario damselfly nymph (suborder Zygoptera), Ontario shrimp (infraorder Caridea), Ontario sunfish (Centrarchidae spp.), Ontario bullhead (Ameiurus spp.), Ontario turtle (Chelydra), plasma, Ontario | 2007-2010 | <0.1  - 0.6 ng/g<br><br>7 – 65.51  ng/g<br><br>5.08 ng/g<br><br>0.78 – 3.89 ng/g<br><br>3.76 ng/g<br><br>10.82 ng/g<br><br>0.1 ng/g | Solla et al., 2011 |
| **Biota** | crocodile (Crocodylus niloticus), plasma, South Africa | 2012-2013 | 0.366  - 0.477 ng/g | Christie et al., 2016 |
| **Biota** | several fish species, USA | 2002/2003 | < 0.5  - 4.3 ng/g | Houde et al., 2006 |
| | bottlenose dolphin, South Carolina USA | 2004 | 79 ng/g | |

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|---|---|---|---|---|---|
| | | several fish species, Florida USA | | < 0.5 ng/g | |
| | | bottlenose dolphin, Florida USA | | 13 ng/g | |
| **Biota** | | different fish species, Canada | 2001 | 0.8 – 57 ng/g | Martin et al., 2004 |
| **Biota** | | Penguin, dung, Antarctic | 2010 | 2.128 ng/g | Llorca et al., 2012 |
| | | Penguin, tissue, Antarctic | | 0.31 ng/g | |
| | | Fish, skin, South America | | 2.815 ng/g | |
| | | Fish, liver,South America | | < LOQ | |
| | | Fish, muscle, South America | | 0.37 ng/g | |
| | | Fish, roe, South America | | 1.67 ng/g | |
| **Biota** | | Beaver, liver, Poland | 2003 | 0.24 ng/g | Falandysz et al., 2007 |
| | | Cod, blood, Poland | | 1.2 ng/L | |
| | | Velvet scoter, blood, Poland | | 1 ng/L | |
| | | Eider duck, blood, Poland | | 0.4 ng/L | |
| | | Long-tailed duck, blood, Poland | | 0.59 ng/L | |
| | | Red-throated diver, blood, Poland | | 1.1 ng/L | |
| | | Razorbill, blood, Poland | | 0.25 ng/L | |
| **Biota** | | Arctic Fox, liver, Norwegen | 2010-2012 | 14 ng/g | Aas et al., 2014 |
| | | Arctic Fox, blood, Norwegen | | 3.8 ng/g | |
| | | Arctic Fox, kidney, Norwegen | | 1.9 ng/g | |
| | | Arctic Fox, adipose, Norwegen | | 0.33 ng/g | |
| | | Arctic Fox, muscle, Norwegen | | 0.41 ng/g | |
| **Biota** | | wild boar, liver,Germany | 2011-2012 | 8.7 ng/g | Klei et al., 2016 |
| **Biota** | | Common kestrel, eggs, Sweden | 2014 | 0.52 ng/g | Eriksson et al., 2016 |
| | | Tawny owl, eggs, Sweden | 2014 | 0.33 ng/g | |
| | | Osprey, eggs, Sweden | 2013 | 1.5 ng/g | |
| | | Osprey, eggs, Sweden | 2008-2009 | 1.1 ng/g | |
| | | Osprey, eggs, Sweden | 1997-2001 | 0.88 ng/g | |
| **Biota** | | Fox (V. vulpes), Germany | 2013 | 1.7 ng/g | Riebe et al., 2015 |
| | | Chamois (R. rupicapra), Germany | | 2 ng/g | |
| **Biota** | | Wild boar (S. scrofa), Germany | 2010 | 2.6 ng/g | Stahl et al., 2012 |
| **Biota** | | Roe deer (C. capreolus), Germany | 2010 | 1.3 ng/g | Falk et al., 2012 |
| **Biota** | | wastewater treatment plant A influent, Greece, Athen | 2009-2011 | 1.2 ng/L | Avaniti et al., 2011 |
| | | wastewater treatment plant A effluent, Greece, Athen | | 2.3 ng/L | |
| | | wastewater treatment plant B influent, Greece, Mytilene | | <LOQ | |
| | | wastewater treatment plant B effluent, Greece, Mytilene | | <LOD | |

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|---|---|---|---|---|---|
| C10-PFCA | household dust | Czech Republic | 2013 | 5.2 ng/g | Karásková et al., 2016 |
| | | Canada | | 8.5 ng/g | |
| | | USA | | 6.9 ng/g | |

| C10-PFCA | household dust | Greece, Athens | 2013–2014 | <1.85 ng/g–20.6 ng/g | Eriksson et al., 2015 |
|---|---|---|---|---|---|
| | | Spain,Catalonia | 2009 | 2.12 ng/g–80.6 ng/g | |
| | | Sweden, Örebro, Växjö | 2013–2014 | <1.8 ng/g5–35.1 ng/g | |
| C10-PFCA | household dust | Norway, Oslo | 2008 | 1.1 ng/g–12.0 ng/g | Haug et al., 2011 |
| C10-PFCA | household dust | Norway, Tromsø | 2007/2008 | 2 ng/g–10.5 ng/g | Huber et al., 2011 |
| C10-PFCA | household dust | Belgium, Flanders | 2008 | – | D'Hollander et al., 2010 |
| C10-PFCA | indoor dust | Korea | 2009 | 2.2 ng/g | Tian et al., 2016 |
| C10-PFCA | sediment | Baltic Sea | 2013-2014 | 0.129 ng/g | Gebbink et al., 2014 |
| C10-PFCA | sediment | China | 2010-2012 | 0.01 - 0.05 ng/g | Lam et al., 2014 |
| C10-PFCA | sediment | U.S. military installations | 2014 | 1.9 ng/g | Anderson et al., 2016 |
| C10-PFCA | sediment | China, Liao River | 2009 | 0.1 ng/g | Yang et al., 2010 |
| C10-PFCA | | China, Taihu Lake | 2009 | 0.06 ng/g | |
| C10-PFCA | sediment | German Bight (North Sea) | 2004-2009 | Median, 0.064 ng/g | Theobald et al., 2011 |
| C10-PFCA | | Baltic Sea | 2004-2010 | Median, 0.066 ng/g | |
| C10-PFCA | sediment | Czech aquatic ecosystem | 2010 | 2.01 ng/g | Hloušková et al., 2013 |
| C10-PFCA | sediment | France, lake and river sediment | 2012 | <0.005-2.4 | Munoz et al., 2015 SciTotEnv |
| C10-PFCA | surface soil | U.S. military installations | 2014 | 0.98 ng/g | Anderson et al., 2016 |
| C10-PFCA | soil | U.S. military installations | 2014 | 1.4 ng/g | Anderson et al., 2016 |
| C10-PFCA | sewage sludge | Germany, Bavarian | 2008 | 9.2 ng/g-16 ng/g | Ulrich et al., 2016 |
| | | | 2009 | 6.9 ng/g-14 ng/g | |
| | | | 2010 | 4.3 ng/g-12 ng/g | |
| | | | 2011 | 3.4 ng/g-12 ng/g | |
| | | | 2012 | 2.8 ng/g-11 ng/g | |
| | | | 2013 | 1.3 ng/g-11 ng/g | |
| C10-PFCA | dissolved phase surface water | France, lake and river water | 2012 | <0.07-10 | Munoz et al., 2015 SciTotEnv |
| C10-PFCA | water | Baltic Sea | 2013-2014 | 0.015 ng/L | Gebbink et al., 2014 |
| C10-PFCA | water | China | 2010-2012 | 0.02 – 2.13 ng/L | Lam et al., 2014 |
| C10-PFCA | water | Ontario, Tyneside Road | 2007-2011 | <0.25 ng/L | Solla et al., 2011 |
| C10-PFCA | water | China, Liao River | 2009 | ND | Yang et al., 2011 |
| C10-PFCA | | China, Taihu Lake | | ND | |
| C10-PFCA | surface water | U.S. military installations | 2014 | 0.67 ng/g | Anderson et al., 2016 |
| C10-PFCA | groundwater | U.S. military installations | 2014 | 0.023 ng/g | Anderson et al., 2016 |
| C10-PFCA | groundwater | French | 2011 | 13.4 ng/L | Lopez et al., 2014 |
| C10-PFCA | **Biota** | zooplankton, Baltic Sea | 2013-2014 | 0.0014 ng/g | Gebbink et al., 2014 |
| | | herring (Clupea harengus membras), Baltic Sea | | 0.25 ng/g | |
| | | sprat (Sprattus sprattus), Baltic Sea | | 0.16 ng/g | |
| | | guillemot (Uria aalge), egg, Baltic Sea | | 6.8 ng/g | |
| C10-PFCA | **Biota** | albatross (Phoebastria nigripes), liver, Midway Atoll | 2011 | 2.97 ng/g | Chu et al., 2015 |
| | | albatross (Phoebastria nigripes), muscle, Midway Atoll | | 0.73 ng/g | |
| | | albatross (Phoebastria nigripes), adipose, Midway Atoll | | 0.27 ng/g | |

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|---|---|---|---|---|---|
| C10-PFCA | **Biota** | Several fish species, Australia | 2015 | <0.5 ng/g | Taylor et al., 2016 |
| C10-PFCA | **Biota** | Phytoplankton, Korean | 2010-2012 | 0.1 ng/g | Lam et al., 2014 |
| | | Micro-zooplankton, Korean | | ND | |
| | | Meso-zooplankton, Korean | | ND | |
| | | Crucian carp (Carassius auratus), blood, Korean | | 5.15 ng/g | |
| | | Crucian carp (Carassius auratus), liver, Korean | | 0.75 ng/g | |
| | | Mandarin fish (Siniperca scherzeri), blood, Korean | | 12.2 ng/g | |
| | | Mandarin fish (Siniperca scherzeri), liver, Korean | | 1.68 ng/g | |
| C10-PFCA | **Biota** | European Honey samples | 2006-2012 | ND – 0.278 ng/g | Surma et al., 2016 |
| C10-PFCA | **Biota** | Minke whales (Balaenoptera acutorostrata) (immature males), liver, Korean | 2006 | 8.3 ng/g | Moon et al., 2010 |
| | | Minke whales (Balaenoptera acutorostrata) (mature males), liver, Korean | | 11 ng/g | |
| | | Minke whales (Balaenoptera acutorostrata) (immature females), liver,Korean | | 7.7 ng/g | |
| | | Long-beaked dolphins (Delphinus capensis) (mature males), liver, Korean | | 11 ng/g | |
| | | Long-beaked dolphins (Delphinus capensis)(mature females), liver | | 9.7 ng/g | |
| C10-PFCA | **Biota** | snapping turtles (Chelydra), plasma, Canada | 2007-2010 | 1.2 – 4.5 ng/g | Solla et al., 2011 |
| | | amphipod(Gammarus or Hyalella), Ontario | | 3.6 – 51.9 ng/g | |
| | | damselfly nymph (suborder Zygoptera), Ontario | | 1.31 ng/g | |
| | | shrimp (infraorder Caridea), Ontario | | 0.39 – 1.18 ng/g | |
| | | sunfish (Centrarchidae spp.), Ontario | | 4.85 ng/g | |
| | | bullhead (Ameiurus spp.), Ontario | | 11.64 ng/g | |
| | | turtle (Chelydra), plasma, Ontario | | 2 ng/g | |
| C10-PFCA | **Biota** | crocodile (Crocodylus niloticus), plasma, South Africa | 2012-2013 | 0.226 – 3.4 ng/g | Christie et al., 2016 |
| C10-PFCA | **Biota** | several fish species, South Carolina USA | 2002/2003 | 1.5 – 5.5 ng/g | Houde et al., 2006 |
| | | bottlenose dolphin, South Carolina USA | 2004 | 160 ng/g | |
| | | several fish species, Florida USA | | < 0.8 ng/g | |
| | | bottlenose dolphin, Florida USA | | 19 ng/g | |
| C10-PFCA | **Biota** | several fish species, Canada | 2001 | 1.3 – 32 ng/g | Martin et al., 2004 |
| C10-PFCA | **Biota** | Penguin, dung, Antarctic | 2010 | < LOD | Llorca et al., 2012 |
| | | Penguin, tissue, Antarctic | | < LOD | |
| | | Fish, skin, South America | | 0.5 ng/g | |
| | | Fish, liver, South America | | 0.22 ng/g | |

| | | Fish, muscle, South America | | < LOQ | |
|---|---|---|---|---|---|
| | | Fish, roe, South America | | < LOD | |
| C10-PFCA | **Biota** | Beaver, liver, Poland | 2003 | 0.17 ng/g | Falandysz et al., 2007 |
| | | Cod, blood, Poland | | 0.95 ng/L | |
| | | Velvet scoter, blood, Poland | | 0.18 ng/L | |
| | | Eider duck, blood, Poland | | 0.11 ng/L | |
| | | Long-tailed duck, blood, Poland | | 0.15 ng/L | |
| | | Red-throated diver, blood, Poland | | 0.55 ng/L | |
| | | Razorbill, blood, Poland | | 0.35 ng/L | |
| C10-PFCA | **Biota** | Arctic Fox, Norway (several tissues) | 2010-2012 | n.d. – 4.15 ng/g | Aas et al., 2014 |
| C10-PFCA | **Biota** | wild boar, liver, Germany | 2011-2012 | 7.3 ng/g | Klei et al., 2016 |
| C10-PFCA | **Biota** | Common kestrel, eggs, Sweden | 2014 | 0.9 ng/g | Eriksson et al., 2012 |
| | | Tawny owl, eggs, Sweden | 2014 | 0.86 ng/g | |
| | | Osprey, eggs, Sweden | 2013 | 7.5 ng/g | |
| | | Osprey, eggs, Sweden | 2008-2009 | 7.6 ng/g | |
| | | Osprey, eggs, Sweden | 1997-2001 | 3.2 ng/g | |
| C10-PFCA | **Biota** | Fox (V. vulpes), Germany | 2013 | 2.4 ng/g | Riebe et al., 2015 |
| | | Chamois (R. rupicapra), Germany | | <1.0 | |
| C10-PFCA | **Biota** | Wild boar (S. scrofa), Germany | 2010 | - | Stahl et al., 2012 |
| C10-PFCA | **Biota** | Roe deer (C. capreolus), Germany | 2010 | 0.4 ng/g | Falk et al., 2012 |
| C10-PFCA | **Biota** | wastewater treatment plant A influent, Greece, Athen | 2009-2011 | 1 ng/L | Avaniti et al., 2011 |
| | | wastewater treatment plant A effluent, Greece, Athen | | 3.1 ng/L | |
| | | wastewater treatment plant B influent, Greece, Mytilene | | 5.6 ng/L | |
| | | wastewater treatment plant B effluent, Greece, Mytilene | | <LOD | |

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|---|---|---|---|---|---|
| C11-PFCA | household dust | Czech Republic | 2013 | 4.3 ng/g | Karásková et al., 2016 |
| | | Canada | | 8.7 ng/g | |
| | | USA | | 3.6 ng/g | |
| C11-PFCA | household dust | Greece, Athens | 2013–2014 | 0.72 ng/g–7.88 ng/g | Eriksson et al., 2015 |
| | | Spain,Catalonia | 2009 | <0.42 ng/g–33.4 ng/g | |
| | | Sweden, Örebro, Växjö | 2013–2014 | <0.42 ng/g–6.08 ng/g | |
| C11-PFCA | household dust | Norway, Oslo | 2008 | – | Haug et al., 2011 |
| C11-PFCA | household dust | Norway, Tromsø | 2007/2008 | 0.9–322 ng/g | Huber et al., 2011 |
| C11-PFCA | household dust | Belgium, Flanders | 2008 | – | D'Hollander et al., 2010 |
| C11-PFCA | indoor dust | Korea | 2009 | 1.3 ng/g | Tian et al., 2016 |
| C11-PFCA | sediment | Baltic Sea | 2013-2014 | 0.128 ng/g | Gebbink et al., 2014 |
| C11-PFCA | sediment | China | 2010-2012 | 0.03 – 0.06 ng/g | Lam et al., 2014 |
| C11-PFCA | sediment | U.S. military installations | 2014 | 1.6 ng/g | Anderson et al., 2016 |
| C11-PFCA | sediment | China, Liao River | 2009 | 0.02 ng/g | Yang et al., 2011 |
| C11-PFCA | | China, Taihu Lake | | 0.07 ng/g | |
| C11-PFCA | sediment | Czech aquatic ecosystem | 2010 | 1.56 ng/g | Hloušková et al., 2013 |

| C11-PFCA | sediment | France, lake and river sediment | 2012 | <0.01-2,6 | Munoz et al., 2015 SciTotEnv |
|---|---|---|---|---|---|
| C11-PFCA | surface soil | U.S. military installations | 2014 | 0.798 ng/g | Anderson et al., 2016 |
| C11-PFCA | soil | U.S. military installations | 2014 | 1.15 ng/g | Anderson et al., 2016 |
| C11-PFCA | water | Baltic Sea | 2013-2014 | 0.0025 ng/L | Gebbink et al., 2014 |
| C11-PFCA | water | China | 2010-2012 | n.d. – 0.59 ng/L | Lam et al., 2014 |
| C11-PFCA | water | Ontario, Tyneside Road | 2007-2011 | <0.25 ng/L | Solla et al., 2011 |
| C11-PFCA | water | China, Liao River | 2009 | ND | Yang et al., 2011 |
| C11-PFCA | | China, Taihu Lake | | ND | |
| C11-PFCA | surface water | U.S. military installations | 2014 | 0.021 ng/g | Anderson et al., 2016 |
| C11-PFCA | dissolved phase surface water | France, lake and river water | 2012 | <0.05-13 | Munoz et al., 2015 SciTotEnv |
| C11-PFCA | groundwater | U.S. military installations | 2014 | 0.025 ng/g | Anderson et al., 2016 |
| C11-PFCA | groundwater | French | 2011 | 15 ng/L | Lopez et al., 2014 |
| C11-PFCA | **Biota** | zooplankton, Baltic Sea<br><br>herring (Clupea harengus membras), Baltic Sea<br><br>sprat (Sprattus sprattus), Baltic Sea<br><br>guillemot (Uria aalge), egg, Baltic Sea | 2013-2014 | <0.008 ng/g<br><br>0.55 ng/g<br><br>0.41 ng/g<br><br>21 ng/g | Gebbink et al., 2014 |
| C11-PFCA | **Biota** | albatross (Phoebastria nigripes), liver, Midway Atoll<br>albatross (Phoebastria nigripes), muscle, Midway Atoll<br>albatross (Phoebastria nigripes), adipose, Midway Atoll | 2011 | 13.96 ng/g<br><br>4.81 ng/g<br><br>1.46 ng/g | Chu et al., 2015 |
| C11-PFCA | **Biota** | several fish species, Australia | 2015 | <0.5 ng/g | Taylor et al., 2016 |
| C11-PFCA | **Biota** | Phytoplankton, Korean<br>Micro-zooplankton, Korean<br>Meso-zooplankton, Korean<br>Crucian carp (Carassius auratus), blood, Korean<br>Crucian carp (Carassius auratus), liver, Korean<br>Mandarin fish (Siniperca scherzeri), blood, Korean<br>Mandarin fish (Siniperca scherzeri), liver, Korean | 2010-2012 | 0.13 ng/g<br>0.17 ng/g<br>0.1 ng/g<br>7.11 ng/g<br>0.8 ng/g<br>20.32 ng/g<br>4.53 ng/g | Lam et al., 2014 |
| C11-PFCA | **Biota** | Minke whales (Balaenoptera acutorostrata) (immature males), liver, Korean<br>Long-beaked dolphins (Delphinus capensis) (mature males), liver, Korean | 2006 | 40 – 69 ng/g<br><br><br>50 – 52 ng/g | Moon et al., 2010 |
| C11-PFCA | **Biota** | snapping turtles (Chelydra), plasma, Canada<br>amphipod(Gammarus or Hyalella), Ontario<br>damselfly nymph (suborder Zygoptera), Ontario<br>shrimp (infraorder Caridea), Ontario | 2007-2010 | 0.8 – 3.6 ng/g<br><br>1.1 – 49  ng/g<br><br>0.35 ng/g<br><br>0.5 ng/g | Solla et al., 2011 |

| | | shrimp (infraorder Caridea), Ontario | | 0.07 ng/g | |
| | | sunfish (Centrarchidae spp.), Ontario | | 1.33 ng/g | |
| | | bullhead (Ameiurus spp.), Ontario | | 5.26 ng/g | |
| | | turtle (Chelydra), plasma, Ontario | | 1.6 ng/g | |
| C11-PFCA | **Biota** | crocodile (Crocodylus niloticus), plasma, South Africa | 2012-2013 | 0.163 – 2.19 ng/g | Christie et al., 2016 |
| C11-PFCA | **Biota** | several fish species, South Carolina USA | 2002/2003 | 3.1 – 6.2 ng/g | Houde et al., 2006 |
| | | bottlenose dolphin, South Carolina USA | 2004 | 132 ng/g | |
| | | several fish species, Florida USA | | < 0.8 ng/g | |
| | | bottlenose dolphin, Florida USA | | 33 ng/g | |
| C11-PFCA | **Biota** | several fish species, Canada | 2001 | 1.3 – 41 ng/g | Martin et al., 2004 |
| C11-PFCA | **Biota** | Penguin, dung, Antarctic | 2010 | <LOQ | Llorca et al., 2012 |
| | | Penguin, tissue, Antarctic | | 0.09 ng/g | |
| | | Fish, skin, Südamerika | | < LOQ | |
| | | Fish, liver, Südamerika | | < LOQ | |
| | | Fish, muscle, Südamerika | | < LOQ | |
| | | Fish, roe, Südamerika | | < LOQ | |
| C11-PFCA | **Biota** | Arctic Fox, Norway (different tissues) | 2010-2012 | 0.09 – 5.2 ng/g | Aas et al., 2014 |
| C11-PFCA | **Biota** | Wildschwein, liver, Ingolstadt | 2011-2012 | 6.6 ng/g | Klei et al., 2016 |
| C11-PFCA | **Biota** | Common kestrel, eggs, Schweden | 2014 | 1.4 ng/g | Eriksson et al., 2016 |
| | | Tawny owl, eggs, Schweden | 2014 | 1.3 ng/g | |
| | | Osprey, eggs, Schweden | 2013 | 10.3 ng/g | |
| | | Osprey, eggs, Schweden | 2008-2009 | 11.3 ng/g | |
| | | Osprey, eggs, Schweden | 1997-2001 | 5.1 ng/g | |
| C11-PFCA | **Biota** | wastewater treatment plant A influent, Greece, Athen | 2009-2011 | 2.5 ng/L | Avaniti et al., 2011 |
| | | wastewater treatment plant A effluent, Greece, Athen | | 5.9 ng/L | |
| | | wastewater treatment plant B influent, Greece, Mytilene | | 9.4 ng/L | |
| | | wastewater treatment plant B effluent, Greece, Mytilene | | 2.1 ng/L | |

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|---|---|---|---|---|---|
| C12-PFCA | household dust | Czech Republic | 2013 | 2.5 ng/g | Karásková et al., 2016 |
| | | Canada | | 6.3 ng/g | |
| | | USA | | 2 ng/g | |
| C12-PFCA | household dust | Greece, Athens | 2013–2014 | 1.09 ng/g–8.01 ng/g | Eriksson et al., 2015 |
| | | Spain,Catalonia | 2009 | 1.04 ng/g–59.7 ng/g | |
| | | Sweden, Örebro, Växjö | 2013–2014 | 0.58 ng/g–17.4 ng/g | |
| C12-PFCA | household dust | Norway, Oslo | 2008 | 1.40 ng/g–78 ng/g | Haug et al., 2011 |
| C12-PFCA | household dust | Norway, Tromsø | 2007/2008 | 0.2 ng/g–3 ng/g | Huber et al., 2011 |
| C12-PFCA | household dust | Belgium, Flanders | 2008 | – | D'Hollander et al., 2010 |
| C12-PFCA | indoor dust | Korea | 2009 | 1.2 ng/g | Tian et al., 2016 |

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|---|---|---|---|---|---|
| C12-PFCA | sediment | Baltic Sea | 2013-2014 | 0.081 ng/g | Gebbink et al., 2014 |
| C12-PFCA | sediment | China | 2010-2012 | 0.03 – 0.09 ng/g | Lam et al., 2014 |
| C12-PFCA | sediment | U.S. military installations | 2014 | 2.8 ng/g | Anderson et al., 2016 |
| C12-PFCA | sediment | China, Liao River | 2009 | 0.01 ng/g | Yang et al., 2011 |
| C12-PFCA | | China, Taihu Lake | | 0.03 ng/g | |
| C12-PFCA | sediment | Czech aquatic ecosystem | 2010 | 1.26 ng/g | Hloušková et al., 2013 |
| C12-PFCA | sediment | France, lake and river sediment | 2012 | <0.06-1.9 | Munoz et al., 2015 SciTotEnv |
| C12-PFCA | surface soil | U.S. military installations | 2014 | 1.95 ng/g | Anderson et al., 2016 |
| C12-PFCA | soil | U.S. military installations | 2014 | 2.4 ng/g | Anderson et al., 2016 |
| C12-PFCA | sewage sludge | Germany, Bavarian | 2008 | 2.5 ng/g-12 ng/g | Ulrich et al., 2016 |
| | | | 2009 | 2.1 ng/g-11 ng/g | |
| | | | 2010 | 1.4 ng/g-11 ng/g | |
| | | | 2011 | 0.89-11 ng/g | |
| | | | 2012 | 0.34 ng/g-10 ng/g | |
| | | | 2013 | 0.24 ng/g-10 ng/g | |
| C12-PFCA | water | Baltic Sea | 2013-2014 | <0.04 ng/L | Gebbink et al., 2014 |
| C12-PFCA | water | China | 2010-2012 | n.d. – 0.21 ng/L | Lam et al., 2014 |
| C12-PFCA | water | Ontario, Tyneside Road | 2007-2011 | <0.25 ng/L | Solla et al., 2011 |
| C12-PFCA | water | China, Liao River | 2009 | ND | Yang et al., 2011 |
| | | China, Taihu Lake | | 0.6 ng/L | |
| C12-PFCA | surface water | U.S. military installations | 2014 | 0.058 ng/g | Anderson et al., 2016 |
| C12-PFCA | dissolved phase surface water | France, lake and river water | 2012 | <0.7 - 0.94 | Munoz et al., 2015 SciTotEnv |
| C12-PFCA | groundwater | U.S. military installations | 2014 | 0.022 ng/g | Anderson et al., 2016 |
| C12-PFCA | groundwater | French | 2011 | 18.8 ng/L | Lopez et al., 2014 |
| C12-PFCA | **Biota** | zooplankton, Baltic Sea herring (Clupea harengus membras), Baltic Sea sprat (Sprattus sprattus), Baltic Sea guillemot (Uria aalge), egg, Baltic Sea | 2013-2014 | 0.0072 ng/g 0.13 ng/g 0.094 ng/g 5.9 ng/g | Gebbink et al., 2014 |
| C12-PFCA | **Biota** | albatross (Phoebastria nigripes), liver, Midway Atoll albatross (Phoebastria nigripes), muscle, Midway Atoll albatross (Phoebastria nigripes), adipose, Midway Atoll | 2011 | 2.54 ng/g 0.99 ng/g 0.28 ng/g | Chu et al., 2015 |
| C12-PFCA | **Biota** | several fish species, Australia | 2015 | <0.5 ng/g | Taylor et al., 2016 |
| C12-PFCA | **Biota** | Phytoplankton, Korean Micro-zooplankton, Korean Meso-zooplankton, Korean Crucian carp (Carassius auratus), blood, Korean Crucian carp (Carassius auratus), liver, Korean Mandarin fish (Siniperca scherzeri), blood, Korean | 2010-2012 | 0.26 ng/g 0.43 ng/g 0.39 ng/g 3.2 ng/g 0.43 ng/g 6.74 ng/g | Lam et al., 2014 |

| | | Mandarin fish (Siniperca scherzeri), liver, Korean | | 1.76 ng/g | |
|---|---|---|---|---|---|
| C12-PFCA | **Biota** | snapping turtles (Chelydra), plasma, Canada<br>amphipod(Gammarus or Hyalella), Ontario<br>damselfly nymph (suborder Zygoptera), Ontario<br>shrimp (infraorder Caridea), Ontario<br>sunfish (Centrarchidae spp.), Ontario<br>bullhead (Ameiurus spp.), Ontario<br>turtle (Chelydra), plasma, Ontario | 2007-2010 | <0.1 – 2.4 ng/g<br><br>0.2 – 1.1 ng/g<br><br><0,.25 ng/g<br><br><0.25 ng/g<br><br><0.25 ng/g<br><br>1.55 ng/g<br><br><0.1 ng/g | Solla et al., 2011 |
| C12-PFCA | **Biota** | crocodile (Crocodylus niloticus), plasma, South Africa | 2012-2013 | n.d. – 0.55 ng/g | Christie et al., 2016 |
| C12-PFCA | **Biota** | several fish species, South Carolina USA | 2002/2003 | 1.1 – 12.1 ng/g | Houde et al., 2006 |
| | | bottlenose dolphin, South Carolina USA<br>several fish species, Florida USA | 2004 | 20 ng/g<br><br><0.5 – 8.9 ng/g | |
| C12-PFCA | **Biota** | several fish species, Canada | 2001 | 1.8 – 14 ng/g | Martin et al., 2004 |
| C12-PFCA | **Biota** | Penguin, dung, Antarctic<br>Penguin, tissue, Antarctic<br>Fish, skin, South America<br>Fish, liver, South America<br>Fish, muscle, South America<br>Fish, roe, South America | 2010 | < LOQ<br>< LOD<br>< .LOQ<br>< LOD<br>< LOD<br>< LOQ | Llorca et al., 2012 |
| C12-PFCA | **Biota** | Arctic Fox (sveral tissues), Norway | 2010-2012 | n.d. – 0.72 ng/g | Aas et al., 2014 |
| C12-PFCA | **Biota** | Wild boar, liver, Germany | 2011-2012 | 5.6 ng/g | Klei et al., 2016 |
| C12-PFCA | **Biota** | Common kestrel, eggs, Schweden<br>Tawny owl, eggs, Schweden<br>Osprey, eggs, Schweden<br>Osprey, eggs, Schweden<br>Osprey, eggs, Schweden | 2014<br>2014<br>2013<br>2008-2009<br>1997-2001 | 1.2 ng/g<br>1 ng/g<br>5.3 ng/g<br>3.7 ng/g<br>2 ng/g | Eriksson et al., 2016 |
| C12-PFCA | **Biota** | Fox (V. vulpes), Germany<br>Chamois (R. rupicapra), Germany | 2013 | 2.4 ng/g<br><br><1.0 ng/g | Riebe et al., 2015 |
| C12-PFCA | **Biota** | Wild boar (S. scrofa), Germany | 2010 | - | Stahl et al., 2012 |
| C12-PFCA | **Biota** | Roe deer (C. capreolus), Germany | 2010 | <0.5 ng/g | Falk et al., 2012 |
| C12-PFCA | **Biota** | Beaver (C. fiber), Poland | 2005 | - | Falandysz et al., 2007 |
| C12-PFCA | **Biota** | wastewater treatment plant A influent, Greece, Athen<br>wastewater treatment plant A effluent, Greece, Athen<br>wastewater treatment plant B influent, Greece, Mytilene<br>wastewater treatment plant B effluent, Greece, Mytilene | 2009-2011 | 1.2 ng/L<br><br>5.7 ng/L<br><br>13.,8 ng/L<br><br><LOD | Avaniti et al., 2011 |

| C13-PFCA | household dust | Czech Republic<br>Canada<br>USA | 2013 | 3.5 ng/g<br>8.2 ng/g<br>1.8 ng/g | Karásková et al., 2016 |
|---|---|---|---|---|---|
| C13-PFCA | household dust | Greece, Athens<br>Spain,Catalonia<br>Sweden, Örebro, Växjö | 2013–2014<br>2009<br>2013–2014 | 0.6 ng/g–3.02 ng/g<br>0.36 ng/g–12.6 ng/g<br><0.02 ng/g–3.45 ng/g | Eriksson et al., 2015 |
| C13-PFCA | household dust | Norway, Oslo | 2008 | 1.1 ng/g–46.0 ng/g | Haug et al., 2011 |
| C13-PFCA | household dust | Norway, Tromsø | 2007/2008 | – | Huber et al., 2011 |
| C13-PFCA | household dust | Belgium, Flanders | 2008 | – | D'Hollander et al., 2010 |
| C13-PFCA | indoor dust | Korea | 2009 | 1.3 ng/g | Tian et al., 2016 |
| C13-PFCA | sediment | Baltic Sea | 2013-2014 | 0.078 ng/g | Gebbink et al., 2016 |
| C13-PFCA | sediment | Czech aquatic ecosystem | 2010 | 1.48 ng/g | Hloušková et al., 2013 |
| C13-PFCA | sediment | France, lake and river sediment | 2012 | <0.02-5.0 | Munoz et al., 2015 SciTotEnv |
| C13-PFCA | water | Baltic Sea | 2013-2014 | <0.02 ng/L | Gebbink et al., 2016 |
| C13-PFCA | water | Ontario, Tyneside Road | 2007-2011 | <0.25 ng/L | Solla et al., 2011 |
| C13-PFCA | dissolved phase surface water | France, lake and river water | 2012 | <0.2-0,29 | Munoz et al., 2015 SciTotEnv |
| C13-PFCA | **Biota** | zooplankton, Baltic Sea<br>herring (Clupea harengus membras), Baltic Sea<br>sprat (Sprattus sprattus), Baltic Sea<br>guillemot (Uria aalge), egg, Baltic Sea | 2013-2014 | <0.004 ng/g<br><br>0.075 ng/g<br><br>0.051 ng/g<br><br>4.7 ng/g | Gebbink et al., 2014 |
| C13-PFCA | **Biota** | albatross (Phoebastria nigripes), liver, Midway Atoll<br>albatross (Phoebastria nigripes), muscle, Midway Atoll<br>albatross (Phoebastria nigripes), adipose, Midway Atoll | 2011 | 8.77 ng/g<br><br>4.06 ng/g<br><br>1.16 ng/g | Chu et al., 2015 |
| C13-PFCA | **Biota** | snapping turtles (Chelydra), plasma, Canada<br>damselfly nymph (suborder Zygoptera), Ontario<br>shrimp (infraorder Caridea), Ontario<br>shrimp (infraorder Caridea), Ontario<br>sunfish (Centrarchidae spp.), Ontario<br>bullhead (Ameiurus spp.), Ontario<br>turtle (Chelydra), plasma, Ontario | 2007-2010 | <0.1 – 1.4 ng/g<br><br><0.25 ng/g<br><br><0.25 ng/g<br><br><0.25 ng/g<br><br><0.25 ng/g<br><br><0.25 ng/g<br><br>0.1 ng/g | Solla et al., 2011 |
| C13-PFCA<br>C13-PFCA | **Biota**<br>**Biota** | several fish species, Canada<br>Penguin, dung, Antarctic<br>Penguin, tissue, Antarctic<br>Fish, skin, Südamerika<br>Fish, liver, Südamerika<br>Fish, muscle, Südamerika<br>Fish, roe, Südamerika | 2001<br>2010 | 1.5 – 15 ng/g<br>< LOD<br><LOQ<br>< LOD<br>< LOD<br>< LOQ<br>< LOQ | Martin et al., 2004<br>Llorca et al., 2012 |

| C13-PFCA | Biota | Arctic Fox, several tissues, Norway | 2010-2012 | n.d. – 6 ng/g | Aas et al., 2014 |
|---|---|---|---|---|---|
| C13-PFCA | Biota | Common kestrel, eggs, Schweden | 2014 | 1.2 ng/g | Eriksson et al., 2016 |
| | | Tawny owl, eggs, Schweden | 2014 | 1.4 ng/g | |
| | | Osprey, eggs, Schweden | 2013 | 4.6 ng/g | |
| | | Osprey, eggs, Schweden | 2008-2009 | 5.6 ng/g | |
| | | Osprey, eggs, Schweden | 1997-2001 | 1.7 ng/g | |
| C13-PFCA | Biota | wastewater treatment plant A influent, Greece, Athen | 2009-2011 | 1.8 ng/L | Avaniti et al., 2011 |
| | | wastewater treatment plant A effluent, Greece, Athen | | 7.8 ng/L | |
| | | wastewater treatment plant B influent, Greece, Mytilene | | 75.7 ng/L | |
| | | wastewater treatment plant B effluent, Greece, Mytilene | | <LOD ng/L | |

| C14-PFCA | household dust | Czech Republic | 2013 | 3.6 ng/g | Karásková et al., 2016 |
|---|---|---|---|---|---|
| | | Canada | | 4.8 ng/g | |
| | | USA | | 1.4 ng/g | |
| C14-PFCA | household dust | Greece, Athens | 2013–2014 | 0.55 ng/g–6.29 ng/g | Eriksson et al., 2015 |
| | | Spain,Catalonia | 2009 | <0.02 ng/g–14.6 ng/g | |
| | | Sweden, Örebro, Växjö | 2013–2014 | <0.02 ng/g–12.7 ng/g | |
| C14-PFCA | household dust | Norway, Oslo | 2008 | 1.1 ng/g–35.0 ng/g | Haug et al., 2011 |
| C14-PFCA | household dust | Norway, Tromsø | 2007/2008 | – | Huber et al., 2011 |
| C14-PFCA | household dust | Belgium, Flanders | 2008 | – | D'Hollander et al., 2010 |
| C14-PFCA | sediment | Baltic Sea | 2013-2014 | 0.046 ng/g | Gebbink et al., 2014 |
| C14-PFCA | sediment | U.S. military installations | 2014 | 1.66 ng/g | Anderson et al., 2016 |
| C14-PFCA | sediment | Czech aquatic ecosystem | 2010 | 0.47 | Hloušková et al., 2013 |
| C14-PFCA | sediment | France, lake and river sediment | 2012 | <0.02-1,3 | Munoz et al., 2015 SciTotEnv |
| C14-PFCA | surface soil | U.S. military installations | 2014 | 1.1 ng/g | Anderson et al., 2016 |
| C14-PFCA | soil | U.S. military installations | 2014 | 3.4 ng/g | Anderson et al., 2016 |
| C14-PFCA | water | Baltic Sea | 2013-2014 | <0.03 ng/L | Gebbink et al., 2014 |
| C14-PFCA | water | Ontario, Tyneside Road | 2007-2011 | <0.25 ng/L | Solla et al., 2011 |
| C14-PFCA | surface water | U.S. military installations | 2014 | - | Anderson et al., 2016 |
| C14-PFCA | dissolved phase surface water | France, lake and river water | 2012 | <0.07 | Munoz et al., 2015 SciTotEnv |
| C14-PFCA | groundwater | U.S. military installations | 2014 | 0.021 ng/g | Anderson et al., 2016 |
| C14-PFCA | Biota | zooplankton, Baltic Sea | 2013-2014 | <0.1 ng/g | Gebbink et al., 2014 |
| | | herring (Clupea harengus membras), Baltic Sea | | 0.0087 ng/g | |
| | | sprat (Sprattus sprattus), Baltic Sea | | 0.0027 ng/g | |
| | | guillemot (Uria aalge), egg, Baltic Sea | | 0.48 ng/g | |
| C14-PFCA | Biota | albatross (Phoebastria nigripes), liver, Midway Atoll | 2011 | 1.57 ng/g | Chu et al., 2015 |
| | | albatross (Phoebastria nigripes), muscle, Midway Atoll | | 0.72 ng/g | |
| | | albatross (Phoebastria nigripes), adipose, Midway Atoll | | 0.11 ng/g | |

| C14-PFCA | **Biota** | snapping turtles (Chelydra), plasma, Canada | 2007-2010 | <0.,1 – 0.6ng/g | Solla et al., 2011 |
|---|---|---|---|---|---|
| | | damselfly nymph (suborder Zygoptera), Ontario | | <0.25 ng/g | |
| | | shrimp (infraorder Caridea), Ontario | | <0.25 ng/g | |
| | | shrimp (infraorder Caridea), Ontario | | <0.25 ng/g | |
| | | sunfish (Centrarchidae spp.), Ontario | | <0.25 ng/g | |
| | | bullhead (Ameiurus spp.), Ontario | | <0.25 ng/g | |
| | | turtle (Chelydra), plasma, Ontario | | <0.1 ng/g | |
| C14-PFCA | **Biota** | Penguin, dung, Antarctic | 2010 | < LOD | Llorca et al., 2012 |
| | | Penguin, tissue, Antarctic | | 0.031 ng/g | |
| | | Fish, skin, Südamerika | | < LOD | |
| | | Fish, liver, Südamerika | | < LOD | |
| | | Fish, muscle, Südamerika | | < LOD | |
| | | Fish, roe, Südamerika | | < LOQ | |
| C14-PFCA | **Biota** | Arctic Fox, several tissues, Norway | 2010-2012 | n.d. – 2.3 ng/g | Aas et al., 2014 |
| C14-PFCA | **Biota** | wastewater treatment plant A influent, Greece, Athen | 2009-2011 | 3.1 ng/L | Avaniti et al., 2011 |
| | | wastewater treatment plant A effluent, Greece, Athen | | 10.4 ng/L | |
| | | wastewater treatment plant B influent, Greece, Mytilene | | <LOD | |
| | | wastewater treatment plant B effluent, Greece, Mytilene | | <LOD | |

# Appendix H: Use information from patent

The following tables summarize the information on C9-C14 PFCAs found on the market.

27 C9-C14 PFCAs was found on the market. Patent information was found for 13 of these in the PubChem database (Table F1).

The most abundant patent types (on the IPC class level 3) are summerized in Table F2.

In Table F3 the patents was categorized into four age groups:

- "New" patents             Granted ≤2years ago

- "Recent" patents          Granted 2-4 years ago

- "Ongoing" patents        Granted 4-20 years ago

- "Expired" patents          Granted >20 years ago


Source: PubChem searched February 2017
https://pubchem.ncbi.nlm.nih.gov/search/search.cgi.

**Table F1:** C9-C14 Perfluoro carboxylic acids searched for patent information in PubChem (Feb. 2017)

| CAS No | EC No | C9-C14 PFCAs on the world market | Search | Found patent |
|--------|-------|----------------------------------|--------|--------------|
| 307-55-1 | 206-203-2 | Dodecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-tricosafluoro- | x | x |
| 335-76-2 | 206-400-3 | Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro- | x | x |
| 375-95-1 | 206-801-3 | Nonanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro- | x | x |
| 376-06-7 | 206-803-4 | Tetradecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptacosafluoro- | x | x |
| 2058-94-8 | 218-165-4 | Undecanoic acid, heneicosafluoro- | x | x |
| 3108-42-7 | - | Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro-, ammonium salt | x | x |
| 3793-74-6 | - | Dodecanoic acid, tricosafluoro-, ammonium salt | x | x |
| 4149-60-4 | - | Nonanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluoro-, ammonium salt (1:1) | x | x |
| 15899-31-7 | - | Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,8,8,8-tetradecafluoro-7-(trifluoromethyl)- | x | x |
| 34598-33-9 | 252-108-4 | Undecanoic acid, 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro- | x | x |
| 72629-94-8 | - | Tridecanoic acid, pentacosafluoro- | x | x |
| 172155-07-6 | - | Octanoic acid, 2,2,3,4,4,5,5,6,6,7,8,8,8-tridecafluoro-3,7-bis(trifluoromethyl)- | x | x |
| 238403-51-5 | - | Hexanoic acid, 2,2,3,4,4,6,6,6-octafluoro-3,5,5-tris(trifluoromethyl)- | x | x |
| 3658-62-6 | - | Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,8,8,8-tetradecafluoro-7-(trifluoromethyl)-, ammonium salt | x | |
| 3658-63-7 | - | Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10-octadecafluoro-9-(trifluoromethyl)-, ammonium salt | x | |
| 3830-45-3 | - | Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro-, sodium salt | x | |
| 16486-94-5 | - | Decanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,10,10,10-octadecafluoro-9-(trifluoromethyl)- | x | |
| 16486-96-7 | - | Dodecanoic acid, docosafluoro-11-(trifluoromethyl)- | x | |
| 68015-86-1 | - | Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,8,8,8-tetradecafluoro-7-(trifluoromethyl)-, compd. With ethanamine (1:1) | x | |
| 68333-92-6 | - | Fatty acids, C7-13, perfluoro- | x | |
| 69278-80-4 | - | Fatty acids, C7-13, perfluoro, compds. With ethylamine | x | |
| 72623-77-9 | - | Fatty acids, C6-18, perfluoro, ammonium salts | x | |
| 72968-38-8 | 277-138-5 | Fatty acids, C7-13, perfluoro, ammonium salts | x | |
| 76199-70-7 | - | Surflon S 113 (perfluoroalkylcarboxylate) | x | |
| 83310-58-1 | 280-373-6 | Undecanoic acid, 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-, potassium salt | x | |
| 91032-01-8 | - | Fatty acids, C7-19, perfluoro- | X | |
| 212013-54-2 | - | Fatty acids, C7-19, perfluoro, ammonium salts | x | |

| **Table F2**: The most abundant (n>100) patent types connected to C9-C14 perfluoro carboxylic acids (PubChem Feb. 2017) | | |
|---|---|---|
| **International Patent class text (level 3)** | **IPC class** | **Number of patents** |
| Macromolecular compounds obtained by reactions only involving carbon-to-carbon unsaturated bonds | C08F | 913 |
| Photomechanical production of textured or patterned surfaces, e.g. for printing, for processing of semiconductor devices; materials therefor; originals therefor; apparatus specially adapted therefor | G03F | 748 |
| Preparations for medical, dental, or toilet purposes | A61K | 475 |
| Acyclic or carbocyclic compounds | C07C | 338 |
| Compositions of macromolecular compounds | C08L | 305 |
| Semiconductor devices; electric solid state devices not otherwise provided for | H01L | 187 |
| Coating compositions, e.g. paints, varnishes or lacquers; filling pastes; chemical paint or ink removers; inks; correcting fluids; woodstains; pastes or solids for colouring or printing; use of materials therefor | C09D | 179 |
| Use of inorganic or non-macromolecular organic substances as compounding ingredients | C08K | 160 |
| Macromolecular compounds obtained otherwise than by reactions only involving unsaturated carbon-to-carbon bonds | C08G | 159 |
| Heterocyclic compounds | C07D | 144 |
| Specific therapeutic activity of chemical compounds or medicinal preparations | A61P | 136 |
| Chemical or physical processes, e.g. catalysis, colloid chemistry; their relevant apparatus | B01J | 121 |

| Table F3: Patent types for <u>new</u> patents connected to C9-C14 perfluoro carboxylic acids (PubChem Feb. 2017) | | |
|---|---|---|
| **Patent class text on new patents (IPC class level 3)** | **IPC class** | **Number of patents** |
| EARTH DRILLING, e.g. DEEP DRILLING; OBTAINING OIL, GAS, WATER, SOLUBLE OR MELTABLE MATERIALS OR A SLURRY OF MINERALS FROM WELLS | E21B | 36 |
| STRUCTURAL ELEMENTS; BUILDING MATERIALS | E04C | 6 |
| GENERAL BUILDING CONSTRUCTIONS; WALLS, e.g. PARTITIONS; ROOFS; FLOORS; CEILINGS; INSULATION OR OTHER PROTECTION OF BUILDINGS | E04B | 5 |
| LIME, MAGNESIA; SLAG; CEMENTS; COMPOSITIONS THEREOF, e.g. MORTARS, CONCRETE OR LIKE BUILDING MATERIALS; ARTIFICIAL STONE; CERAMICS; REFRACTORIES; TREATMENT OF NATURAL STONE | C04B | 3 |
| CRACKING HYDROCARBON OILS; PRODUCTION OF LIQUID HYDROCARBON MIXTURES, e.g. BY DESTRUCTIVE HYDROGENATION, OLIGOMERISATION, POLYMERISATION; RECOVERY OF HYDROCARBON OILS FROM OIL-SHALE, OIL-SAND, OR GASES; REFINING MIXTURES MAINLY CONSISTING OF HYDROCARBONS; | C10G | 3 |
| DETAILS OF LIGHTING DEVICES, OF GENERAL APPLICATION | F21V | 2 |
| TREATMENT OR CHEMICAL MODIFICATION OF RUBBERS | C08C | 1 |
| MECHANICAL METHODS OR APPARATUS IN THE MANUFACTURE OF ARTIFICIAL FILAMENTS, THREADS, FIBRES, BRISTLES OR RIBBONS | D01D | 1 |
| MANUFACTURE, SHAPING, OR SUPPLEMENTARY PROCESSES | C03B | 1 |

# Appendix I: Summary of European human biomonitoring data on C9-C14 PFCA

**Summary of studies on C9-C14 PFCA in serum (data from 2007 -)**

| Compound | Publications retreived (snapshot + temporal trend) | Detection in samples | Concentrations | Temporal trends |
|---|---|---|---|---|
| C9-PFCA | 21 + 8 | High (often ~100%) | High pg/ml – low ng/ml | Increasing 1980 – 2010. Levelling out or decreasing after that. |
| C10-PFCA | 17 + 8 | High (often > 90%) | High pg/ml – low ng/ml | Increasing 1980 – 2010. Levelling out or decreasing after that. |
| C11-PFCA | 11 + 8 | Average (often > 75%) | High pg/ml – low ng/ml | Increasing 1980 – 2010. Levelling out or decreasing after that. |
| C12-PFCA | 7 + 3 | Fairly low (often 25 – 75%) | pg/ml | Increasing 1980 – 2010. |
| C13-PFCA | 6 + 2 | Fairly low (often 25 – 75%) | pg/ml | Increasing 1980 – 2010. |
| C14-PFCA | 4 + 2 | Low (0 – 25%) | pg/ml | No data. |

**Summary of studies on C9-C14 PFCA in breast milk (data from 2007 -)**

| Compound | Publications retrieved (snapshot + temporal trend) | Detection in samples | Concentrations | Temporal trends |
|---|---|---|---|---|
| C9-PFCA | 8 + 1 | Low (0-10%) | < LOD – low pg/ml | Increasing 1972 to around 2010. Levelling out or decreasing after that. |
| C10-PFCA | 8 + 1 | Low (0-10%) | < LOD – low pg/ml | Increasing 1972 to around 2010. Levelling out or decreasing after that. |
| C11-PFCA | 6 + 1 | Low (0-10%) | < LOD – low pg/ml | Increasing 1972 to around 2010. Levelling out or decreasing after that. |
| C12-PFCA | 4 + 1 | Very low (0-3%) | < LOD – low pg/ml | Increasing after 2000 and likely decreasing after around 2010. |
| C13-PFCA | 1 + 1 | Low (0-10%) | < LOD – low pg/ml | Increasing 1972 to around 2010. Levelling out or decreasing after that. |
| C14-PFCA | 0 + 1 | Low (0-10%) | < LOD – low pg/ml | Slight increase since around 2007. |

**C9-PFCA in serum – snapshot studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2015 | Adult blood donors | 40.8 ± 10.2 | 300 | LOQ = 0,013 | 99,7 | 0,43 ± 0,57[*] | <LOQ – 6.55 | (Sochorova et al., 2017) |
| Denmark | 2008-2013 | Pregnant women | 29[¤] | 1533 | LOQ = 0,27 | 99 | 0,83 ± 0,37[*] | <LOQ – 4,69 | (Bjerregaard-Olesen et al., 2016) |
| Denmark | 2010 | Mothers | 41 | 143 | LOD = 0,03 | 100 | 0,75 ± 0,39 | 0,26 – 2,55 | (Morck et al., 2015) |
| Denmark | 2010 | Children | 8,7 | 116 | LOD = 0,03 | 100 | 0,88 ± 0,35 | 0,28 – 2,16 | (Morck et al., 2015) |
| Denmark | 2010-2012 | Pregnant women | 29,9 ± 4,7 | 392 | LOD = 0,03 | 100 | 0,84 ± 0,48 | 0,18 – 4,40 | (Jensen et al., 2015) |
| Faroe Islands | 2007-2009 | Mothers 2 weeks postpartum | 30,1 ± 5,4 | 441 | LOD = 0,03 | 100 | 0,67 ± 1,5[*] | 0,18 – 4,30 | (Karlsen et al., 2016) |
| Faroe Islands | 2007-2009 | Children 5 years | 5,0 ± 0,07 | 371 | LOD = 0,03 | 100 | 1,12 ± 1,7[*] | 0,12 – 5,75 | (Karlsen et al., 2016) |
| Faroe Islands | 2004-2007 | Children 7 years | 7,5 ± 1,2 | 491 | LOD = 0,03 | 100 | 1,2[*] | 0,47 – 9,49 | (Oulhote et al., 2016) |
| France | 2008 | Adult fishermen | 44,8 | 478 | N.A. | N.A. | 1,4 ± 0,9[*]<br>1,6 ± 0,9[#] | 0,2 – 8 | (Denys et al., 2014) |
| France | 2010-2013 | Pregnant women | 33 ± 5 | 100 | LOQ = 0,3 | 21 | 0,519 ± 0,402[#] | < LOD – 3,29 | (Cariou et al., 2015) |
| France | 2010-2013 | Umbilical cord serum | 33 ± 5 | 100 | LOQ = 0,3 | 22 | 0,266 ± 0,242[#] | < LOD – 2,25 | (Cariou et al., 2015) |
| Germany | 2007-2008 | Children 6-7 years | 6,6 ± 0,5 | 112 | LOQ = 0,4 | 100 | 0,84 ± <0,4[*] | 0,42 – 2,38 | (Wilhelm et al., 2015) |
| Germany | 2007-2008 | Children 8-10 years | 8,5 ± 0,3 | 101 | LOQ = 0,4 | 94 | 0,70 ± <0,4[*] | < LOQ – 1,59 | (Wilhelm et al., 2015) |
| Germany | 2007-2008 | Mothers | 31,6 ± 5,1 | 81 | LOQ = 0,4 | 54 | 0,69 ± <0,4[*] | < LOQ – 2,59 | Wilhelm et al. 2015 |
| Greenland | 2010-2013 | Pregnant women | 27,5 ± 5,2 | 209 | LOQ = 0,27 | 100 | 1,49 ± 0,99 | 0,41 – 7,71 | (Long et al., 2015) |
| Greenland | 2011-2014 | Adult women | 51.7 ± 13,3 | 99 | LOD = 0,09 | 100 | 4,60 ± 5,35[#] | 0,33 – 38,6 | (Wielsoe et al., 2017) |
| Norway | 2007-2008 | Mothers at delivery | 32,5 ± 4,3 | 99 | LOQ = 0,05 | 72 | 0,10 ± 0,79[*] | < LOQ – 0,44 | (Papadopoulou et al., 2016) |
| Norway | 2010-2011 | Children 3 years | 2,9 ± 0,2 | 112 | LOQ = 0,05 | 79 | 0,14 ± 0,97[*] | < LOQ – 1,08 | Papadopoulou et al. 2016 |
| Norway | 2012-2014 | Non-consumers of contaminated fish | 54,6 ± 12,2 | 15 | LOD = 0,05 | 100 | 0,80[*] ± 0,55<br>0,95[#] ± 0,55 | 0,19 – 2,14 | (Hansen et al., 2016) |

[*] = Geometic mean, [#] = Arithmetic mean, [¤] = Median. N.A. = information not retrieved

**C9-PFCA in serum – snapshot studies (cont.)**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Norway | 2012-2014 | Low consumers of contaminated fish | 55,5 ± 8,3 | 27 | LOD = 0,05 | 100 | 0,75 ± 0,62[*] 0,93 ± 0,62[#] | 0,12 – 2,98 | (Hansen et al., 2016) |
| Norway | 2012-2014 | Moderate consumers of contaminated fish | 57,2 ± 13,9 | 16 | LOD = 0,05 | 100 | 0,87 ± 0,48[*] 0,99 ± 0,48[#] | 0,25 – 2,02 | (Hansen et al., 2016) |
| Norway | 2012-2014 | High consumers of contaminated fish | 59,6 ± 7,2 | 16 | LOD = 0,05 | 100 | 1,57 ± 2,60[*] 2,18 ± 2,60[#] | 0,37 – 1,72 | (Hansen et al., 2016) |
| Norway | 2007-2009 | Pregnant women | 31 ± 4,8 | 391 | LOD = 0,04 | 100 | 0,67 ± 0,46[#] | 0,15 – 4,36 | (Berg et al., 2014) |
| Spain | 2003-2008 | Pregnant women | 30,7± 4,0 | 1216 | LOD = 0,1 | 99,3 | 0,64 ± 0,41[*] | 0,03 – 5,51 | (Manzano-Salgado et al., 2016) |
| Spain | 2009-2010 | Adults | 37,4 ± 10,2 | 46 | LOD = 0,05 | 39 | 0,12 ± 0,43 | < LOD – 2,94 | (Gomez-Canela et al., 2015) |
| Spain | 2009-2010 | Adults | 39.6 ± 10,1 | 755 | LOQ = 0,16-0,34 | 99,9 | 1,11[#] 0,96[*] | < LOQ – 8,32 | (Bartolome et al., 2017) |
| Sweden | 2001-2007 | Adult men with prostate cancer | 66,8 ± 5,3 | 201 | LOD = 0,05 – 0,7 | 93 | 0,68 ± 0,45[#] | 0,05 – 4,6 | (Hardell et al., 2014) |
| Sweden | 2001-2007 | Adult men without prostate cancer | 66,8 ± 5,5 | 186 | LOD = 0,05 – 0,7 | 91 | 0,63 ± 0,36[#] | 0,0850 – 2,1 | (Hardell et al., 2014) |
| Sweden | 2012-2014 | Adult women | 29 | 60 | LOQ = 0,03 | 100 | 0,57 | 0,22 – 1,5 | (Glynn et al., 2015) |
| Sweden | 2008 | Children 4 years | 3,9 | 78 | LOQ = 0,08 | 100 | 0,85 | 0,26 – 5,5 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 8-9 years | 8,4 | 56 | LOQ = 0,08 | 100 | 0,76 | 0,34 – 2,1 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 12 years | 12,2 | 121 | LOQ = 0,08 | 99 | 0,67 | < LOQ – 3,9 | (Gyllenhammar et al., 2016) |
| Sweden | 2013 | Young women | 18,1 ± 0,58 | 104 | LOD = 0,01 | 100 | 0,56[¤] | 0,148 – 2,422 | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | | 97 | LOD = 0,01 | 100 | 0,49[¤] | 0,249 – 2,231 | (Jönsson et al., 2014) |

[*] = Geometic mean, [#] = Arithmetic mean, [¤] = median, N.A. = information not retrieved

**C10-PFCA in serum – snapshot studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2015 | Adult blood donors | 40.8 ± 10.2 | 300 | LOQ = 0,013 | 100 | 0,19 ± 0,19[*] | 0,013 – 1,81 | (Sochorova et al., 2017) |
| Denmark | 2010-2012 | Pregnant women | 29,9 ± 4,7 | 392 | LOD = 0,03 | 100 | 0,30 ± 0,17 | 0,18 – 4,40 | (Jensen et al., 2015) |
| Denmark | 2010 | Mothers | 41 | 143 | LOD = 0,03 | 100 | 0,75 ± 0,39 | 0,26 – 2,55 | (Morck et al., 2015) |
| Denmark | 2010 | Children | 8,7 | 116 | LOD = 0,03 | 100 | 0,88 ± 0,35 | 0,28 – 2,16 | (Morck et al., 2015) |
| Faroe Islands | 2004-2007 | Children 7 years | 7,5 ± 1,2 | 491 | LOD = 0,03 | 100 | 0,36[*] | 0,07 – 2,02 | (Oulhote et al., 2016) |
| France | 2008 | Adult fishermen | 44,8 | 478 | N.A. | N.A. | 0,6 ± 0,7[*]<br>0,7 ± 0,7[#] | 0,0 – 11,2 | (Denys et al., 2014) |
| France | 2010-2013 | Pregnant women | 33 ± 5 | 100 | LOQ = 0,4 | 19 | 0,277 ± 0,280[#] | < LOD – 1,99 | (Cariou et al., 2015) |
| France | 2010-2013 | Umbilical cord serum | 33 ± 5 | 100 | LOQ = 0,3 | 4,5 | 0,103 ± 0,081[#] | < LOD – 0,602 | (Cariou et al., 2015) |
| Germany | 2007-2008 | Children 6-7 years | 6,6 ± 0,5 | 112 | LOQ = 0,4 | ~100 | < LOQ | < LOQ | (Wilhelm et al., 2015) |
| Germany | 2007-2008 | Children 8-10 years | 8,5 ± 0,3 | 101 | LOQ = 0,4 | ~100 | < LOQ | < LOQ | (Wilhelm et al., 2015) |
| Germany | 2007-2008 | Mothers | 31,6 ± 5,1 | 81 | LOQ = 0,4 | ~100 | < LOQ | < LOQ | Wilhelm et al. 2015 |
| Greenland | 2010-2013 | Pregnant women | 27,5 ± 5,2 | 209 | LOQ = 0,09 | 100 | 0,99 ± 0,88[*] | 0,12 – 7,84 | (Long et al., 2015) |
| Greenland | 2011-2014 | Adult women | 51.7 ± 13,3 | 158 | LOD = 0,03 | 100 | 2,23 ± 2,10 | 0,113 – 11,1[#] | (Wielsoe et al., 2017) |
| Norway | 2007-2009 | Pregnant women | 31 ± 4,8 | 391 | LOD = 0,03 | 100 | 0,26 ± 0,16[#] | 0,05-2,34 | (Berg et al., 2014) |
| Norway | 2012-2014 | Non-consumers of contaminated fish | 54,6 ± 12,2 | 15 | LOD = 0,05 | 88 | 0,31[*] ± 0,21<br>0,22[#] ± 0,21 | < LOQ – 0,79 | (Hansen et al., 2016) |
| Norway | 2012-2014 | Low consumers of contaminated fish | 55,5 ± 8,3 | 27 | LOD = 0,05 | | 0,31 ± 0,29[*]<br>0,20 ± 0,29[#] | < LOQ – 1,21 | (Hansen et al., 2016) |
| Norway | 2012-2014 | Moderate consumers of contaminated fish | 57,2 ± 13,9 | 16 | LOD = 0,05 | | 0,25 ± 0,25[*]<br>0,15 ± 0,25[#] | < LOQ – 0,93 | (Hansen et al., 2016) |
| Norway | 2012-2014 | High consumers of contaminated fish | 59,6 ± 7,2 | 16 | LOD = 0,05 | | 0,59 ± 0,53[*]<br>0,43 ± 0,53[#] | < LOQ – 2,29 | (Hansen et al., 2016) |

[*] = Geometic mean, [#] = Arithmetic mean, N.A. = information not retrieved

**C10-PFCA in serum – snapshot studies (cont.)**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Spain | 2009-2010 | Adults | 37,4 ± 10,2 | 46 | LOD = 0,05 | 39 | 0,12 ± 0,43 | < LOD – 2,94 | (Gomez-Canela et al., 2015) |
| Spain | 2009-2010 | Adults | 39.6 ± 10,1 | 755 | LOQ = 0,16-0,34 | 86,4 | 0,49[#] <br> 0,42[*] | < LOQ – 2,33 | (Bartolome et al., 2017) |
| Sweden | 2007-2001 | Adult men with prostate cancer | 66,8 ± 5,3 | 200 | LOD = 0,06 – 0,4 | 86 | 0,34 ± 0,21[#] | 0,03 – 1,2 | (Hardell et al., 2014) |
| Sweden | 2007-2001 | Adult men without prostate cancer | 66,8 ± 5,5 | 181 | LOD = 0,06 – 0,4 | 80 | 0,29 ± 0,19[#] | 0,02 – 1,0 | (Hardell et al., 2014) |
| Sweden | 2012-2014 | Adult women | 29 | 60 | LOQ = 0,01 | 88 | 0,22 | < LOQ – 1,3 | (Glynn et al., 2015) |
| Sweden | 2008 | Children 4 years | 3,9 | 78 | LOQ = 0,10 | 98 | 0,26 | < LOQ – 0,54 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 8-9 years | 8,4 | 56 | LOQ = 0,10 | 96 | 0,30 | < LOQ – 0,67 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 12 years | 12,2 | 121 | LOQ = 0,10 | 99 | 0,25 | < LOQ – 0,52 | (Gyllenhammar et al., 2016) |
| Sweden | 2013 | Young women | 18,1 ± 0,58 | 104 | LOD = 0,01 | 100 | 0,25[¤] | 0,075 – 1,026 | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | | 97 | LOD = 0,01 | 100 | 0,20[¤] | 0,087 – 0,423 | (Jönsson et al., 2014) |

[*] = Geometic mean, [#] = Arithmetic mean

**C11-PFCA in serum – snapshot studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2015 | Adult blood donors | 40.8 ± 10.2 | 300 | LOQ = 0,013 | 96,0 | 0,073 ± 0,058[*] | < LOQ – 0,417 | (Sochorova et al., 2017) |
| Denmark | 2008-2013 | Pregnant women | 29[¤] | 1533 | LOQ = 0,15 | 87 | 0,36 ± 0,25[*] | <LOQ – 2,47 | (Bjerregaard-Olesen et al., 2016) |
| France | 2010-2013 | Pregnant women | 33 ± 5 | 100 | LOQ = 0,35 | 8 | 0,213 ± 0,285[#] | < LOD – 2,60 | (Cariou et al., 2015) |
| France | 2010-2013 | Umbilical cord serum | 33 ± 5 | 100 | LOQ = 0,3 | 1 | 0,106 ± 0,085[#] | < LOD – 0,743 | (Cariou et al., 2015) |
| Greenland | 2010-2013 | Pregnant women | 27,5 ± 5,2 | 209 | LOQ = 0,15 | 100 | 2,58 ± 2,82 | 0,18 – 18,2 | (Long et al., 2015) |
| Greenland | 2011-2014 | Adult women | 51.7 ± 13,3 | 158 | LOD = 0,05 | 100 | 4,44 – 4,54[#] | 0,031 – 24,9 | (Wielsoe et al., 2017) |
| Norway | 2012-2014 | Non-consumers of contaminated fish | 54,6 ± 12,2 | 15 | LOD = 0,05 | | 0,25 ± 0,40[*] 0,45 ± 0,40[#] | < LOQ – 1,10 | (Hansen et al., 2016) |
| Norway | 2012-2014 | Low consumers of contaminated fish | 55,5 ± 8,3 | 27 | LOD = 0,05 | | 0,23 ± 0,46[*] 0,42 ± 0,46[#] | < LOQ – 1,63 | (Hansen et al., 2016) |
| Norway | 2012-2014 | Moderate consumers of contaminated fish | 57,2 ± 13,9 | 16 | LOD = 0,05 | 88 | 0,22 ± 0,41[*] 0,38 ± 0,41[#] | < LOQ – 1,33 | (Hansen et al., 2016) |
| Norway | 2012-2014 | High consumers of contaminated fish | 59,6 ± 7,2 | 16 | LOD = 0,05 | | 0,66 ± 1,45[*] 1,10 ± 1,45[#] | 0,09 – 6,24 | (Hansen et al., 2016) |
| Norway | 2007-2009 | Pregnant women | 31 ± 4,8 | 391 | LOD = 0,02 | 100 | 0,30 ± 0,19[#] | 0,03-1,46 | (Berg et al., 2014) |
| Sweden | 2007-2001 | Adult men with prostate cancer | 66,8 ± 5,3 | 198 | LOD = 0,05 – 0,37 | 79 | 0,31 ± 0,23[#] | 0,0150 – 1,3 | (Hardell et al., 2014) |
| Sweden | 2007-2001 | Adult men without prostate cancer | 66,8 ± 5,5 | 174 | LOD = 0,05 – 0,37 | 80 | 0,29 ± 0,21[#] | 0,0250 – 1,5 | (Hardell et al., 2014) |
| Sweden | 2012-2014 | Adult women | 29 | 60 | LOQ = 0,01 | 93 | 0,26 | < LOQ – 1,3 | (Glynn et al., 2015) |
| Sweden | 2008 | Children 4 years | 3,9 | 78 | LOQ = 0,10 | 74 | 0,21 | < LOQ – 0,77 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 8-9 years | 8,4 | 56 | LOQ = 0,10 | 78 | 0,20 | < LOQ – 0,46 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 12 years | 12,2 | 121 | LOQ = 0,10 | 65 | 0,17 | < LOQ – 0,51 | (Gyllenhammar et al., 2016) |
| Sweden | 2013 | Young women | 18,1 ± 0,58 | 104 | LOD = 0,04 | 96 | 0,14[¤] | < LOQ – 0,657 | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | | 97 | LOD = 0,04 | 99 | 0,13[¤] | < LOQ – 0,643 | (Jönsson et al., 2014) |

[*] = Geometric mean, [#] = Arithmetic mean

**C12-PFCA in serum- snapshot studies**

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2015 | Adult blood donors | 40.8 ± 10.2 | 300 | LOQ = 0,013 | 47,3 | - | <LOQ – 0,196 | (Sochorova et al., 2017) |
| Greenland | 2010-2013 | Pregnant women | 27,5 ± 5,2 | 209 | LOQ = 0,41 | 37,8 | 0,39 ± 0,29 | 0,20- 1,85 | (Long et al., 2015) |
| Greenland | 2011-2014 | Adult women | 51.7 ± 13,3 | 158 | LOD = 0,14 | 58,6 | 0,91 ± 1,10[#] | 0,21 – 6,5 | (Wielsoe et al., 2017) |
| Norway | 2007-2009 | Pregnant women | 31 ± 4,8 | 391 | LOD = 0,03 | 50 | 0,04 ± 0,03[#] | < LOD – 0,20 | (Berg et al., 2014) |
| Sweden | 2012-2014 | Adult women | 29 | 60 | LOQ = 0,01 | 60 | 0,032 | < LOQ – 0,24 | (Glynn et al., 2015) |
| Sweden | 2008 | Children 4 years | 3,9 | 78 | LOQ = 0,08 | 12 | - | < LOQ – 0,21 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 8-9 years | 8,4 | 56 | LOQ = 0,08 | 0 | - | < LOQ | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 12 years | 12,2 | 121 | LOQ = 0,08 | 1 | - | < LOQ – 0,061 | (Gyllenhammar et al., 2016) |
| Sweden | 2013 | Young women | 18,1 ± 0,58 | 104 | LOD = 0,03 | 24 | - | < LOD – 0,172 | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | | 97 | LOD = 0,03 | 20 | - | < LOD – 0,117 | (Jönsson et al., 2014) |

[*] = Geometric mean, [#] = Arithmetic mean

**C13-PFCA in serum – snapshot studies**

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD (ng/ml) | < LOD (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2015 | Adult blood donors | 40.8 ± 10.2 | 300 | LOQ = 0,013 | 36,3 | - | < LOQ – 0,094 | (Sochorova et al., 2017) |
| Greenland | 2010-2013 | Pregnant women | 27,5 ± 5,2 | 209 | LOQ = 0,41 | 1,9 | 0,21 ± 0,06 | 0,21 – 0,90 | (Long et al., 2015) |
| Greenland | 2011-2014 | Adult women | 51.7 ± 13,3 | 158 | LOD = 0,14 | 14,1 | - | - | (Wielsoe et al., 2017) |
| Sweden | 2012-2014 | Adult women | 29 | 60 | LOQ = 0,03 | 87 | 0,036 | < LOQ – 0,19 | (Glynn et al., 2015) |
| Sweden | 2008 | Children 4 years | 3,9 | 78 | LOQ = 0,02 | 35 | - | < LOQ – 0,35 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 8-9 years | 8,4 | 56 | LOQ = 0,02 | 51 | - | < LOQ – 0,13 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 12 years | 12,2 | 121 | LOQ = 0,02 | 29 | - | < LOQ – 0,10 | (Gyllenhammar et al., 2016) |
| Sweden | 2013 | Young women | 18,1 ± 0,58 | 104 | LOD = 0,01 | 82 | 0,03[¤] | < LOD – 0,224 | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | | 97 | LOD = 0,01 | 56 | 0,02[¤] | < LOD – 0,089 | (Jönsson et al., 2014) |

[*] = Geometric mean, [#] = Arithmetic mean

**C14-PFCA in serum – snapshot studies**

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD (ng/ml) | > LOD (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2015 | Adult blood donors | 40.8 ± 10.2 | 300 | LOQ = 0,013 | 4,3 | - | < LOQ – 0,029 | (Sochorova et al., 2017) |
| Greenland | 2011-2014 | Adult women | 51.7 ± 13,3 | 158 | LOD = 0,14 | 0 | - | - | (Wielsoe et al., 2017) |
| Sweden | 2008 | Children 4 years | 3,9 | 78 | LOQ = 0,06 | 11 | - | < LOQ – 0,43 | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 8-9 years | 8,4 | 56 | LOQ = 0,06 | 0 | - | < LOQ | (Gyllenhammar et al., 2016) |
| Sweden | 2008 | Children 12 years | 12,2 | 121 | LOQ = 0,06 | 3 | - | < LOQ – 0,094 | (Gyllenhammar et al., 2016) |
| Sweden | 2013 | Young women | 18,1 ± 0,58 | 97 | LOD = 0,01 | 38 | - | < LOD – 0,42 | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | | 104 | LOD = 0,01 | 19 | - | < LOD – 0,037 | (Jönsson et al., 2014) |

[*] = Geometric mean, [#] = Arithmetic mean

## C9-PFCA in serum – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Denmark | 2008 | Pregnant women | 29$^\square$ | 244 | LOQ = 0,27 | 100 | 0,96 ± 0,35$^*$ | 0,31 – 3,05 | (Bjerregaard-Olesen et al., 2016) |
| Denmark | 2009 | Pregnant women | 29$^\square$ | 243 | LOQ = 0,27 | 100 | 0,88 ± 0,41$^*$ | 0,27 – 4,56 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2010 | Pregnant women | 29$^\square$ | 246 | LOQ = 0,27 | 99 | 0,85 ± 0,33$^*$ | <LOQ – 2,19 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2011 | Pregnant women | 29$^\square$ | 284 | LOQ = 0,27 | 99 | 0,82 ± 0,41$^*$ | <LOQ – 4,69 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2012 | Pregnant women | 29$^\square$ | 288 | LOQ = 0,27 | 99 | 0,73 ± 0,29$^*$ | <LOQ – 2,03 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2013 | Pregnant women | 29$^\square$ | 228 | LOQ = 0,27 | 98 | 0,72 ± 0,36$^*$ | <LOQ – 3,46 | Bjerregaard-Olesen et al. 2016 |
| Germany | 1982-2009 | Adult males | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | (Yeung et al., 2013) |
| Germany | 1982-2009 | Adult females | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Norway | 1979 | Adult men | 42 ± 6 | 53 | LOD = 0,05 | 81 | 0,1 ± 0 | < LOD – 0,2 | (Nost et al., 2014) |
| Norway | 1986 | Adult men | 49 ± 6 | 52 | LOD = 0,05 | 100 | 0,6 ± 0,2 | 0,2 – 1,3 | (Nost et al., 2014) |
| Norway | 1994 | Adult men | 57 ± 6 | 48 | LOD = 0,05 | 100 | 0,8 ± 0,3 | 0,2 – 1,6 | (Nost et al., 2014) |
| Norway | 2001 | Adult men | 64 ± 6 | 49 | LOD = 0,05 | 100 | 1,2 ± 0,3 | 0,5 – 1,9 | (Nost et al., 2014) |
| Norway | 2007 | Adult men | 70 ± 6 | 52 | LOD = 0,05 | 100 | 1,6 ± 0,6 | 0,7 – 3,4 | (Nost et al., 2014) |
| Sweden | 1987-1990 | Adult women | 47 ± 4 | 24 | LOD = 0,1 | 98 | 0,28 ± 0,13$^*$ | <LOQ – 0,64 | (Axmon et al., 2014) |
| Sweden | 1991-2000 | Adult women | 46 ± 5 | 30 | LOD = 0,1 | 98 | 0,36 ± 0,15$^*$ | <LOQ – 0,89 | Axmon et al. 2014 |
| Sweden | 2001-2007 | Adult women | 49 ± 5 | 26 | LOD = 0,1 | 9 | 0,76 ± 0,34$^*$ | <LOQ – 1,59 | Axmon et al. 2014 |
| Sweden | 1997-2012 | Adult women | 27-31 | 9-10 | LOQ = 0,03 | See Table I-1 below | | | (Gebbink et al., 2015) |
| Sweden | 2010 | Young men | N.A. | 306 | LOD = 0,01 | N.A. | 0,72$^\square$ | N.A. | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | N.A. | 97 | LOD = 0,01 | N.A. | 0,49$^\square$ | N.A. | (Jönsson et al., 2014) |
| Sweden | 1996-1999 | Adult women | 28,6 | 147 | LOD = 0,05 | 100 | 0,41 ± 0,02 | 0,062 – 1,4 | (Gyllenhammar et al., 2015) |
| Sweden | 2008-2011 | Adult women | 30,2 | 149 | LOD = 0,05 | 100 | 0,52 ± 0,02 | 0,064 – 2,2 | (Gyllenhammar et al., 2015) |
| Sweden | 2001-2004 | Elderly men and women | 70 | 579 | LOQ = 0,05 | 99 | 0,84 ± 0,47 | < LOQ – 4,8 | (Stubleski et al., 2016) |
| Sweden | 2006-2009 | Elderly men and women | 75 | 579 | LOQ = 0,05 | 100 | 1,3 ± 0,84 | 0,08 – 5,9 | Stubleski et al. 2016 |
| Sweden | 2011-2014 | Elderly men and women | 80 | 579 | LOQ = 0,05 | 100 | 1,1 ± 0,71 | 0,07 – 6,9 | Stubleski et al. 2016 |

$^*$ = Geometic mean, $^\#$ = Arithmetic mean, $^\square$ = Median, N.A. = information not retrieved.

**C10-PFCA in serum – temporal trend studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Denmark | 2008 | Pregnant women | 29[¤] | 244 | LOQ = 0.09 | 100 | 0.43 ± 0.18 | 0.13 – 1.48 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2009 | Pregnant women | 29[¤] | 243 | LOQ = 0.09 | 100 | 0.38 ± 0.17 | 0.12 – 1.70 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2010 | Pregnant women | 29[¤] | 246 | LOQ = 0.09 | 99 | 0.34 ± 0.16 | <LOQ – 1.47 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2011 | Pregnant women | 29[¤] | 284 | LOQ = 0.09 | 100 | 0.36 ± 0.21 | <LOQ – 2.67 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2012 | Pregnant women | 29[¤] | 288 | LOQ = 0.09 | 100 | 0.31 ± 0.15 | (0.12 – 1.08 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2013 | Pregnant women | 29[¤] | 228 | LOQ = 0.09 | 97 | 0.33 ± 0.25 | <LOQ – 2.87 | Bjerregaard-Olesen et al. 2016 |
| Germany | 1982-2009 | Adult males | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Germany | 1982-2009 | Adult females | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Norway | 1979 | Adult men | 42 ± 6 | 53 | LOD = 0,03 | 91 | 0,1 ± 0 | < LOD – 0,2 | (Nost et al., 2014) |
| Norway | 1986 | Adult men | 49 ± 6 | 53 | LOD = 0,03 | 100 | 0,3 ± 0,1 | 0,1 – 0,7 | (Nost et al., 2014) |
| Norway | 1994 | Adult men | 57 ± 6 | 53 | LOD = 0,03 | 100 | 0,5 ± 0,2 | 0,1 – 1,1 | (Nost et al., 2014) |
| Norway | 2001 | Adult men | 64 ± 6 | 53 | LOD = 0,03 | 100 | 0,7 ± 0,3 | 0,2 – 1,7 | (Nost et al., 2014) |
| Norway | 2007 | Adult men | 70 ± 6 | 53 | LOD = 0,03 | 100 | 0,8 ± 0,3 | 0,2 – 1,8 | (Nost et al., 2014) |
| Sweden | 1987-1990 | Adult women | 47 ± 4 | 24 | LOD = 0,1 | 100 | 0,11 ± 0,05[*] | 0,05 – 0,21 | (Axmon et al., 2014) |
| Sweden | 1991-2000 | Adult women | 46 ± 5 | 30 | LOD = 0,1 | 100 | 0,17 ± 0,08[*] | 0,05 – 0,42 | Axmon et al. 2014 |
| Sweden | 2001-2007 | Adult women | 49 ± 5 | 26 | LOD = 0,1 | 100 | 0,31 ± 0,15[*] | 0,11 – 0,59 | Axmon et al. 2014 |
| Sweden | 1997-2012 | Adult women | 27-31 | 9-10 | LOQ = 0,03 | See Table I-1 below | | | (Gebbink et al., 2015) |
| Sweden | 2010 | Young men | N.A. | 306 | LOD = 0,01 | N.A. | 0,29[¤] | N.A. | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | N.A. | 97 | LOD = 0,01 | N.A. | 0,20[¤] | N.A. | (Jönsson et al., 2014) |
| Sweden | 1996-1999 | Adult women | 28,6 | 147 | LOD = 0,05 | 95 | 0,20 ± 0,009 | < LOD – 0,72 | (Gyllenhammar et al., 2015) |
| Sweden | 2008-2011 | Adult women | 30,2 | 149 | LOD = 0,05 | 98 | 0,28 ± 0,012 | < LOD – 1,1 | (Gyllenhammar et al., 2015) |
| Sweden | 2001-2004 | Elderly men and women | 70 | 579 | LOQ = 0,22 | 90 | 0.35 ± 0.15 | < LOQ – 1,3 | Stubleski et al. 2016 |
| Sweden | 2006-2009 | Elderly men and women | 75 | 579 | LOQ = 0,22 | 100 | 0.54 ± 0.34 | < LOQ – 3,9 | Stubleski et al. 2016 |
| Sweden | 2011-2014 | Elderly men and women | 80 | 579 | LOQ = 0,22 | 99 | 0.40 ± 0.26 | 0,07 – 2,0 | Stubleski et al. 2016 |

[*] = Geometic mean, [#] = Arithmetic mean, [¤] = Median, N.A. = information not retrieved.

**C11-PFCA in serum – temporal trend studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Denmark | 2008 | Pregnant women | 29[¤] | 244 | LOQ = 0,15 | 95 | 0,45 ± 0,29[*] | <LOQ – 2,15 | (Bjerregaard-Olesen et al., 2016) |
| Denmark | 2009 | Pregnant women | 29[¤] | 243 | LOQ = 0,15 | 91 | 0,37 ± 0,37[*] | <LOQ – 1,71 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2010 | Pregnant women | 29[¤] | 246 | LOQ = 0,15 | 86 | 0,32 ± 0,19[*] | <LOQ – 1,19 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2011 | Pregnant women | 29[¤] | 284 | LOQ = 0,15 | 88 | 0,38 ± 0,30[*] | <LOQ – 2,47 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2012 | Pregnant women | 29[¤] | 288 | LOQ = 0,15 | 81 | 0,29 ± 0,23[*] | <LOQ – 1,94 | Bjerregaard-Olesen et al. 2016 |
| Denmark | 2013 | Pregnant women | 29[¤] | 228 | LOQ = 0,15 | 84 | 0,33 ± 0,23[*] | <LOQ – 1,63 | Bjerregaard-Olesen et al. 2016 |
| Germany | 1982-2009 | Adult males | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Germany | 1982-2009 | Adult females | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Norway | 1979 | Adult men | 42 ± 6 | 53 | LOD = 0,04 | 87 | 0,1 ± 0,1 | < LOD – 0,7 | (Nost et al., 2014) |
| Norway | 1986 | Adult men | 49 ± 6 | 53 | LOD = 0,04 | 100 | 0,9 ± 0,5 | 0,3 – 3,0 | (Nost et al., 2014) |
| Norway | 1994 | Adult men | 57 ± 6 | 53 | LOD = 0,04 | 100 | 0,9 ± 0,5 | 0,1 – 2,4 | (Nost et al., 2014) |
| Norway | 2001 | Adult men | 64 ± 6 | 53 | LOD = 0,04 | 100 | 1,3 ± 0,7 | 0,4 – 4,5 | (Nost et al., 2014) |
| Norway | 2007 | Adult men | 70 ± 6 | 53 | LOD = 0,04 | 100 | 1,4 ± 0,8 | 0,3 – 3,9 | (Nost et al., 2014) |
| Sweden | 1987-1990 | Adult women | 47 ± 4 | 24 | LOD = 0,1 | 100 | 0,17 ± 0,07[*] | 0,05 – 0,31 | (Axmon et al., 2014) |
| Sweden | 1991-2000 | Adult women | 46 ± 5 | 30 | LOD = 0,1 | 100 | 0,16 ± 0,08[*] | 0,05 – 0,38 | Axmon et al. 2014 |
| Sweden | 2001-2007 | Adult women | 49 ± 5 | 26 | LOD = 0,1 | 100 | 0,26 ± 0,14[*] | 0,05 – 0,68 | Axmon et al. 2014 |
| Sweden | 1997-2012 | Adult women | 27-31 | 9-10 | LOQ = 0,03 | See Table I-1 below | | | (Gebbink et al., 2015) |
| Sweden | 2010 | Young men | N.A | 306 | LOD = 0,04 | N.A | 0,14[¤] | N.A | (Jönsson et al., 2014) |
| Sweden | 2013 | Young men | N.A | 97 | LOD = 0,04 | N.A | 0,13[¤] | N.A | (Jönsson et al., 2014) |
| Sweden | 1996-1999 | Adult women | 28,6 | 147 | LOD = 0,05 | 66 | 0,14 ± 0,008 | < LOD – 0,58 | (Gyllenhammar et al., 2015) |
| Sweden | 2008-2011 | Adult women | 30,2 | 149 | LOD = 0,05 | 95 | 0,26 ± 0,012 | < LOD – 0,91 | (Gyllenhammar et al., 2015) |
| Sweden | 2001-2004 | Elderly men and women | 70 | 579 | LOQ = 0,22 | 82 | 0.35 ± 0.15 | < LOQ – 1,3 | Stubleski et al. 2016 |
| Sweden | 2006-2009 | Elderly men and women | 75 | 579 | LOQ = 0,22 | 91 | 0.54 ± 0.34 | < LOQ – 3,9 | Stubleski et al. 2016 |
| Sweden | 2011-2014 | Elderly men and women | 80 | 579 | LOQ = 0,22 | 92 | 0.40 ± 0.26 | 0,07 – 2,0 | Stubleski et al. 2016 |

[*] = Geometric mean, [#] = Arithmetic mean, N.A. = information not retrieved.

## C12-PFCA in serum – temporal trend studies

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD/LOQ (ng/ml) | > LOD/LOQ (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Germany | 1982-2009 | Adult males | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Germany | 1982-2009 | Adult females | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Sweden | 1997-2012 | Adult women | 27-31 | 9-10 | LOQ = 0,03 | See Table I-1 below | | | (Gebbink et al., 2015) |
| Sweden | 1996-1999 | Adult women | 28,6 | 147 | LOD = 0,05 | 18 | - | < LOD – 0,22 | (Gyllenhammar et al., 2015) |
| Sweden | 2008-2011 | Adult women | 30,2 | 149 | LOD = 0,05 | 33 | - | < LOD – 0,25 | (Gyllenhammar et al., 2015) |

[*] = Geometric mean, [#] = Arithmetic mean, N.A. = information not retrieved.

## C13-PFCA in serum – temporal trend studies

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD (ng/ml) | > LOD (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Germany | 1982-2009 | Adult males | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Germany | 1982-2009 | Adult females | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Sweden | 1997-2012 | Adult women | 27-31 | 9-10 | LOQ = 0,03 | See Table I-1 below | | | (Gebbink et al., 2015) |

[*] = Geometric mean, [#] = Arithmetic mean, N.A. = information not retrieved.

## C14-PFCA in serum – temporal trend studies

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD (ng/ml) | > LOD (%) | Mean ± SD (ng/ml) | Range (min – max) (ng/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Germany | 1982-2009 | Adult males | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Germany | 1982-2009 | Adult females | N.A. | 3-7 | N.A. | See Figure I-1 and I-2 below | | | Yeung et al. 2013 |
| Sweden | 1997-2012 | Adult women | 27-31 | 9-10 | LOQ = 0,03 | See Table I-1 below | | | (Gebbink et al., 2015) |

[*] = Geometric mean, [#] = Arithmetic mean, N.A. = information not retrieved.

**C9-PFCA in breast milk – snapshot studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2010 | Nursing mothers | 30 | 50 | LOQ = 6 | < 70% | - | < LOQ – 15 | Lankova et al. 2013 |
| France | 2007 | Nursing mothers | 31,8 ± 3,4 | 48 | LOD = 50 | 2 | - | < LOD – 64 | (Antignac et al., 2013) |
| France | 2010 | Nursing mothers | N.A. | 30 | LOD = 7 | 0 | - | < LOD | (Kadar et al., 2011) |
| France | 2010-2013 | Nursing mothers | N.A. | 61 | LOQ = 50 | 0 | - | < LOD | (Cariou et al., 2015) |
| Spain | 2007 | Nursing mothers | 30-39 (range) | 10 | LOQ = 0,03 | 0 | - | < LOD | Karrman et al. 2010 |
| Spain | 2008 | Nursing mothers | N.A. | 200 | LOQ = 11,5 | 0 | - | < LOD | (Llorca et al., 2010) |
| Spain | 2014 | Nursing mothers | 33 ± 5 | 67 | LOQ = 10 | 6 | 41 ± 29 | 15 – 70 | (Motas Guzman et al., 2016) |
| Sweden | 2011 | Nursing mothers | N.A. | 13 | LOQ = 28 | 62 | - | < LOQ – 42 | Kärrman et al. 2013 |

* = Geometric mean, # = Arithmetic mean, N.A. = information not retrieved.

**C10-PFCA in breast milk – snapshot studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Czech Republic | 2010 | Nursing mothers | 30 | 50 | LOQ = 6 | < 70 | - | < LOQ – 12 | (Lankova et al., 2013) |
| France | 2007 | Nursing mothers | 31,8 ± 3,4 | 48 | LOD = 50 | 0 | - | < LOD | (Antignac et al., 2013) |
| France | 2010 | Nursing mothers | N.A. | 30 | LOD = 10 | 0 | - | < LOD | (Kadar et al., 2011) |
| France | 2010-2013 | Nursing mothers | N.A. | 61 | LOQ = 30 | 0 | - | < LOD | (Cariou et al., 2015) |
| Spain | 2007 | Nursing mothers | 30-39 (range) | 10 | LOQ = 0,06 | 0 | - | < LOD | (Karrman et al., 2010) |
| Spain | 2008 | Nursing mothers | N.A. | 200 | LOQ = 85 | 10 | 666 | 237 – 1095 | (Llorca et al., 2010) |
| Spain | 2014 | Nursing mothers | 33 ± 5 | 67 | LOQ = 12 | 4 | 24 ± 8 | < LOQ – 34 | (Motas Guzman et al., 2016) |
| Sweden | 2011 | Nursing mothers | N.A. | 13 | LOQ = 19 | 0 | - | - | (Kärrman et al., 2013) |

* = Geometric mean, # = Arithmetic mean, N.A. = information not retrieved.

**C11-PFCA in breast milk – snapshot studies**

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---------|------------------|------------------|------------------|---|-----------------|---------------|-------------------|---------------|-----------|
| France | 2007 | Nursing mothers | 31,8 ± 3,4 | 48 | LOD = 100 | 0 | - | < LOD | (Antignac et al., 2013) |
| France | 2010 | Nursing mothers | N.A. | 30 | LOD = 25 | 0 | - | - | (Kadar et al., 2011) |
| France | 2010-2013 | Nursing mothers | N.A | 61 | LOQ = 100 | 0 | - | - | (Cariou et al., 2015) |
| Spain | 2007 | Nursing mothers | 30-39 (range) | 10 | LOQ = 0,03 | 0 | - | - | Karrman et al. 2010 |
| Spain | 2014 | Nursing mothers | 33 ± 5 | 67 | LOQ = 15 | 10 | 29 ± 18 | 16 -57 | (Motas Guzman et al., 2016) |
| Sweden | 2011 | Nursing mothers | N.A. | 13 | LOQ = 32 | 0 | - | - | Kärrman et al. 2013 |

* = Geometic mean, # = Arithmetic mean, N.A. = information not 236etrieved

**C12-PFCA in breast milk – snapshot studies**

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---------|------------------|------------------|------------------|---|-----------------|---------------|-------------------|---------------|-----------|
| France | 2007 | Nursing mothers | 31,8 ± 3,4 | 48 | LOD = 50 | 0 | - | < LOD | (Antignac et al., 2013) |
| France | 2010 | Nursing mothers | N.A | 30 | LOD = 50 | 0 | - | - | (Kadar et al., 2011) |
| Spain | 2007 | Nursing mothers | 30-39 (range) | 10 | LOQ = 0,03 | 0 | - | - | Karrman et al. 2010 |
| Spain | 2014 | Nursing mothers | 33 ± 5 | 67 | LOQ = 15 | 3 | 21¤ | 16 – 26 | (Motas Guzman et al., 2016) |

¤ = median; N.A. = information not 236etrieved

**C13-PFCA in breast milk – snapshot studies**

| Country | Sampling year(s) | Study population | Age (mean ± SD) | N | LOD (ng/ml) | < LOD (%) | Mean ± SD (ng/ml) | Range (ng/ml) | Reference |
|---------|------------------|------------------|------------------|---|-------------|-----------|-------------------|---------------|-----------|
| Spain | 2007 | Nursing mothers | 30-39 (range) | 10 | LOQ = 0,03 | 0 | - | - | Karrman et al. 2010 |

N.A. = information not retreived

**C14-PFCA in breast milk – snapshot studies**

No data.

## C9-PFCA in breast milk – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Sweden | 2007-2015 | Nursing mothers | 26-31 | 14-21 | 2 pg/ml | 100 | See Figure I3 below | 3,4 - 51 | Nyberg et al. 2017 |

## C10-PFCA in breast milk – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Sweden | 2007-2015 | Nursing mothers | 26-31 | 14-21 | 2 pg/ml | 71-100 | See Figure I4 below | < LOD – 12 | Nyberg et al. 2017 |

## C11-PFCA in breast milk – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Sweden | 2007-2015 | Nursing mothers | 26-31 | 14-21 | 1 pg/ml | 86-100 | See Figure I5 below | < LOD – 8,6 | Nyberg et al. 2017 |

## C12-PFCA in breast milk – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Sweden | 2007-2015 | Nursing mothers | 26-31 | 14-21 | 1 pg/ml | 21-60 | See Figure I6 below | < LOD – 2,7 | Nyberg et al. 2017 |

## C13-PFCA – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Sweden | 2007-2015 | Nursing mothers | 26-31 | 14-21 | 0,8 pg/ml | 65-93 | See Figure I7 below | < LOD – 8,8 | Nyberg et al. 2017 |

## C14-PFCA – temporal trend studies

| Country | Sampling year(s) | Study population | Age (Mean ± SD) | N | LOD/LOQ (pg/ml) | > LOD/LOQ (%) | Mean ± SD (pg/ml) | Range (pg/ml) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Sweden | 2007-2015 | Nursing mothers | 26-31 | 14-21 | 0,8 pg/ml | 36-67 | See Figure I8 below | < LOD – 7,0 | Nyberg et al. 2017 |
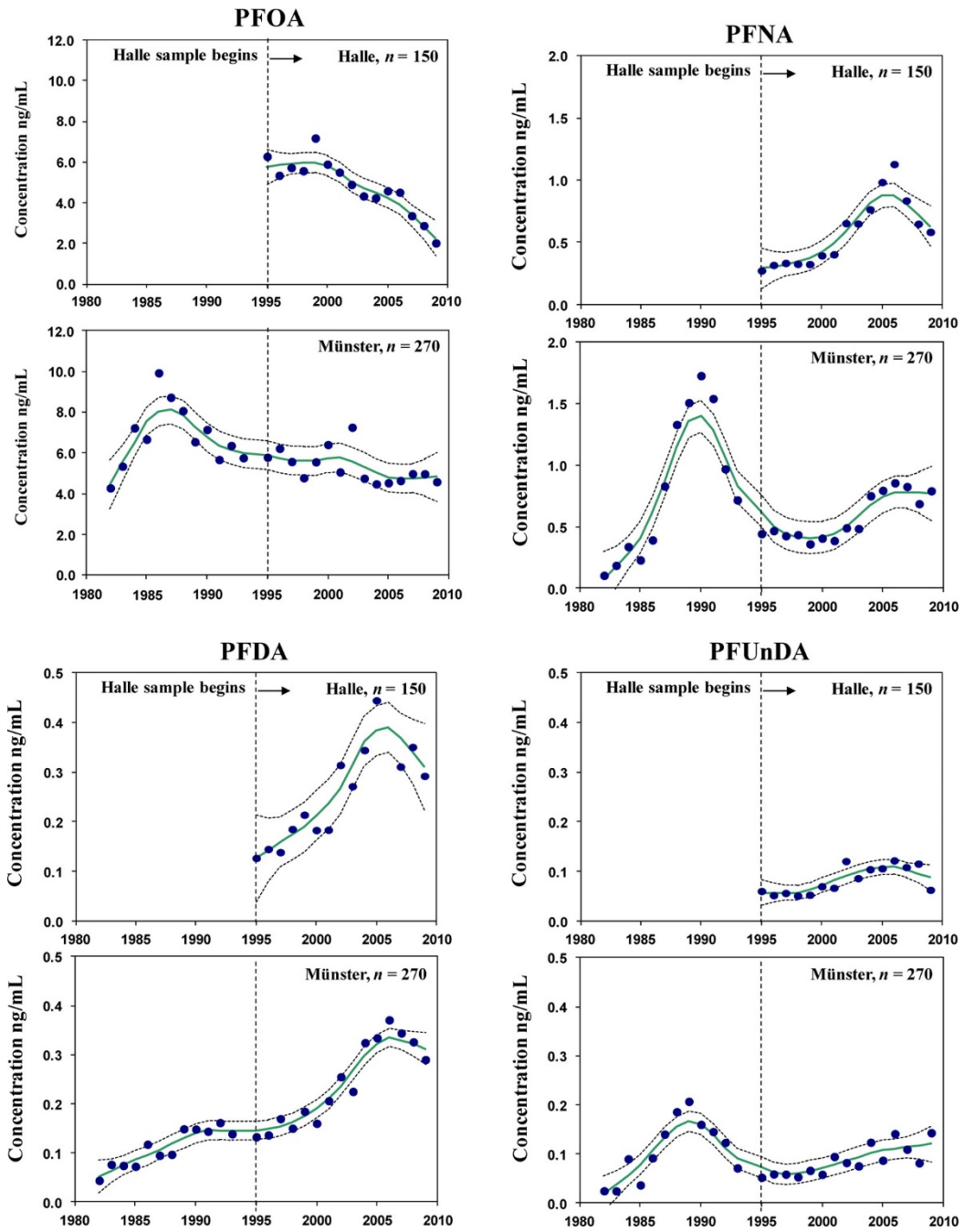
*Figure I- 1. Concentrations of C8-C11 PFCA (ng/ml) in human plasma between 1982 and 2009 in the German cities Halle and Münster (from (Yeung et al., 2013)).*
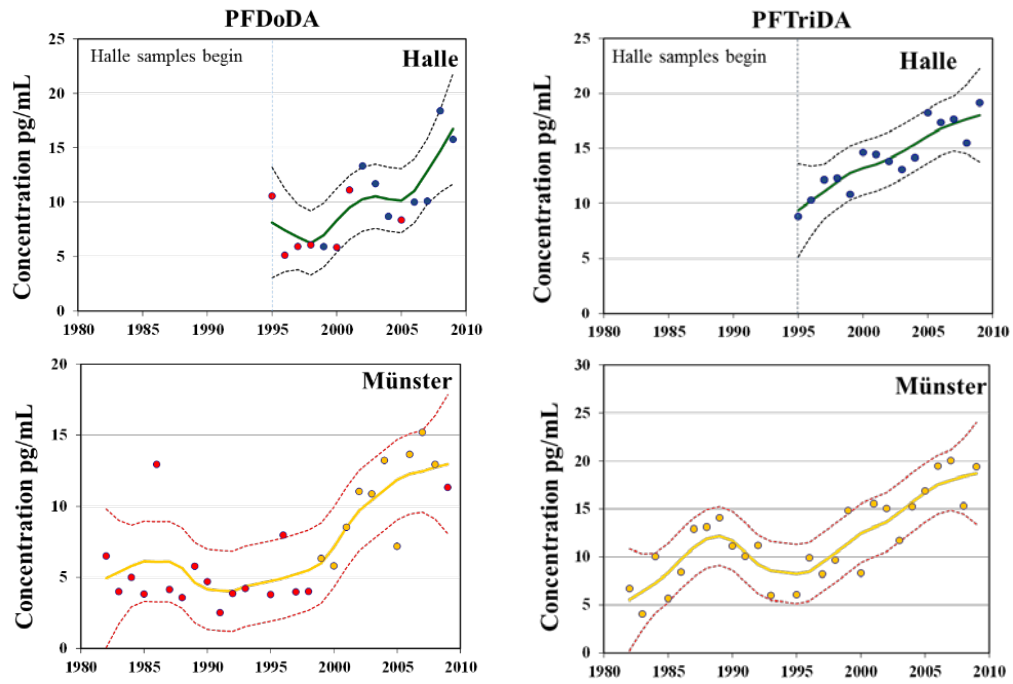
*Figure I- 2. Concentrations of C8-C11 PFCA (ng/ml) in human plasma between 1982 and 2009 in the German cities Halle and Münster. (Young, 2017) (data based on (Yeung et al., 2013)).*
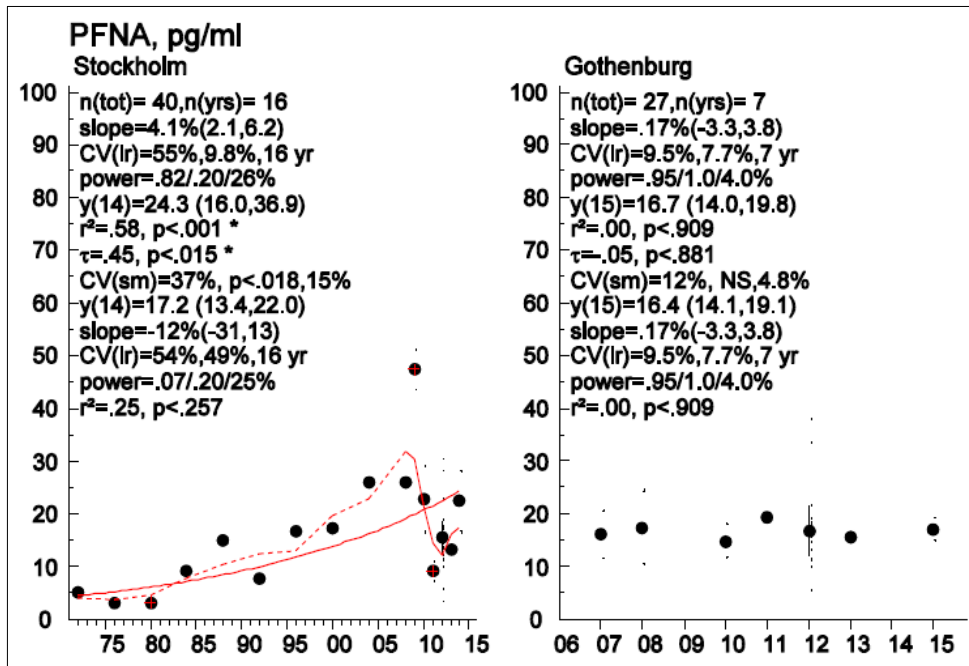
*Figure I- 3. Temporal trend of C9-PFCA (pg/ml) in human milk from Stockholm (1972-2014) and Gothenburg (2007-2015). From Nyberg et al. 2017.*
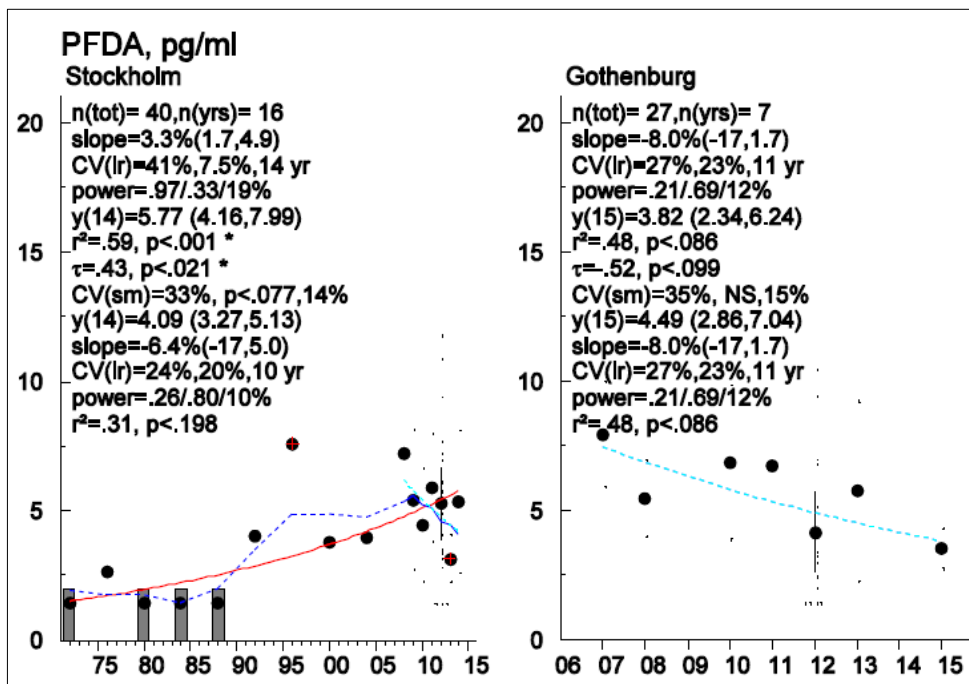


*Figure I- 4. Temporal trend of C10-PFCA (pg/ml) in human milk from Stockholm (1972-2014) and Gothenburg (2007-2015). The grey bars represent years where all values are below LOQ. From Nyberg et al. 2017.*
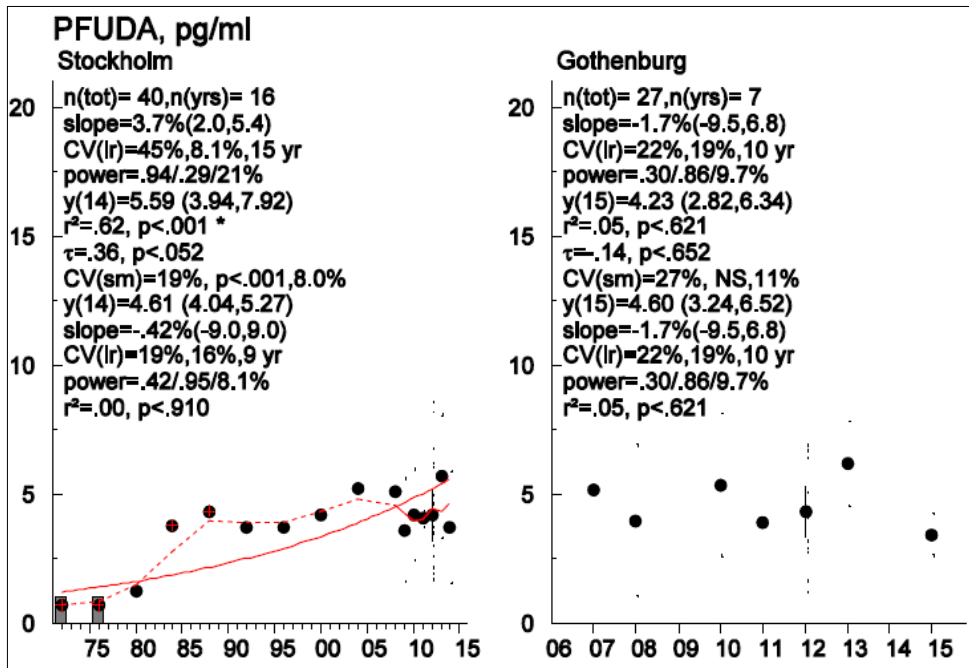
*Figure I- 5. Temporal trend of C11-PFCA (pg/ml) in human milk from Stockholm (1972-2014) and Gothenburg (2007-2015). The grey bars represent years where all values are below LOQ. From Nyberg et al. 2017.*
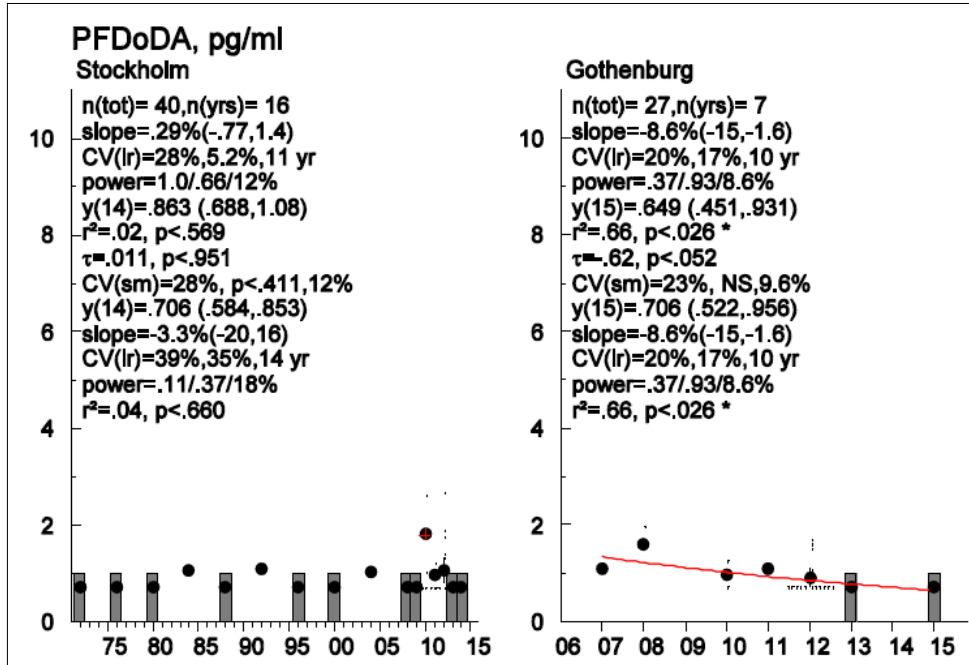


*Figure I- 6. Temporal trend of C12-PFCA (pg/ml) in human milk from Stockholm (1972-2014) and Gothenburg (2007-2015). The grey bars represent years where all values are below LOQ. From Nyberg et al. 2017.*
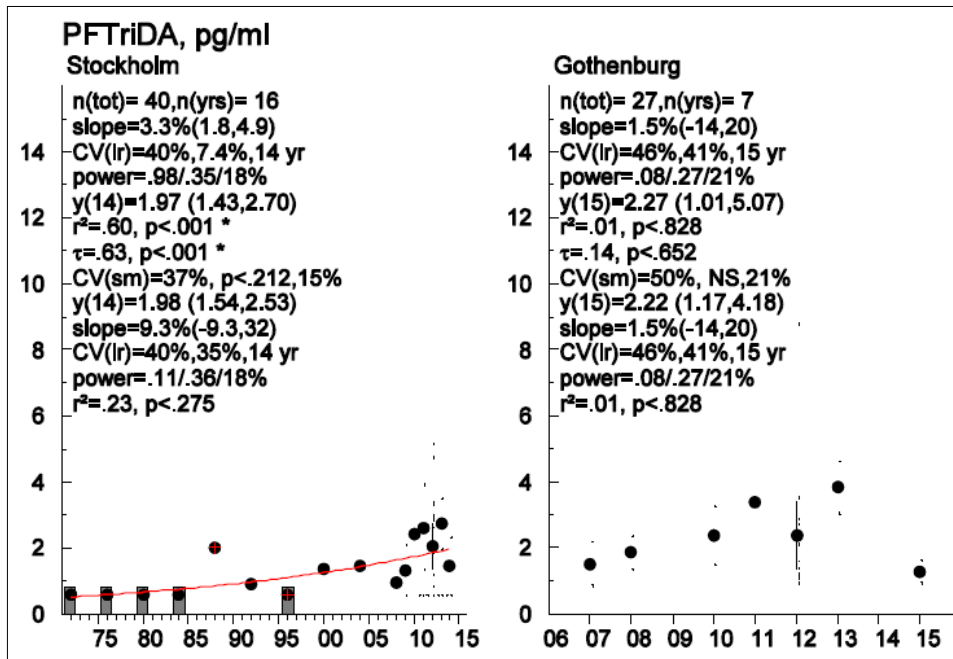
*Figure I- 7. Temporal trend of C13-PFCA (pg/ml) in human milk from Stockholm (1972-2014) and Gothenburg (2007-2015). The grey bars represent years where all values are below LOQ. From Nyberg et al. 2017.*



*Figure I- 8. Temporal trend of C14-PFCA (pg/ml) in human milk from Stockholm (1972-2014) and Gothenburg (2007-2015). The grey bars represent years where all values are below LOQ. From Nyberg et al. 2017.*

**Table 1.** Concentrations of perfluoroalkyl carboxylic acids (ng/g) in pooled blood serum samples from primiparous women in Sweden.[1]

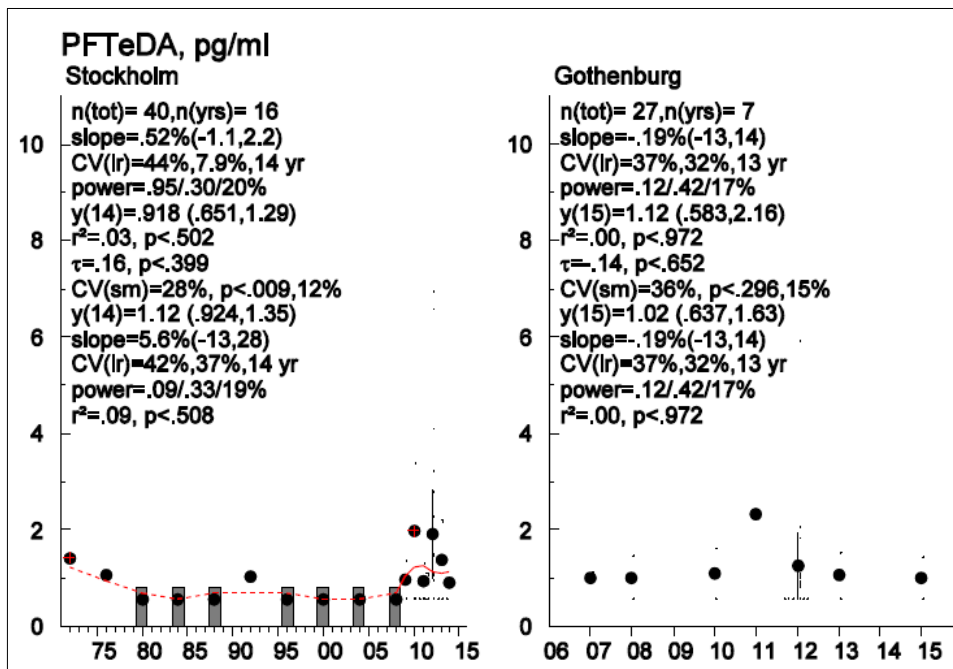| Year | C4-PFCA | C5-PFCA | C6-PFCA | C7-PFCA | br-C8-PFCA | lin-C8-PFCA | tot-C8-PFCA | C9-PFCA | C10-PFCA | C11-PFCA | C12-PFCA | C13-PFCA | C14-PFCA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1997 | <0.3[2] | <0.1 | <0.05 | 0.031 | 0.05 | 2.25 | 2.30 | 0.29 | 0.14 | 0.14 | 0.026 | 0.038 | <0.002 |
| 1997 | <0.3 | <0.1 | <0.05 | 0.038 | 0.07 | 2.53 | 2.60 | 0.34 | 0.18 | 0.14 | 0.025 | 0.022 | <0.002 |
| 1997 | <0.3 | <0.1 | <0.05 | 0.023 | 0.04 | 2.19 | 2.23 | 0.26 | 0.14 | 0.11 | 0.017 | 0.016 | <0.002 |
| 1998 | <0.3 | <0.1 | <0.05 | 0.034 | 0.06 | 2.47 | 2.53 | 0.37 | 0.18 | 0.17 | 0.018 | 0.021 | <0.002 |
| 1998 | <0.3 | <0.1 | <0.05 | 0.022 | 0.04 | 2.58 | 2.62 | 0.39 | 0.23 | 0.21 | 0.031 | 0.028 | <0.002 |
| 1998 | <0.3 | <0.1 | <0.05 | 0.040 | 0.05 | 2.33 | 2.38 | 0.36 | 0.19 | 0.14 | 0.016 | 0.019 | <0.002 |
| 2000 | <0.3 | <0.1 | <0.05 | 0.019 | 0.04 | 2.59 | 2.62 | 0.39 | 0.19 | 0.17 | 0.023 | 0.026 | <0.002 |
| 2000 | <0.3 | <0.1 | <0.05 | 0.028 | 0.05 | 2.64 | 2.70 | 0.39 | 0.20 | 0.23 | 0.030 | 0.037 | <0.002 |
| 2000 | <0.3 | <0.1 | <0.05 | 0.043 | 0.05 | 2.54 | 2.59 | 0.31 | 0.17 | 0.16 | 0.020 | 0.027 | <0.002 |
| 2002 | <0.3 | <0.1 | <0.05 | 0.105 | 0.05 | 2.85 | 2.91 | 0.45 | 0.24 | 0.22 | 0.031 | 0.037 | <0.002 |
| 2002 | <0.3 | <0.1 | <0.05 | 0.045 | 0.03 | 2.64 | 2.68 | 0.43 | 0.24 | 0.23 | 0.027 | 0.021 | <0.002 |
| 2002 | <0.3 | <0.1 | <0.05 | 0.050 | 0.04 | 2.84 | 2.88 | 0.41 | 0.23 | 0.18 | 0.024 | 0.022 | <0.002 |
| 2004 | <0.3 | <0.1 | <0.05 | 0.044 | 0.04 | 2.31 | 2.35 | 0.38 | 0.20 | 0.18 | 0.026 | 0.030 | <0.002 |
| 2004 | <0.3 | <0.1 | <0.05 | 0.039 | 0.03 | 2.47 | 2.50 | 0.66 | 0.38 | 0.30 | 0.040 | 0.046 | <0.002 |
| 2004 | <0.3 | <0.1 | <0.05 | 0.029 | 0.02 | 2.67 | 2.69 | 0.56 | 0.37 | 0.29 | 0.038 | 0.044 | <0.002 |
| 2006 | <0.3 | <0.1 | <0.05 | 0.058 | 0.04 | 2.08 | 2.12 | 0.54 | 0.25 | 0.21 | 0.026 | 0.022 | <0.002 |
| 2006 | <0.3 | <0.1 | <0.05 | 0.032 | 0.03 | 2.18 | 2.22 | 0.52 | 0.29 | 0.25 | 0.034 | 0.045 | <0.002 |
| 2006 | <0.3 | <0.1 | <0.05 | 0.038 | 0.02 | 1.99 | 2.01 | 0.46 | 0.24 | 0.24 | 0.029 | 0.032 | <0.002 |
| 2008 | <0.3 | <0.1 | <0.05 | 0.038 | 0.03 | 1.65 | 1.67 | 0.56 | 0.26 | 0.25 | 0.036 | 0.049 | <0.002 |
| 2008 | <0.3 | <0.1 | <0.05 | 0.014 | 0.02 | 1.82 | 1.84 | 0.51 | 0.28 | 0.24 | 0.031 | 0.039 | <0.002 |
| 2008 | <0.3 | <0.1 | <0.05 | 0.014 | 0.02 | 2.19 | 2.21 | 0.72 | 0.39 | 0.26 | 0.035 | 0.039 | <0.002 |
| 2010 | <0.3 | <0.1 | <0.05 | 0.014 | 0.01 | 1.61 | 1.62 | 0.63 | 0.31 | 0.28 | 0.032 | 0.038 | <0.002 |
| 2010 | <0.3 | <0.1 | <0.05 | 0.030 | 0.02 | 1.93 | 1.95 | 0.75 | 0.38 | 0.31 | 0.040 | 0.047 | <0.002 |
| 2010 | <0.3 | <0.1 | <0.05 | 0.021 | 0.02 | 1.79 | 1.80 | 0.60 | 0.38 | 0.31 | 0.042 | 0.042 | <0.002 |
| 2012 | <0.3 | <0.1 | <0.05 | 0.026 | 0.01 | 1.28 | 1.29 | 0.48 | 0.27 | 0.23 | 0.027 | 0.030 | <0.002 |
| 2012 | <0.3 | <0.1 | <0.05 | 0.030 | 0.02 | 1.71 | 1.73 | 0.56 | 0.27 | 0.25 | 0.031 | 0.030 | <0.002 |
| 2012 | <0.3 | <0.1 | <0.05 | 0.022 | 0.01 | 1.40 | 1.41 | 0.54 | 0.29 | 0.27 | 0.033 | 0.038 | <0.002 |

[1] Reported concentrations are the average of duplicate analyses. [2] Value indicating the method quantification limit (MQL).

# References

3M. Co (2001): Hydrolysis Reactions of Perfluorooctanoic Acid (PFOA). 3M Lab Request Number E00-1851. U.S. Environmental Protection Agency Administrative Record 226-1030a090

Agency S.C. (2013): Harmonized Classification and Labeling Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2. Substance Name: 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononanoic acid and its sodium and ammonium salts. . https://echa.europa.eu/documents/10162/d34820f9-bcc7-44f9-b0bc-f5353258a66e (last accessed 2017-08-08)

Agency" S.C. (2015): Proposal for Harmonised Classification and Labelling Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2. International Chemical Identification: Nonadecaflourodecanoic Acid (PFDA) and its ammonium and sodium salts. . https://echa.europa.eu/documents/10162/3e08ce73-4b1a-444f-ac15-2c130616341c (last accessed 2017-08-08)

Ahrens L. (2011): Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. J Environ Monit 13 (1), 20-31. DOI: 10.1039/c0em00373e

Ahrens L., Felizeter S., Sturm R., Xie Z., and Ebinghaus R. (2009a): Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany. Mar Pollut Bull 58 (9), 1326-1333. DOI: 10.1016/j.marpolbul.2009.04.028

Ahrens L., Gerwinski W., Theobald N., and Ebinghaus R. (2010a): Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water. Mar Pollut Bull 60 (2), 255-260. DOI: 10.1016/j.marpolbul.2009.09.013

Ahrens L., Siebert U., and Ebinghaus R. (2009b): Temporal trends of polyfluoroalkyl compounds in harbor seals (Phoca vitulina) from the German Bight, 1999-2008. Chemosphere 76 (2), 151-158. DOI: 10.1016/j.chemosphere.2009.03.053

Ahrens L., Taniyasu S., Yeung L.W., Yamashita N., Lam P.K., and Ebinghaus R. (2010b): Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. Chemosphere 79 (3), 266-272. DOI: 10.1016/j.chemosphere.2010.01.045

Aldrich: Handbook of fine Chemicals and Laboratory Equipment 2007-2008

Antignac J.P., Veyrand B., Kadar H., Marchand P., Oleko A., Le Bizec B., and Vandentorren S. (2013): Occurrence of perfluorinated alkylated substances in breast milk of French women and relation with socio-demographical and clinical parameters: results of the ELFE pilot study. Chemosphere 91 (6), 802-808. DOI: 10.1016/j.chemosphere.2013.01.088

Armstrong D.L., Lozano N., Rice C.P., Ramirez M., and Torrents A. (2016): Temporal trends of perfluoroalkyl substances in limed biosolids from a large municipal water resource recovery facility. Journal of Environmental Management 165, 88-95. DOI: https://doi.org/10.1016/j.jenvman.2015.09.023

Arp H.P., Niederer C., and Goss K.U. (2006): Predicting the partitioning behavior of various highly fluorinated compounds. Environ.Sci Technol. 40 (23), 7298-7304. DOI: 10.1021/es101384w

Arvaniti O.S., Andersen H.R., Thomaidis N.S., and Stasinakis A.S. (2014): Sorption of Perfluorinated Compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment. Chemosphere 111 (0), 405-411. DOI: 10.1016/j.chemosphere.2014.03.087

Arvaniti O.S. and Stasinakis A.S. (2015): Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. Science of The Total Environment 524–525 (0), 81-92. DOI: 10.1016/j.scitotenv.2015.04.023

Arvaniti O.S., Ventouri E.I., Stasinakis A.S., and Thomaidis N.S. (2012): Occurrence of different classes of perfluorinated compounds in Greek wastewater treatment plants and determination of their solid-water distribution coefficients. J Hazard Mater 239-240, 24-31. DOI: 10.1016/j.jhazmat.2012.02.015

ATSDR (2015): Draft toxicological profile for perfluoroalkyls. , U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES. https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf (last accessed 2017-08-08)

Axmon A., Axelsson J., Jakobsson K., Lindh C.H., and Jonsson B.A. (2014): Time trends between 1987 and 2007 for perfluoroalkyl acids in plasma from Swedish women. Chemosphere 102, 61-67. DOI: 10.1016/j.chemosphere.2013.12.021

Ballschmiter K. (1992): Transport and fate of organic compounds in the global environment. Angewandte Chemie International Edition in English 31 (5), 487-515

Barmentlo S.H., Stel J.M., van Doorn M., Eschauzier C., de Voogt P., and Kraak M.H.S. (2015): Acute and chronic toxicity of short chained perfluoroalkyl substances to Daphnia magna. Environmental Pollution 198 (0), 47-53. DOI: 10.1016/j.envpol.2014.12.025

Bartolome M., Gallego-Pico A., Cutanda F., Huetos O., Esteban M., Perez-Gomez B., Bioambient.es, and Castano A. (2017): Perfluorinated alkyl substances in Spanish adults: Geographical distribution and determinants of exposure. Sci Total Environ 603-604, 352-360. DOI: 10.1016/j.scitotenv.2017.06.031

Benskin J.P., Muir D.C., Scott B.F., Spencer C., De Silva A.O., Kylin H., Martin J.W., Morris A., Lohmann R., Tomy G., Rosenberg B., Taniyasu S., and Yamashita N. (2012): Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. Environ Sci Technol 46 (11), 5815-5823. DOI: 10.1021/es300578x

Benskin J.P., Phillips V., St Louis V.L., and Martin J.W. (2011): Source elucidation of perfluorinated carboxylic acids in remote alpine lake sediment cores. Environ Sci Technol 45 (17), 7188-7194. DOI: 10.1021/es2011176

Berg V., Nost T.H., Huber S., Rylander C., Hansen S., Veyhe A.S., Fuskevag O.M., Odland J.O., and Sandanger T.M. (2014): Maternal serum concentrations of per- and polyfluoroalkyl substances and their predictors in years with reduced production and use. Environ Int 69, 58-66. DOI: 10.1016/j.envint.2014.04.010

BIG Database. https://www.big.be/nl-nl/

Bischel H.N., Macmanus-Spencer L.A., Zhang C., and Luthy R.G. (2011): Strong associations of short-chain perfluoroalkyl acids with serum albumin and investigation of binding mechanisms. Environ Toxicol Chem 30 (11), 2423-2430. DOI: 10.1002/etc.647

Bjerregaard-Olesen C., Bach C.C., Long M., Ghisari M., Bossi R., Bech B.H., Nohr E.A., Henriksen T.B., Olsen J., and Bonefeld-Jorgensen E.C. (2016): Time trends of perfluorinated alkyl acids in serum from Danish pregnant women 2008-2013. Environ Int 91, 14-21. DOI: 10.1016/j.envint.2016.02.010

Blom C. and Hanssen L. (2015): Analysis of per- and polyfluorinated substances in articles, date: 2015. Nordisk Ministerråd, Copenhagen. DOI: 10.6027/NA2015-911

Borg D. (2013): Tissue distribution studies and risk assessment of perfluoroalkylated and polyfluoroalkylated substances (PFASs). Karolinska Institutet

Borg D. and Håkansson H. (2012): Environmental and health risk assessment of perfluoroalkylated and polyfluoroalkylated substances (PFASs) in Sweden. 6513

Borg D. and Ivarsson J. (2017): Analysis of PFASs and TOF in products. Nordisk Ministerråd, Copenhagen. ISBN: 978-92-893-5068-6. DOI: 10.6027/TN2017-543

Bossi R., Dam M., and Riget F.F. (2015): Perfluorinated alkyl substances (PFAS) in terrestrial environments in Greenland and Faroe Islands. Chemosphere 129, 164-169. DOI: 10.1016/j.chemosphere.2014.11.044

Buck R.C., Franklin J., Berger U., Conder J.M., Cousins I.T., de Voogt P., Astrup Jensen A., Kannan K., Mabury S.A., and van Leeuwen S.P. (2011):

Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins. Integr Environ Assess Manag 7 (4), 513-541. DOI: 10.1002/ieam.258

Butt C.M., Berger U., Bossi R., and Tomy G.T. (2010): Levels and trends of poly- and perfluorinated compounds in the arctic environment. Sci Total Environ 408 (15), 2936-2965. DOI: 10.1016/j.scitotenv.2010.03.015

Butt C.M., Muir D.C.G., and Mabury S.A. (2014): Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: A review. Environmental Toxicology and Chemistry 33 (2), 243-267. DOI: 10.1002/etc.2407

Bytingsvik J., van Leeuwen S.P., Hamers T., Swart K., Aars J., Lie E., Nilsen E.M., Wiig O., Derocher A.E., and Jenssen B.M. (2012): Perfluoroalkyl substances in polar bear mother-cub pairs: a comparative study based on plasma levels from 1998 and 2008. Environ Int 49, 92-99. DOI: 10.1016/j.envint.2012.08.004

Cai M., Xie Z., Moller A., Yin Z., Huang P., Cai M., Yang H., Sturm R., He J., and Ebinghaus R. (2012): Polyfluorinated compounds in the atmosphere along a cruise pathway from the Japan Sea to the Arctic Ocean. Chemosphere 87 (9), 989-997. DOI: 10.1016/j.chemosphere.2011.11.010

Cariou R., Veyrand B., Yamada A., Berrebi A., Zalko D., Durand S., Pollono C., Marchand P., Leblanc J.C., Antignac J.P., and Le Bizec B. (2015): Perfluoroalkyl acid (PFAA) levels and profiles in breast milk, maternal and cord serum of French women and their newborns. Environ Int 84, 71-81. DOI: 10.1016/j.envint.2015.07.014

Casal P., Zhang Y., Martin J.W., Pizarro M., Jimenez B., and Dachs J. (2017): The Role of Snow Deposition of Perfluoroalkylated Substances at Coastal Livingston Island (Maritime Antarctica). Environ Sci Technol. DOI: 10.1021/acs.est.7b02521

Chen H., Reinhard M., Nguyen V.T., and Gin K.Y.-H. (2016): Reversible and irreversible sorption of perfluorinated compounds (PFCs) by sediments of an urban reservoir. Chemosphere 144, 1747-1753. DOI: 10.1016/j.chemosphere.2015.10.055

Chengelis C.P., Kirkpatrick J.B., Myers N.R., Shinohara M., Stetson P.L., and Sved D.W. (2009): Comparison of the toxicokinetic behavior of perfluorohexanoic acid (PFHxA) and nonafluorobutane-1-sulfonic acid (PFBS) in cynomolgus monkeys and rats. Reprod Toxicol 27 (3–4), 400-406. DOI: 10.1016/j.reprotox.2009.01.013

Clara M., Scharf S., Weiss S., Gans O., and Scheffknecht C. (2008): Emissions of perfluorinated alkylated substances (PFAS) from point sources-identification of relevant branches. Water Sci Technol. 58 (1), 59-66. DOI: 10.2166/wst.2008.641

D'eon J.C. and Mabury S.A. (2007): Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): exploring routes of human contamination. Environ.Sci Technol. 41 (13), 4799-4805. DOI: 10.1021/es070126x

D'eon J.C. and Mabury S.A. (2011a): Exploring indirect sources of human exposure to perfluoroalkyl carboxylates (PFCAs): evaluating uptake, elimination, and biotransformation of polyfluoroalkyl phosphate esters (PAPs) in the rat. Environ Health Perspect 119 (3), 344-350. DOI: 10.1289/ehp.1002409

D'eon J.C. and Mabury S.A. (2011b): Is indirect exposure a significant contributor to the burden of perfluorinated acids observed in humans? Environ Sci Technol 45 (19), 7974-7984. DOI: 10.1021/es200171y

Das K.P., Grey B.E., Rosen M.B., Wood C.R., Tatum-Gibbs K.R., Zehr R.D., Strynar M.J., Lindstrom A.B., and Lau C. (2015): Developmental toxicity of perfluorononanoic acid in mice. Reprod Toxicol 51, 133-144. DOI: 10.1016/j.reprotox.2014.12.012

Dasu K. and Lee L.S. (2016): Aerobic biodegradation of toluene-2,4-di(8:2 fluorotelomer urethane) and hexamethylene-1,6-di(8:2 fluorotelomer urethane) monomers in soils. Chemosphere 144, 2482-2488. DOI: 10.1016/j.chemosphere.2015.11.021

Dasu K., Lee L.S., Turco R.F., and Nies L.F. (2013): Aerobic biodegradation of 8:2 fluorotelomer stearate monoester and 8:2 fluorotelomer citrate triester in forest soil. Chemosphere 91 (3), 399-405. DOI: 10.1016/j.chemosphere.2012.11.076

Dasu K., Liu J., and Lee L.S. (2012): Aerobic soil biodegradation of 8:2 fluorotelomer stearate monoester. Environ Sci Technol 46 (7), 3831-3836. DOI: 10.1021/es203978g

Dauchy X., Boiteux V., Bach C., Rosin C., and Munoz J.F. (2017): Per- and polyfluoroalkyl substances in firefighting foam concentrates and water samples collected near sites impacted by the use of these foams. Chemosphere 183, 53-61. DOI: 10.1016/j.chemosphere.2017.05.056

Denys S., Fraize-Frontier S., Moussa O., Le Bizec B., Veyrand B., and Volatier J.L. (2014): Is the fresh water fish consumption a significant determinant of the internal exposure to perfluoroalkylated substances (PFAS)? Toxicol Lett 231 (2), 233-238. DOI: 10.1016/j.toxlet.2014.07.028

Deutsches Institut für Normung e.V. (DIN) (2011): DIN 38407-42: 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)

DeWitt J.C. (2015). Toxicological effects of perfluoroalkyl and polyfluoroalkyl substances. Humana Press. ISBN: 978-3-319-15517-3

Ding L., Hao F., Shi Z., Wang Y., Zhang H., Tang H., and Dai J. (2009): Systems biological responses to chronic perfluorododecanoic acid exposure by integrated metabonomic and transcriptomic studies. J Proteome Res 8 (6), 2882-2891. DOI: 10.1021/pr9000256

Dinglasan M.J., Ye Y., Edwards E.A., and Mabury S.A. (2004): Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. Environ.Sci Technol. 38 (10), 2857-2864. DOI: 10.1021/es0350177

Ebnesajjad S. (2013): Introduction to Fluoropolymers - Material, Technology, and Applications. Elsevier

Ehresman D.J., Froehlich J.W., Olsen G.W., Chang S.C., and Butenhoff J.L. (2007): Comparison of human whole blood, plasma, and serum matrices for the determination of perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other fluorochemicals. Environ Res 103 (2), 176-184. DOI: 10.1016/j.envres.2006.06.008

Ellis D., Mabury S., Martin J., and Stock N. (2004a): Environmental Review of Other (non-C8) Perfluorocarboxylic Acids (PFCAs). Prepared under contract for Existing Substances Branch, Environment Canada. Gatineau (QC)

Ellis D.A., Martin J.W., De Silva A.O., Mabury S.A., Hurley M.D., Sulbaek Andersen M.P., and Wallington T.J. (2004b): Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. Environ.Sci Technol. 38 (12), 3316-3321. DOI: 10.1021/es049860w

Ellis D.A., Martin J.W., Mabury S.A., Hurley M.D., Andersen M.P., and Wallington T.J. (2003): Atmospheric lifetime of fluorotelomer alcohols. Environ Sci Technol 37 (17), 3816-3820. DOI: 10.1021/es034136j

Eriksson U., Roos A., Lind Y., Hope K., Ekblad A., and Karrman A. (2016): Comparison of PFASs contamination in the freshwater and terrestrial environments by analysis of eggs from osprey (Pandion haliaetus), tawny owl (Strix aluco), and common kestrel (Falco tinnunculus). Environ Res 149, 40-47. DOI: 10.1016/j.envres.2016.04.038

Eschauzier C., Raat K.J., Stuyfzand P.J., and De Voogt P. (2013): Perfluorinated alkylated acids in groundwater and drinking water: identification, origin and mobility. Sci Total Environ 458-460, 477-485. DOI: 10.1016/j.scitotenv.2013.04.066

European Chemicals Agency (2012a): Inclusion of substances of very high concern in the Candidate List ED/169/2012, date: 18.12.2012

European Chemicals Agency (2012b): Member State Committee support document for identification of henicosafluoroundecanoic acid as a substance of

very high concern because of its vPvB properties.
https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807dd43c

European Chemicals Agency (2012c): Member State Committee support document for identification of heptacosafluorotetradecanoic acid as a substance of very high concern because of its vPvB properties.
https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807dd647

European Chemicals Agency (2012d): Member State Committee support document for identification of pentacosafluorotridecanoic acid as a substance of very high concern because of its vPvB properties.
https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807dd5ad

European Chemicals Agency (2012e): Member State Committee support document for identification of tricosafluorododecanoic acid as a substance of very high concern because of its vPvB properties.
https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807dd4ef

European Chemicals Agency (2013): Member State Committee support document for identification of pentadecafluorooctanoic acid (PFOA) as a substance of very high concern because of its CMR and PBT properties.
https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1807db2ba

European Chemicals Agency (2015a): Background document to the Opinion on the Annex XV dossier proposing restrictions on Perfluorooctanoic acid (PFOA), PFOA salts and PFOA-related substances.
https://echa.europa.eu/documents/10162/61e81035-e0c5-44f5-94c5-2f53554255a8

European Chemicals Agency (2015b): Inclusion of substances of very high concern in the Candidate List for eventual includion in Annex XIV ED/79/2015, date: 15.12.2015

European Chemicals Agency (2015c): Member State Committee support document for identification of perfluorononan-1-oic acid and its sodium and ammoinium salts as a substance of very high concern because of its toxic for reproduction, PBT properties. https://echa.europa.eu/candidate-list-table/-/dislist/details/0b0236e1808db499

European Chemicals Agency, (2016). Annex XV restriction report, proposal for restriction. "Lead compounds-PVC" European Chemicals Agency Annankatu 18, Helsinki, Finland.

European Chemicals Agency (2016a): Guidance on information requirements and Chemical Safety Assessment Chapter R.16: Environmental exposure

assessment. https://echa.europa.eu/documents/10162/13632/information_requirements_r16_en.pdf/b9f0f406-ff5f-4315-908e-e5f83115d6af

European Chemicals Agency (2016b): Member State Committee support document for identification of nonadecafluorodecanoic acid and its sodium and ammoinium salts as a substance of very high concern because of its toxic for reproduction, PBT properties. https://echa.europa.eu/de/candidate-list-table/-/dislist/details/0b0236e180e22a1a

European Chemicals Agency (2017a): Guidance on Information Requirements and Chemical Safety Assessment. Chapter R.11: PBT Assessment. European Chemicals Agency. https://echa.europa.eu/documents/10162/13632/information_requirements_r11_en.pdf/a8cce23f-a65a-46d2-ac68-92fee1f9e54f

European Chemicals Agency (2017b): Inclusion of substances of very high concern in the Candidate List for eventual inclusion in Annex XIV D/01/2017

Fang X., Gao G., Xue H., Zhang X., and Wang H. (2012a): Exposure of perfluorononanoic acid suppresses the hepatic insulin signal pathway and increases serum glucose in rats. Toxicology 294 (2-3), 109-115. DOI: 10.1016/j.tox.2012.02.008

Fang X., Gao G., Xue H., Zhang X., and Wang H. (2012b): In vitro and in vivo studies of the toxic effects of perfluorononanoic acid on rat hepatocytes and Kupffer cells. Environ Toxicol Pharmacol 34 (2), 484-494. DOI: 10.1016/j.etap.2012.06.011

Fang X., Zhang L., Feng Y., Zhao Y., and Dai J. (2008): Immunotoxic effects of perfluorononanoic acid on BALB/c mice. Toxicol Sci 105 (2), 312-321. DOI: 10.1093/toxsci/kfn127

Faxneld S., Berger U., Helander B., Danielsson S., Miller A.A., Nyberg E., Persson J.-O., and Bignert A. (2016): Temporal trends and geographical differences of perfluoroalkyl acids in Baltic Sea herring and white-tailed sea eagle eggs in Sweden. Environmental Science & Technology 50 (23), 13070-13079. DOI: 10.1021/acs.est.6b03230

Felizeter S., McLachlan M.S., and De Voogt P. (2014): Root uptake and translocation of perfluorinated alkyl acids by three hydroponically grown crops. J Agric Food Chem 62 (15), 3334-3342. DOI: 10.1021/jf500674j

Frömel T. and Knepper T.P. (2010): Fluorotelomer ethoxylates: sources of highly fluorinated environmental contaminants part I: biotransformation. Chemosphere 80 (11), 1387-1392. DOI: 10.1016/j.chemosphere.2010.06.002

Fujii Y., Harada K.H., and Koizumi A. (2013): Occurrence of perfluorinated carboxylic acids (PFCAs) in personal care products and compounding agents. Chemosphere 93 (3), 538-544. DOI: 10.1016/j.chemosphere.2013.06.049

Gannon S.A., Johnson T., Nabb D.L., Serex T.L., Buck R.C., and Loveless S.E. (2011): Absorption, distribution, metabolism, and excretion of [1-14C]-perfluorohexanoate ([14C]-PFHx) in rats and mice. Toxicology 283 (1), 55-62. DOI: 10.1016/j.tox.2011.02.004

Gauthier S.A. and Mabury S.A. (2005): Aqueous photolysis of 8:2 fluorotelomer alcohol. Environ.Toxicol.Chem 24 (8), 1837-1846. DOI: 10.1897/04-591R.1

Gebbink W.A., Glynn A., and Berger U. (2015): Temporal changes (1997-2012) of perfluoroalkyl acids and selected precursors (including isomers) in Swedish human serum. Environ Pollut 199, 166-173. DOI: 10.1016/j.envpol.2015.01.024

Gellrich V., Stahl T., and Knepper T.P. (2012): Behavior of perfluorinated compounds in soils during leaching experiments. Chemosphere 87 (9), 1052-1056. DOI: 10.1016/j.chemosphere.2012.02.011

Glynn A., Benskin J.P., Lignell S., Gyllenhammar I., Aune M., Cantillana T., Darnerud P.O., Kärsrud A.-S., and Sandblom O. (2015): Levels of perfluoroalkyl substances (PFAS) in individual serum samples from first-time mothers in Uppsala 2012 and 2014. Report to the Swedish EPA (the Health-Related Environmental Monitoring Program). http://www.imm.ki.se/Datavard/rapporter/Levels%20of%20perfluoroalkyl%20substances%20PFAS%20in%20individual%20serum%20samples%20from%20first%20time%20mothers%20in%20Uppsala%202012%20and%202014.pdf

Glynn A., Berger U., Bignert A., Ullah S., Aune M., Lignell S., and Darnerud P.O. (2012): Perfluorinated alkyl acids in blood serum from primiparous women in Sweden: serial sampling during pregnancy and nursing, and temporal trends 1996-2010. Environ Sci Technol 46 (16), 9071-9079. DOI: 10.1021/es301168c

Glynn A. and Sand S. (2014): Intagsberäkningar som underlag för framtagande av hälsobaserad åtgärdsgräns för perfluorerade alkylsyror (PFAA) i dricksvatten (In Swedish). https://www.livsmedelsverket.se/globalassets/livsmedel-innehall/oonskade-amnen/pfaa/intagsberakningar-for-atgardsgrans-for-pfaa-i-dricksvatten (last accessed 2017-08-08)

Gomez-Canela C., Barth J.A., and Lacorte S. (2012): Occurrence and fate of perfluorinated compounds in sewage sludge from Spain and Germany. Environ Sci Pollut Res Int 19 (9), 4109-4119. DOI: 10.1007/s11356-012-1078-7

Gomez-Canela C., Fernandez-Sanjuan M., Farres M., and Lacorte S. (2015): Factors affecting the accumulation of perfluoroalkyl substances in human blood. Environ Sci Pollut Res Int 22 (2), 1480-1486. DOI: 10.1007/s11356-014-3439-x

Gomis Ferreira, MI., Vestergren R., Borg D., and Cousins I. (2017): Comparing the potency in vivo of PFAS alternatives and their predecessors. http://su.diva-portal.org/smash/record.jsf?pid=diva2%3A1085755&dswid=-4384

Gonzalez-Gaya B., Dachs J., Roscales J.L., Caballero G., and Jimenez B. (2014): Perfluoroalkylated substances in the global tropical and subtropical surface oceans. Environ Sci Technol 48 (22), 13076-13084. DOI: 10.1021/es503490z

Gremmel C., Fromel T., and Knepper T.P. (2016): Systematic determination of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in outdoor jackets. Chemosphere 160, 173-180. DOI: 10.1016/j.chemosphere.2016.06.043

Guelfo J.L. and Higgins C.P. (2013): Subsurface transport potential of perfluoroalkyl acids at aqueous film-forming foam (AFFF)-impacted sites. Environ Sci Technol 47 (9), 4164-4171. DOI: 10.1021/es3048043

Günther T., Strauss M., Kopp J., and Hartmann R. (2009): Identifizierung und Verminderung der PFT-Belastung im Klärschlamm der Kläranlagen Hann, Münden und Hedemünden. KA Korrespondenz Abwasser, Abfall 56, 690-695

Guo R., Sim W.-J., Lee E.-S., Lee J.-H., and Oh J.-E. (2010): Evaluation of the fate of perfluoroalkyl compounds in wastewater treatment plants. Water Research 44 (11), 3476-3486

Gyllenhammar I., Benskin J.P., Lignell S., Kärsrud A.-S., Sandblom O., and Glynn A. (2016): Temporal trends of poly- and perfluoroalkyl substances (PFASs) in serum from children at 4, 8, and 12 years of age, in Uppsala 2008-2015. Report to the Swedish EPA (the Health-Related Environmental Monitoring Program). Contract no. 2215-15-011 and 2215-16-001

Gyllenhammar I., Berger U., Sundstrom M., McCleaf P., Euren K., Eriksson S., Ahlgren S., Lignell S., Aune M., Kotova N., and Glynn A. (2015): Influence of contaminated drinking water on perfluoroalkyl acid levels in human serum--A case study from Uppsala, Sweden. Environ Res 140, 673-683. DOI: 10.1016/j.envres.2015.05.019

Hansen S., Vestergren R., Herzke D., Melhus M., Evenset A., Hanssen L., Brustad M., and Sandanger T.M. (2016): Exposure to per- and polyfluoroalkyl substances through the consumption of fish from lakes affected by aqueous film-forming foam emissions - A combined epidemiological and exposure modeling approach. The SAMINOR 2 Clinical Study. Environ Int 94, 272-282. DOI: 10.1016/j.envint.2016.05.030

Hardell E., Karrman A., van Bavel B., Bao J., Carlberg M., and Hardell L. (2014): Case-control study on perfluorinated alkyl acids (PFAAs) and the risk of prostate cancer. Environ Int 63, 35-39. DOI: 10.1016/j.envint.2013.10.005

Harding-Marjanovic K.C., Houtz E.F., Yi S., Field J.A., Sedlak D.L., and Alvarez-Cohen L. (2015): Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. Environ Sci Technol 49 (13), 7666-7674. DOI: 10.1021/acs.est.5b01219

Hare E.F., Shafrin E.G., and Zisman W.A. (1954): Properties of films of adsorbed fluorinated acids. The Journal of Physical Chemistry A 58 (3), 236-239

Harris M.W. and Birnbaum L.S. (1989): Developmental toxicity of perfluorodecanoic acid in C57BL/6N mice. Fundam Appl Toxicol 12 (3), 442-448. https://www.ncbi.nlm.nih.gov/pubmed/2731659

Haug L.S., Huber S., Becher G., and Thomsen C. (2011): Characterisation of human exposure pathways to perfluorinated compounds--comparing exposure estimates with biomarkers of exposure. Environ Int 37 (4), 687-693. DOI: 10.1016/j.envint.2011.01.011

Heidler J. and Halden R.U. (2008): Meta-analysis of mass balances examining chemical fate during wastewater treatment. Environmental Science & Technology 42 (17), 6324-6332

Hellsing M.S., Josefsson S., Hughes A.V., and Ahrens L. (2016): Sorption of perfluoroalkyl substances to two types of minerals. Chemosphere 159, 385-391. DOI: 10.1016/j.chemosphere.2016.06.016

Henderson W.M. and Smith M.A. (2007a): Perfluorooctanoic acid and perfluorononanoic acid in fetal and neonatal mice following in utero exposure to 8-2 fluorotelomer alcohol. Toxicol Sci 95 (2), 452-461. DOI: 10.1093/toxsci/kfl162

Henderson W.M. and Smith M.A. (2007b): Perfluorooctanoic acid and perfluorononanoic acid in fetal and neonatal mice following in utero exposure to 8-2 fluorotelomer alcohol. Toxicol Sci 95 (2), 452-461. DOI: 10.1093/toxsci/kfl162

Herzke D., Nygård T., Heimstad E.S., Uggerud H.T. (2015): Environmental pollutants in the terrestrial and urban environment, part II. Norwegian Environment Agency report M-354/2015

Higgins C.P. and Luthy R.G. (2006): Sorption of perfluorinated surfactants on sediments. Environ.Sci Technol. 40 (23), 7251-7256. DOI: 10.1021/es061000n

Himmelstein M.W., Serex T.L., Buck R.C., Weinberg J.T., Mawn M.P., and Russell M.H. (2012): 8:2 fluorotelomer alcohol: a one-day nose-only

inhalation toxicokinetic study in the Sprague-Dawley rat with application to risk assessment. Toxicology 291 (1-3), 122-132. DOI: 10.1016/j.tox.2011.11.005

Hirata-Koizumi M., Fujii S., Hina K., Matsumoto M., Takahashi M., Ono A., and Hirose A. (2015): Repeated dose and reproductive/developmental toxicity of long-chain perfluoroalkyl carboxylic acids in rats: perfluorohexadecanoic acid perfluorotetradecanoic acid. . Fundam. Toxicol. Sci. 2 (4), 177-190

Hoke R.A., Bouchelle L.D., Ferrell B.D., and Buck R.C. (2012): Comparative acute freshwater hazard assessment and preliminary PNEC development for eight fluorinated acids. Chemosphere 87 (7), 725-733. DOI: 10.1016/j.chemosphere.2011.12.066

Houtz E.F., Higgins C.P., Field J.A., and Sedlak D.L. (2013): Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. Environ Sci Technol 47 (15), 8187-8195. DOI: 10.1021/es4018877

Houtz E.F. and Sedlak D.L. (2012): Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. Environ Sci Technol 46 (17), 9342-9349. DOI: 10.1021/es302274g

Huang B.-N., Haas A., and Lieb M. (1987): A new method for the preparation of perfluorocarboxylic acids. Journal of Fluorine Chemistry 36 (1), 49-62. DOI: 10.1016/S0022-1139(00)82053-9

Huset C.A., Chiaia A.C., Barofsky D.F., Jonkers N., Kohler H.-P.E., Ort C., Giger W., and Field J.A. (2008): Occurrence and Mass Flows of Fluorochemicals in the Glatt Valley Watershed, Switzerland. Environmental Science & Technology 42 (17), 6369-6377. DOI: 10.1021/es703062f

Ishibashi H., Iwata H., Kim E.Y., Tao L., Kannan K., Amano M., Miyazaki N., Tanabe S., Batoev V.B., and Petrov E.A. (2008): Contamination and Effects of Perfluorochemicals in Baikal Seal (Pusa sibirica). 1. Residue Level, Tissue Distribution, and Temporal Trend. Environmental Science & Technology 42 (7), 2295-2301. DOI: 10.1021/es072054f

Jackson D.A. and Mabury S.A. (2013): Polyfluorinated amides as a historical PFCA source by electrochemical fluorination of alkyl sulfonyl fluorides. Environ Sci Technol 47 (1), 382-389. DOI: 10.1021/es303152m

Jackson D.A., Wallington T.J., and Mabury S.A. (2013): Atmospheric oxidation of polyfluorinated amides: historical source of perfluorinated carboxylic acids to the environment. Environ Sci Technol 47 (9), 4317-4324. DOI: 10.1021/es400617v

Jensen T.K., Andersen L.B., Kyhl H.B., Nielsen F., Christesen H.T., and Grandjean P. (2015): Association between perfluorinated compound exposure and miscarriage in Danish pregnant women. PLoS One 10 (4), e0123496. DOI: 10.1371/journal.pone.0123496

Jönsson B., Axmon A., and Lindh C. (2014): Tidstrender för och halter av perfluorerade alkylsyror (PFAAs) i serum samt ftalatmetaboliter och alkylfenoler i urin hos unga svenska män och kvinnor– Resultat från den fjärde uppföljningsundersökningen år 2013. Rapport till Naturvårdsverket. http://www.imm.ki.se/Datavard/Rapporter/Rapport_NV-13-12_final.pdf

Kadar H., Veyrand B., Barbarossa A., Pagliuca G., Legrand A., Bosher C., Boquien C.Y., Durand S., Monteau F., Antignac J.P., and Le Bizec B. (2011): Development of an analytical strategy based on liquid chromatography-high resolution mass spectrometry for measuring perfluorinated compounds in human breast milk: application to the generation of preliminary data regarding perinatal exposure in France. Chemosphere 85 (3), 473-480. DOI: 10.1016/j.chemosphere.2011.07.077

Kaiser M.A., Larsen B.S., Kao C.-P.C., and Buck R.C. (2005): Vapor Pressures of Perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic Acids. Journal of Chemical & Engineering Data 50 (6), 1841-1843. DOI: 10.1021/je050070r

Karlsen M., Grandjean P., Weihe P., Steuerwald U., Oulhote Y., and Valvi D. (2016): Early-Life Exposures to Persistent Organic Pollutants in Relation to Overweight in Preschool Children. Reprod Toxicol In Press. . DOI: 10.1016/j.reprotox.2016.08.002

Kärrman A., Davies J., and Salihovic S. (2013): PFAAs in matched milk and serum from primipara women

Karrman A., Domingo J.L., Llebaria X., Nadal M., Bigas E., van Bavel B., and Lindstrom G. (2010): Biomonitoring perfluorinated compounds in Catalonia, Spain: concentrations and trends in human liver and milk samples. Environ Sci Pollut Res Int 17 (3), 750-758. DOI: 10.1007/s11356-009-0178-5

Kato H., Fujii S., Takahashi M., Matsumoto M., Hirata-Koizumi M., Ono A., and Hirose A. (2015): Repeated dose and reproductive/developmental toxicity of perfluorododecanoic acid in rats. Environ Toxicol 30 (11), 1244-1263. DOI: 10.1002/tox.21996

Kauck E.A. and Diesslin A.R. (1951): Some properties of perfluorocarboxylic acids. Ind Enf Chem 43, 2332-2334

Kawashima Y., Kobayashi H., Miura H., and Kozuka H. (1995): Characterization of hepatic responses of rat to administration of perfluorooctanoic and perfluorodecanoic acids at low levels. Toxicology 99 (3), 169-178. https://www.ncbi.nlm.nih.gov/pubmed/7610463

Swedish Chemicals Agency (2015a): Chemical Analysis of Selected Fire-fighting Foams on the Swedish Market 2014. PM 6/15, http://www.kemi.se/global/pm/2015/pm-6-15.pdf (last accessed 11.09.2017)

Swedish Chemicals Agency (2015b): Occurence and use of highly fluorinated substances and alternatives, http://www.kemi.se/en/global/rapporter/2015/report-7-15-occurrence-and-use-of-highly-fluorinated-substances-and-alternatives.pdf. www.kemi.se/en/global/rapporter/2015/report-7-15-occurrence-and-use-of-highly-fluorinated-substances-and-alternatives.pdf (last accessed 09.08.2016)

Swedish Chemicals Agency (2016): Proposal for national regulation of highly fluorinated substances in firefighting foam. 1/16 In Swedish with an English summary, https://www.kemi.se/en/global/rapporter/2016/rapport-1-16-forslag-till-nationella-regler-for-hogfluorerade-amnen-i-brandslackningsskum.pdf

Kennedy G.L., Jr., Butenhoff J.L., Olsen G.W., O'Connor J.C., Seacat A.M., Perkins R.G., Biegel L.B., Murphy S.R., and Farrar D.G. (2004): The toxicology of perfluorooctanoate. Crit Rev Toxicol 34 (4), 351-384. https://www.ncbi.nlm.nih.gov/pubmed/15328768

Keutel K. and Koch M. (2016): Untersuchung fluortensidfreier Löschmittel und geeigneter Löschverfahren zur Bekämpfung von Bränden häufig verwendeter polarer (d. h. schaumzerstörender) Flüssigkeiten. 187, date: February 2016. Institut für Brand- und Katastrophenschutz Heyrothsberge, Abteilung Forschung - Institut der Feuerwehr -. Arbeitgemeinschaft der Innenministerien der Bundesländer A.V.A.F., Katastrophenschutz und zivile Verteidigung. http://www.idf.sachsen-anhalt.de/fileadmin/Bibliothek/Politik_und_Verwaltung/MI/IDF/IBK/Dokumente/Forschung/Fo_Publikationen/imk_ber/bericht_187.pdf

Kim S., Choi K., Ji K., Seo J., Kho Y., Park J., Kim S., Park S., Hwang I., Jeon J., Yang H., and Giesy J.P. (2011): Trans-placental transfer of thirteen perfluorinated compounds and relations with fetal thyroid hormones. Environ Sci Technol 45 (17), 7465-7472. DOI: 10.1021/es202408a

Kim S.K. and Kannan K. (2007): Perfluorinated acids in air, rain, snow, surface runoff, and lakes: relative importance of pathways to contamination of urban lakes. Environ.Sci Technol. 41 (24), 8328-8334. http://www.ncbi.nlm.nih.gov/pubmed/18200859

Knepper T.P., Froemel T., Gremmel C., van Driezum I., Weil H., Vestergren R., and Cousins I.T. (2014): Understanding the exposure pathways of per- and polyfluoroalkyl substances (PFASs) via use of PFASs-containing products - risk estimation for man and environment. (Umweltbundesamt) F.E.A., German Federal Environment Agency (Umweltbundesamt), UBA-Texte 47/2014, Project No. (FKZ) 3711 63 418, Report No. (UBA-FB) 001935/E)

Kotthoff M., Muller J., Jurling H., Schlummer M., and Fiedler D. (2015): Perfluoroalkyl and polyfluoroalkyl substances in consumer products. Environ Sci Pollut Res Int 22 (19), 14546-14559. DOI: 10.1007/s11356-015-4202-7

Krämer R. and Schlipf M. (2016): Fluoropolymers. Kunststoff International 10/2016. https://www.kunststoffe.de/en/journal/archive/article/social-megatrends-give-fluoropolymers-a-boost-1800781.html

Kudo N. (2015): Metabolism and pharmacokinetics. . In: Toxicological effects of perfluoroalkylk and polyfluoroalkyl substances. (Dewitt J., ed.), chapter 6, pp. 151-175. ISBN: 978-3-319-15517-3

Kudo N., Iwase Y., Okayachi H., Yamakawa Y., and Kawashima Y. (2005): Induction of Hepatic Peroxisome Proliferation by 8-2 Telomer Alcohol Feeding In Mice: Formation of Perfluorooctanoic Acid in the Liver. Toxicological Sciences 86 (2), 231-238. DOI: 10.1093/toxsci/kfi191

Kunieda H. and Shinoda K. (1976): Krafft points, critical micelle concentrations, surface tension, and solubilizing power of aqueous solutions of fluorinated surfactants. The Journal of physical Chemistry 80 (22), 2468-2470

Kwadijk C.J.A.F., Koryta¦ür P., and Koelmans A.A. (2010): Distribution of Perfluorinated Compounds in Aquatic Systems in The Netherlands. Environmental Science & Technology 44 (10), 3746-3751. DOI: doi: 10.1021/es100485e

Lam J.C., Lyu J., Kwok K.Y., and Lam P.K. (2016): Perfluoroalkyl Substances (PFASs) in Marine Mammals from the South China Sea and Their Temporal Changes 2002 - 2014: Concern for Alternatives of PFOS? Environ Sci Technol. DOI: 10.1021/acs.est.5b06076

Lankova D., Lacina O., Pulkrabova J., and Hajslova J. (2013): The determination of perfluoroalkyl substances, brominated flame retardants and their metabolites in human breast milk and infant formula. Talanta 117, 318-325. DOI: 10.1016/j.talanta.2013.08.040

Lee H., D'Eon J., and Mabury S.A. (2010): Biodegradation of polyfluoroalkyl phosphates as a source of perfluorinated acids to the environment. Environ Sci Technol 44 (9), 3305-3310. DOI: 10.1021/es9028183

Lee H., Tevlin A.G., Mabury S.A., and Mabury S.A. (2014): Fate of polyfluoroalkyl phosphate diesters and their metabolites in biosolids-applied soil: biodegradation and plant uptake in greenhouse and field experiments. Environ Sci Technol 48 (1), 340-349. DOI: 10.1021/es403949z

Lehmler H.-J., Oyewumi M.O., Jay M., and Bummer P.M. (2001): Behavior of partially fluorinated carboxylic acids at the air–water interface. Journal of Fluorine Chemistry 107 (1), 141-146. DOI: https://doi.org/10.1016/S0022-1139(00)00384-5

Liu C. and Liu J. (2016): Aerobic biotransformation of polyfluoroalkyl phosphate esters (PAPs) in soil. Environ Pollut 212, 230-237. DOI: 10.1016/j.envpol.2016.01.069

Liu F., Hashim N.A., Liu Y., Abed M.R.M., and Li K. (2011a): Progress in the production and modification of PVDF membranes. Journal of Membrane Science 375 (1–2), 1-27. DOI: 10.1016/j.memsci.2011.03.014

Liu J. and Lee L.S. (2005): Solubility and Sorption by Soils of 8:2 Fluorotelomer Alcohol in Water and Cosolvent Systems. Environmental Science & Technology 39 (19), 7535-7540. DOI: 10.1021/es051125c (last accessed 2014/06/30)

Liu J., Li J., Liu Y., Chan H.M., Zhao Y., Cai Z., and Wu Y. (2011b): Comparison on gestation and lactation exposure of perfluorinated compounds for newborns. Environ Int 37 (7), 1206-1212. DOI: 10.1016/j.envint.2011.05.001

Liu J. and Mejia Avendano S. (2013): Microbial degradation of polyfluoroalkyl chemicals in the environment: A review. Environ Int 61, 98-114. DOI: 10.1016/j.envint.2013.08.022

Liu J., Wang N., Buck R.C., Wolstenholme B.W., Folsom P.W., Sulecki L.M., and Bellin C.A. (2010a): Aerobic biodegradation of [14C] 6:2 fluorotelomer alcohol in a flow-through soil incubation system. Chemosphere 80 (7), 716-723. DOI: 10.1016/j.chemosphere.2010.05.027

Liu J., Wang N., Szostek B., Buck R.C., Panciroli P.K., Folsom P.W., Sulecki L.M., and Bellin C.A. (2010b): 6-2 Fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture. Chemosphere 78 (4), 437-444. DOI: 10.1016/j.chemosphere.2009.10.044

Llorca M., Farre M., Pico Y., Teijon M.L., Alvarez J.G., and Barcelo D. (2010): Infant exposure of perfluorinated compounds: levels in breast milk and commercial baby food. Environ Int 36 (6), 584-592. DOI: 10.1016/j.envint.2010.04.016

Long M., Knudsen A.K., Pedersen H.S., and Bonefeld-Jorgensen E.C. (2015): Food intake and serum persistent organic pollutants in the Greenlandic pregnant women: The ACCEPT sub-study. Sci Total Environ 529, 198-212. DOI: 10.1016/j.scitotenv.2015.05.022

López-Fontán J.L., Sarmiento F., and Schulz P.C. (2005): The aggregation of sodium perfluorooctanoate in water. Colloid and Polymer Science 283 (8), 862-871. DOI: 10.1007/s00396-004-1228-7

Mackay D. (2001): Multimedia environmental models: the fugacity approach. CRC press. ISBN: 1420032542

Manzano-Salgado C.B., Casas M., Lopez-Espinosa M.J., Ballester F., Basterrechea M., Grimalt J.O., Jimenez A.M., Kraus T., Schettgen T., Sunyer J., and Vrijheid M. (2015): Transfer of perfluoroalkyl substances from mother to fetus in a Spanish birth cohort. Environ Res 142, 471-478. DOI: 10.1016/j.envres.2015.07.020

Manzano-Salgado C.B., Casas M., Lopez-Espinosa M.J., Ballester F., Martinez D., Ibarluzea J., Santa-Marina L., Schettgen T., Vioque J., Sunyer J., and Vrijheid M. (2016): Variability of perfluoroalkyl substance concentrations in pregnant women by socio-demographic and dietary factors in a Spanish birth cohort. Environ Int 92-93, 357-365. DOI: 10.1016/j.envint.2016.04.004

Market Research Store (2016): Polyvinylidene Fluoride (PVDF) Market for Chemical Processing Industry, Construction Industrial, Oil & Gas, New Energies and Other Applications: Global Industry Perspective, Comprehensive Analysis, Size, Share, Growth, Segment, Trends and Forecast, 2014 – 2020. http://www.marketresearchstore.com/report/polyvinylidene-fluoride-market-z46154 (last accessed 29.12.2016)

Martin J.W., Asher B.J., Beesoon S., Benskin J.P., and Ross M.S. (2010): PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure? J Environ Monit 12. DOI: 10.1039/c0em00295j

Martin J.W., Ellis D.A., Mabury S.A., Hurley M.D., and Wallington T.J. (2006): Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-ethyl perfluorobutanesulfonamide. Environ Sci Technol 40 (3), 864-872. DOI: 10.1021/es051362f

Martin J.W., Mabury S.A., and O'Brien P.J. (2005): Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes. Chem Biol Interact 155 (3), 165-180. DOI: 10.1016/j.cbi.2005.06.007

Miljöstyrelsen (2015): Administrative overvejelser og fastlæggelse af grænseværdier for perfluorerede alkylsyreforbindelser (PFAS-forbindelser), inkl. PFOA, PFOS og PFOSA i drikkevand, samt jord og grundvand til vurdering af forurenede grunde (in danish). . http://mst.dk/media/91517/pfas-administrative-graensevaerdier-27-april-2015-final.pdf (last accessed 2017-08-08)

Ministry of Environmental Protection of the People`s Republic of China (2013): Inventory of Exisiting Chemical Substances Produced or Imported in China (IECSC) , Notice 2013 No. 1. Department of the Ministry of Environmental Protection,

Moody C.A., Hebert G.N., Strauss S.H., and Field J.A. (2003): Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA. J Environ Monit. 5 (2), 341-345. DOI: 10.1039/B212497A

Morck T.A., Nielsen F., Nielsen J.K., Siersma V.D., Grandjean P., and Knudsen L.E. (2015): PFAS concentrations in plasma samples from Danish school children and their mothers. Chemosphere 129, 203-209. DOI: 10.1016/j.chemosphere.2014.07.018

Moroi Y., Yano H., Shibata O., and Yonemitsu T. (2001): Determination of acidity constants of perfluoroalkanoic acids. Bulletin of the Chemical Society of Japan 74 (4), 667-672. DOI: 10.1246/bcsj.74.667

Motas Guzman M., Clementini C., Perez-Carceles M.D., Jimenez Rejon S., Cascone A., Martellini T., Guerranti C., and Cincinelli A. (2016): Perfluorinated carboxylic acids in human breast milk from Spain and estimation of infant's daily intake. Sci Total Environ 544, 595-600. DOI: 10.1016/j.scitotenv.2015.11.059

Müller C.E., De Silva A.O., Small J., Williamson M., Wang X., Morris A., Katz S., Gamberg M., and Muir D.C. (2011): Biomagnification of perfluorinated compounds in a remote terrestrial food chain: Lichen-Caribou-wolf. Environ Sci Technol 45 (20), 8665-8673. DOI: 10.1021/es201353v

Munoz G., Giraudel J.L., Botta F., Lestremau F., Devier M.H., Budzinski H., and Labadie P. (2015): Spatial distribution and partitioning behavior of selected poly- and perfluoroalkyl substances in freshwater ecosystems: a French nationwide survey. Sci Total Environ 517, 48-56. DOI: 10.1016/j.scitotenv.2015.02.043

Myers A.L., Crozier P.W., Helm P.A., Brimacombe C., Furdui V.I., Reiner E.J., Burniston D., and Marvin C.H. (2012): Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. Environ Int 44, 92-99. DOI: 10.1016/j.envint.2012.02.002

Myers A.L. and Mabury S.A. (2010): Fate of fluorotelomer acids in a soil-water microcosm. Environ Toxicol Chem 29 (8), 1689-1695. DOI: 10.1002/etc.211

Nabb D.L., Szostek B., Himmelstein M.W., Mawn M.P., Gargas M.L., Sweeney L.M., Stadler J.C., Buck R.C., and Fasano W.J. (2007): In vitro metabolism of 8-2 fluorotelomer alcohol: interspecies comparisons and metabolic pathway refinement. Toxicol.Sci 100 (2), 333-344. DOI: 10.1093/toxsci/kfm230

Neumann P. (2013): Europäische Union: 71.000 kommunale Kläranlagen. wwt - Das Praxismagazin für das Trink- und Abwassermanagement

Nielsen C.J. (2012): PFOA Isomers, salts and precursors - Literature study and evaluation of physico-chemical properties. CTCC, Department of Chemistry, University of Oslo, Klif project no: 3012013. file://\\uba\gruppen\IV2.3\Doc\6-Literatur\6.0-ReferenceManager\Bibliothek\NielsenCL_2012_Klif.pdf

Nielsen C.J. (2014): Potential PFOA Precursors - Literature study and theoretical assessment of abiotic degradation pathways leading to PFOA. CTCC, Department of Chemistry, University of Oslo, , http://www.miljodirektoratet.no/no/Publikasjoner/2014/September-2014/Potential-PFOA-Precursors/

Nilsson H., Karrman A., Rotander A., van Bavel B., Lindstrom G., and Westberg H. (2013): Biotransformation of fluorotelomer compound to perfluorocarboxylates in humans. Environ Int 51, 8-12. DOI: 10.1016/j.envint.2012.09.001

Nilsson H., Karrman A., Westberg H., Rotander A., van Bavel B., and Lindstroem G. (2010): A time trend study of significantly elevated perfluorocarboxylate levels in humans after using fluorinated ski wax. Environ Sci Technol 44 (6), 2150-2155. DOI: 10.1021/es9034733

Norwegian Institute for Water Research (2016): Environmental pollutants in large Norwegian lakes, 2015. Rapport 7062-2016. M548/2016. http://www.miljodirektoratet.no/Documents/publikasjoner/M548/M548.pdf

Norwegian Institute of Air Research (2016): Environmental pollutants in the terrestrial and urban environment 2015. NILU report 27/2016. M-570/2016. http://www.miljodirektoratet.no/Documents/publikasjoner/M570/M570.pdf

Nost T.H., Vestergren R., Berg V., Nieboer E., Odland J.O., and Sandanger T.M. (2014): Repeated measurements of per- and polyfluoroalkyl substances (PFASs) from 1979 to 2007 in males from Northern Norway: Assessing time trends, compound correlations and relations to age/birth cohort. Environ Int 67C, 43-53. DOI: 10.1016/j.envint.2014.02.011

Numata J., Kowalczyk J., Adolphs J., Ehlers S., Schafft H., Fuerst P., Müller-Graf C., Lahrssen-Wiederholt M., and Greiner M. (2014): Toxicokinetics of Seven Perfluoroalkyl Sulfonic and Carboxylic Acids in Pigs Fed a Contaminated Diet. Journal of Agricultural and Food Chemistry 62 (28), 6861-6870. DOI: 10.1021/jf405827u

OECD (2006): SIDS Initial Assessment Report after SIAM 22 - Ammonium Perfluorooctanoate & Perfluorooctanic Acid

OECD (2013): OECD/UNEP Global PFC Group, Synthesis paper on per- and polyfluorinated chemicals (PFCs), http://www.oecd.org/chemicalsafety/risk-management/synthesis-paper-on-per-and-polyfluorinated-chemicals.htm, 2017-02-15

Olofsson U., Brorstrom-Lunden E., Kylin H., and Haglund P. (2013): Comprehensive mass flow analysis of Swedish sludge contaminants. Chemosphere 90 (1), 28-35. DOI: 10.1016/j.chemosphere.2012.07.002

Oulhote Y., Steuerwald U., Debes F., Weihe P., and Grandjean P. (2016): Behavioral difficulties in 7-year old children in relation to developmental exposure to perfluorinated alkyl substances. Environ Int 97, 237-245. DOI: 10.1016/j.envint.2016.09.015

Papadopoulou E., Sabaredzovic A., Namork E., Nygaard U.C., Granum B., and Haug L.S. (2016): Exposure of Norwegian toddlers to perfluoroalkyl

substances (PFAS): The association with breastfeeding and maternal PFAS concentrations. Environ Int 94, 687-694. DOI: 10.1016/j.envint.2016.07.006

PERFORCE (2004): Perfluorinated substances in the European environment, EU project FP6-NEST-508967

Piekarz A.M., Primbs T., Field J.A., Barofsky D.F., and Simonich S. (2007): Semivolatile fluorinated organic compounds in Asian and western U.S. air masses. Environ Sci Technol 41 (24), 8248-8255. http://www.ncbi.nlm.nih.gov/pubmed/18200847

Posner S., Roos S., Brunn Poulsen P., Jörundsdottir H.O., Gunnlaugsdóttir H., Trier X., Jensen A.A., Katsogiannis A.A., Herzke D., Bonefeld-Jörgensen E.C., Jönsson C., Alsing Pedersen G., and Ghisari M. (2013): Per- and polyfluorinated susbtances in the Nordic Countries - use, occurence and toxicology. TemaNord 2013:542. , http://www.norden.org/en/publications/publikationer/2013-542

Posner S., Roos S., and Olsson E. (2009): Survey of the extent of use and occurrence of PFNA (perfluorononanoic acid) in Norway, Swerea IVF, Project report 09/46. TA-2562/2009

Prevedouros K., Cousins I.T., Buck R.C., and Korzeniowski S.H. (2006): Sources, fate and transport of perfluorocarboxylates. Environ.Sci Technol. 40 (1), 32-44. DOI: 10.1021/es0512475

Rankin K., Lee H., Tseng P.J., and Mabury S.A. (2014): Investigating the biodegradability of a fluorotelomer-based acrylate polymer in a soil-plant microcosm by indirect and direct analysis. Environ Sci Technol 48 (21), 12783-12790. DOI: 10.1021/es502986w

Rankin K., Mabury S.A., Jenkins T.M., and Washington J.W. (2016): A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence. Chemosphere 161, 333-341. DOI: 10.1016/j.chemosphere.2016.06.109

Rayne S. and Forest K. (2009): Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. Journal of Environmental Science and Health Part A 44, 1145-1199. DOI: 10.1080/10934520903139811

Rayne S. and Forest K. (2010): Modeling the hydrolysis of perfluorinated compounds containing carboxylic and phosphoric acid ester functions and sulfonamide groups. J Environ Sci Health A Tox Hazard Subst Environ Eng 45 (4), 432-446. DOI: 10.1080/10934520903538731

Renner R. (2008): Do perfluoropolymers biodegrade into PFOA? Environ Sci Technol 42 (3), 648-650. DOI: 10.1021/es087093l

ReportLinker (2016): Polyvinylidene Fluoride (PVDF) - A Global Market Overview. http://www.prnewswire.com/news-releases/polyvinylidene-fluoride-pvdf---a-global-market-overview-300380915.html# (last accessed 29.12.2016)

Riget F., Bossi R., Sonne C., Vorkamp K., and Dietz R. (2013): Trends of perfluorochemicals in Greenland ringed seals and polar bears: indications of shifts to decreasing trends. Chemosphere 93 (8), 1607-1614. DOI: 10.1016/j.chemosphere.2013.08.015

Roos A., Berger U., Jarnberg U., van Dijk J., and Bignert A. (2013): Increasing concentrations of perfluoroalkyl acids in Scandinavian otters (Lutra lutra) between 1972 and 2011: a new threat to the otter population? Environ Sci Technol 47 (20), 11757-11765. DOI: 10.1021/es401485t

Royer L.A., Lee L.S., Russell M.H., Nies L.F., and Turco R.F. (2015): Microbial transformation of 8:2 fluorotelomer acrylate and methacrylate in aerobic soils. Chemosphere 129, 54-61. DOI: 10.1016/j.chemosphere.2014.09.077

Ruan T., Szostek B., Folsom P.W., Wolstenholme B.W., Liu R., Liu J., Jiang G., Wang N., and Buck R.C. (2013): Aerobic soil biotransformation of 6:2 fluorotelomer iodide. Environ Sci Technol 47 (20), 11504-11511. DOI: 10.1021/es4018128

Ruan T., Wang Y., Wang T., Zhang Q., Ding L., Liu J., Wang C., Qu G., and Jiang G. (2010): Presence and partitioning behavior of polyfluorinated iodine alkanes in environmental matrices around a fluorochemical manufacturing plant: another possible source for perfluorinated carboxylic acids? Environ Sci Technol 44 (15), 5755-5761. DOI: 10.1021/es101507s

Russell M.H., Berti W.R., Szostek B., and Buck R.C. (2008): Investigation of the biodegradation potential of a fluoroacrylate polymer product in aerobic soils. Environ Sci Technol 42 (3), 800-807. DOI: 10.1021/es0710499

Russell M.H., Berti W.R., Szostek B., Wang N., and Buck R.C. (2010): Evaluation of PFO formation from the biodegradation of a fluorotelomer-based urethane polymer product in aerobic soils. Polymer Degradation and Stability 95 (1), 79-85. DOI: 10.1016/j.polymdegradstab.2009.10.004

Russell M.H., Nilsson H., and Buck R.C. (2013): Elimination kinetics of perfluorohexanoic acid in humans and comparison with mouse, rat and monkey. Chemosphere 93 (10), 2419-2425. DOI: 10.1016/j.chemosphere.2013.08.060

Savu P.M. (2000): Fluorinated Higher Carboxylic Acids. In: Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. ISBN: 9780471238966. DOI: 10.1002/0471238961.0612211519012221.a01

Scheringer M. (2002): Persistence and spatial range of environmental chemicals. New ethical and scientific concepts for risk assessment. Wiley-VCH: Weinheim

Schroter-Kermani C., Muller J., Jurling H., Conrad A., and Schulte C. (2013): Retrospective monitoring of perfluorocarboxylates and perfluorosulfonates in human plasma archived by the German Environmental Specimen Bank. Int J Hyg Environ Health 216 (6), 633-640. DOI: 10.1016/j.ijheh.2012.08.004

Schwarzenbach R.P., Gschwend P.M., and Imboden D.M. (2003): Transformation Processes. Wiley Online Library. ISBN: 0471649643

Sepulvado J.G., Blaine A.C., Hundal L.S., and Higgins C.P. (2011): Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environ Sci Technol 45 (19), 8106-8112. DOI: 10.1021/es103903d

Shi Z., Ding L., Zhang H., Feng Y., Xu M., and Dai J. (2009): Chronic exposure to perfluorododecanoic acid disrupts testicular steroidogenesis and the expression of related genes in male rats. Toxicol Lett 188 (3), 192-200. DOI: 10.1016/j.toxlet.2009.04.014

Shi Z., Zhang H., Liu Y., Xu M., and Dai J. (2007): Alterations in gene expression and testosterone synthesis in the testes of male rats exposed to perfluorododecanoic acid. Toxicol Sci 98 (1), 206-215. DOI: 10.1093/toxsci/kfm070

Shoeib M., Harner T., and Vlahos P. (2006): Perfluorinated chemicals in the arctic atmosphere. Environ Sci Technol 40 (24), 7577-7583. http://www.ncbi.nlm.nih.gov/pubmed/17256497

Siegemund G., Schwertfeger W., Feiring A., Smart B., Behr F., Vogel H., and McKusick B. (2000): Fluorine Compounds, Organic. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA. ISBN: 9783527306732. DOI: 10.1002/14356007.a11_349

Sinclair E. and Kannan K. (2006): Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ Sci Technol 40 (5), 1408-1414. DOI: 10.1021/es051798v

Sochorova L., Hanzlikova L., Cerna M., Drgacova A., Fialova A., Svarcova A., Gramblicka T., and Pulkrabova J. (2017): Perfluorinated alkylated substances and brominated flame retardants in serum of the Czech adult population. Int J Hyg Environ Health 220 (2 Pt A), 235-243. DOI: 10.1016/j.ijheh.2016.09.003

Stemmler I. and Lammel G. (2010): Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources. Atmospheric Chemistry and Physics 10 (20), 9965-9980

Stock N.L., Furdui V.I., Muir D.C., and Mabury S.A. (2007): Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination. Environ.Sci Technol. 41 (10), 3529-3536. http://www.ncbi.nlm.nih.gov/pubmed/17547174

Stock N.L., Muir D.C.G., and Mabury S. (2010): Perfluoroalkyl Compounds, In:Stuart Harrad. Persistent Organic Pollutants. John Wiley and Sons Ltd, p 25-69. ISBN: 978-1-4051-6930-1

Stubleski J., Salihovic S., Lind L., Lind P.M., van Bavel B., and Karrman A. (2016): Changes in serum levels of perfluoroalkyl substances during a 10-year follow-up period in a large population-based cohort. Environ Int 95, 86-92. DOI: 10.1016/j.envint.2016.08.002

Styler S.A., Myers A.L., and Donaldson D.J. (2013): Heterogeneous photooxidation of fluorotelomer alcohols: a new source of aerosol-phase perfluorinated carboxylic acids. Environ Sci Technol 47 (12), 6358-6367. DOI: 10.1021/es4011509

Sulbaek Andersen M.P., Nielsen O.J., Toft A., Nakayama T., Matsumi Y., Waterland R.L., Buck R.C., Hurley M.D., and Wallington T.J. (2005): Atmospheric chemistry of CxF2x+1CH=CH2(x= ;1, 2, 4, 6, and 8): Kinetics of gas-phase reactions with Cl atoms, OH radicals, and O3. Journal of Photochemistry and Photobiology A: Chemistry 176 (1–3), 124-128. DOI: 10.1016/j.jphotochem.2005.06.015

Takahashi M., Ishida S., Hirata-Koizumi M., Ono A., and Hirose A. (2014): Repeated dose and reproductive/developmental toxicity of perfluoroundecanoic acid in rats. J Toxicol Sci 39 (1), 97-108. https://www.ncbi.nlm.nih.gov/pubmed/24418714

Taniyasu S., Yamashita N., Moon H.B., Kwok K.Y., Lam P.K., Horii Y., Petrick G., and Kannan K. (2013): Does wet precipitation represent local and regional atmospheric transportation by perfluorinated alkyl substances? Environ Int 55, 25-32. DOI: 10.1016/j.envint.2013.02.005

Taylor P.H., Yamada T., Striebich R.C., Graham J.L., and Giraud R.J. (2014): Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment. Chemosphere 110, 17-22. DOI: 10.1016/j.chemosphere.2014.02.037

Thomsen C., Haug L.S., Stigum H., Froshaug M., Broadwell S.L., and Becher G. (2010): Changes in concentrations of perfluorinated compounds, polybrominated diphenyl ethers, and polychlorinated biphenyls in Norwegian breast-milk during twelve months of lactation. Environ Sci Technol 44 (24), 9550-9556. DOI: 10.1021/es1021922

U.S.EPA (2009): Long-Chain perfluorinated Chemicals (PFCs) Action Plan, https://www.epa.gov/sites/production/files/2016-01/documents/pfcs_action_plan1230_09.pdf

US EPA (2015): Significant New Use Rules: Long-Chain Perfluoroalkyl Carboxylate and Perfluoroalkyl Sulfonate Chemical Substances. https://www.regulations.gov/document?D=EPA-HQ-OPPT-2013-0225-0001 (last accessed 2017-10-06)

Ulrich H., Freier K.P., and Gierig M. (2016): Getting on with persistent pollutants: Decreasing trends of perfluoroalkyl acids (PFAAs) in sewage sludge. Chemosphere 161, 527-535. DOI: 10.1016/j.chemosphere.2016.07.048

UNEP (2012): Technical paper on the identification and assessment of alternatives to the use of perfluorooctane sulfonic acid in open applications. UNEP/POPS/POPRC.8/INF/17, http://chm.pops.int/Convention/POPsReviewCommittee/POPRCMeetings/POPRC8/POPRC7WorkingDocuments/tabid/2801/Default.aspx

UNEP (2013): Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals. UNEP/POPS/POPRC.9/INF/11/Rev.1, http://chm.pops.int/Convention/POPsReviewCommittee/LatestMeeting/POPRC9/POPRC9Documents/tabid/3281/Default.aspx

UNEP (2015): Draft consolidated guidance on alternatives to perfluorooctane sulfonic acid and its related chemicals. UNEP/POPS/POPRC.12/INF/15, http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC12/Overview/tabid/5171/Default.aspx

van der Putte I., Murin M., van Velthoven M., and Affourtit F. (2010): Analysis of the risks arising from the industrial use of Perfluorooctanoic Acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO. European Commission, DG Enterprise and Industry, for the European Commission, DG Enterprise and Industry. Report TOX08.7049.FR03. \\uba\gruppen\iv2.3\Doc\6-Literatur\6.0-ReferenceManager\Bibliothek\RPS_van_der_Putte_2010_Report_POFA_PFOS.pdf

Vestergren R., Berger U., Glynn A., and Cousins I.T. (2012): Dietary exposure to perfluoroalkyl acids for the Swedish population in 1999, 2005 and 2010. Environment International 49, 120-127. DOI: 10.1016/j.envint.2012.08.016

Vierke L. (2014a): Environmental Mobility of Short Chain Perfluoroalkyl Carboxylic Acids-Partition Behaviour and Resulting Environmental Concern, Universitätsbibliothek der Leuphana Universität Lüneburg

Vierke L. (2014b): Environmental Mobility of Short Chain Perfluoroalkyl Carboxylic Acids - Partition Behaviour and Resulting Environmental Concern, Dissertation. http://opus.uni-

lueneburg.de/opus/volltexte/2015/14327/pdf/Dissertation_Lena_Vierke_2014.pdf

Vierke L., Ahrens L., Shoeib M., Palm W.U., Webster E.M., Ellis D.A., Ebinghaus R., and Harner T. (2013a): In situ air-water and particle-water partitioning of perfluorocarboxylic acids, perfluorosulfonic acids and perfluorooctyl sulfonamide at a wastewater treatment plant. Chemosphere 92 (8), 941-948. DOI: 10.1016/j.chemosphere.2013.02.067

Vierke L., Ahrens L., Shoeib M., Reiner E.J., Guo R., Palm W.U., Ebinghaus R., and Harner T. (2011): Air concentrations and particlegas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant. Environmental Chemistry 8 (4), 363-371. DOI: 10.1071/EN10133

Vierke L., Berger U., and Cousins I.T. (2013b): Estimation of the acid dissociation constant of perfluoroalkyl carboxylic acids through an experimental investigation of their water-to-air transport. Environ Sci Technol 47 (19), 11032-11039. DOI: 10.1021/es402691z

Vierke L., Moller A., and Klitzke S. (2014): Transport of perfluoroalkyl acids in a water-saturated sediment column investigated under near-natural conditions. Environ Pollut 186, 7-13. DOI: 10.1016/j.envpol.2013.11.011

Wallington T.J., Hurley M.D., Xia J., Wuebbles D.J., Sillman S., Ito A., Penner J.E., Ellis D.A., Martin J., Mabury S.A., Nielsen O.J., and Sulbaek Andersen M.P. (2006): Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8:2 fluorotelomer alcohol. Environ.Sci Technol. 40 (3), 924-930.
http://www.ncbi.nlm.nih.gov/pubmed/16509338

Wang N., Buck R.C., Szostek B., Sulecki L.M., and Wolstenholme B.W. (2012): 5:3 Polyfluorinated acid aerobic biotransformation in activated sludge via novel "one-carbon removal pathways". Chemosphere 87 (5), 527-534. DOI: 10.1016/j.chemosphere.2011.12.056

Wang N., Liu J., Buck R.C., Korzeniowski S.H., Wolstenholme B.W., Folsom P.W., and Sulecki L.M. (2011a): 6:2 fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants. Chemosphere 82 (6), 853-858. DOI: 10.1016/j.chemosphere.2010.11.003

Wang N., Szostek B., Buck R.C., Folsom P.W., Sulecki L.M., Capka V., Berti W.R., and Gannon J.T. (2005a): Fluorotelomer alcohol biodegradation-direct evidence that perfluorinated carbon chains breakdown. Environ.Sci Technol. 39 (19), 7516-7528. DOI: 10.1021/es0506760

Wang N., Szostek B., Buck R.C., Folsom P.W., Sulecki L.M., and Gannon J.T. (2009): 8-2 fluorotelomer alcohol aerobic soil biodegradation: pathways, metabolites, and metabolite yields. Chemosphere 75 (8), 1089-1096. DOI: 10.1016/j.chemosphere.2009.01.033

Wang N., Szostek B., Folsom P.W., Sulecki L.M., Capka V., Buck R.C., Berti W.R., and Gannon J.T. (2005b): Aerobic biotransformation of 14C-labeled 8-2 telomer B alcohol by activated sludge from a domestic sewage treatment plant. Environ Sci Technol 39 (2), 531-538. DOI: 10.1021/es049466y

Wang Z., Cousins I.T., Berger U., Hungerbühler K., and Scheringer M. (2016): Comparative assessment of the environmental hazards of and exposure to perfluoroalkyl phosphonic and phosphinic acids (PFPAs and PFPiAs): Current knowledge, gaps, challenges and research needs. Environment International 89–90, 235-247. DOI: 10.1016/j.envint.2016.01.023

Wang Z., Cousins I.T., Scheringer M., Buck R.C., and Hungerbühler K. (2014): Global Emission Inventories for C4-C14 Perfluoralkyl Carboxylic Acid (PFCA) Homologues from 1951 to 2030, Part I: Production and Emission from Quantifiable Sources. Environment International 70, 62-75

Wang Z., MacLeod M., Cousins I.T., Scheringer M., and Hungerbühler K. (2011b): Using COSMOtherm to predict physicochemical properties of poly- and perfluorinated alkyl substances (PFASs). Environmental Chemistry 8 (4), 389-398. DOI: 10.1071/en10143

Wang Z., Xie Z., Mi W., Möller A., Wolschke H., and Ebinghaus R. (2015): Neutral Poly/Per-Fluoroalkyl Substances in Air from the Atlantic to the Southern Ocean and in Antarctic Snow. Environmental Science & Technology 49 (13), 7770-7775. DOI: 10.1021/acs.est.5b00920

Washington J.W., Ellington J.J., Jenkins T.M., Evans J.J., Yoo H., and Hafner S.C. (2009): Degradability of an Acrylate-Linked, Fluorotelomer Polymer in Soil. Environmental Science & Technology 43 (17), 6617-6623. DOI: doi: 10.1021/es9002668

Washington J.W. and Jenkins T.M. (2015): Abiotic hydrolysis of fluorotelomer-based polymers as a source of perfluorocarboxylates at the global scale. Environmental Science & Technology 49 (24), 14129-14135. DOI: 10.1021/acs.est.5b03686

Washington J.W., Jenkins T.M., Rankin K., and Naile J.E. (2015): Decades-Scale Degradation of Commercial, Side-Chain, Fluorotelomer-based Polymers in Soils & Water. Environ Sci Technol 49 (2), 915-923. DOI: 10.1021/es504347u

Webster E.M. and Ellis D.A. (2011): Equilibrium modeling: a pathway to understanding observed perfluorocarboxylic and perfluorosulfonic acid behavior. Environ Toxicol Chem 30 (10), 2229-2236. DOI: 10.1002/etc.637

Wen B., Li L., Zhang H., Ma Y., Shan X.Q., and Zhang S. (2014): Field study on the uptake and translocation of perfluoroalkyl acids (PFAAs) by wheat (Triticum aestivum L.) grown in biosolids-amended soils. Environ Pollut 184, 547-554. DOI: 10.1016/j.envpol.2013.09.040

Wielsoe M., Kern P., and Bonefeld-Jorgensen E.C. (2017): Serum levels of environmental pollutants is a risk factor for breast cancer in Inuit: a case control study. Environ Health 16 (1), 56. DOI: 10.1186/s12940-017-0269-6

Wilhelm M., Wittsiepe J., Volkel W., Fromme H., and Kasper-Sonnenberg M. (2015): Perfluoroalkyl acids in children and their mothers: Association with drinking water and time trends of inner exposures--Results of the Duisburg birth cohort and Bochum cohort studies. Int J Hyg Environ Health 218 (7), 645-655. DOI: 10.1016/j.ijheh.2015.07.001

Wolf C.J., Zehr R.D., Schmid J.E., Lau C., and Abbott B.D. (2010): Developmental effects of perfluorononanoic Acid in the mouse are dependent on peroxisome proliferator-activated receptor-alpha. PPAR Res 2010. DOI: 10.1155/2010/282896

Yamashita N., Taniyasu S., Petrick G., Wei S., Gamo T., Lam P.K., and Kannan K. (2008): Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70 (7), 1247-1255. http://www.ncbi.nlm.nih.gov/pubmed/17854858

Yaws C.L. (2008): The Yaws handbook of physical properties for hydrocarbons and chemicals. ISBN: 9781933762074

Yeung L.W., Robinson S.J., Koschorreck J., and Mabury S.A. (2013): Part I. A temporal study of PFCAs and their precursors in human plasma from two German cities 1982-2009. Environ Sci Technol 47 (8), 3865-3874. DOI: 10.1021/es303716k

Yeung L.W.Y., Dassuncao C., Mabury S., Sunderland E.M., Zhang X., and Lohmann R. (2017): Vertical Profiles, Sources, and Transport of PFASs in the Arctic Ocean. Environ Sci Technol 51 (12), 6735-6744. DOI: 10.1021/acs.est.7b00788

Yoo H., Washington J.W., Ellington J.J., Jenkins T.M., and Neill M.P. (2010): Concentrations, distribution, and persistence of fluorotelomer alcohols in sludge-applied soils near Decatur, Alabama, USA. Environ Sci Technol 44 (22), 8397-8402. DOI: 10.1021/es100390r

Young C.J., Hurley M.D., Wallington T.J., and Mabury S.A. (2008): Atmospheric chemistry of 4:2 fluorotelomer iodide (n-C4F9CH2CH2I): kinetics and products of photolysis and reaction with OH radicals and Cl atoms. J Phys Chem A 112 (51), 13542-13548. DOI: 10.1021/jp807322x

Young C.J. and Mabury S.A. (2010): Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts. Rev Environ Contam Toxicol 208, 1-109. DOI: 10.1007/978-1-4419-6880-7_1

Young I. (2017), personal communication, 2017-08-10.

Zangl S., Blepp M., Marquardt M., Moch K., Wirth O., Homburg B., and Temme C. (2012): Nationale Umsetzung des Stockholmer Übereinkommens zu persistenten organischen Schadstoffen (POPs) - PBDE und PFOS in Erzeugnissen und im Recyclingkreislauf Reprt No. UBA-FB 001661, Project No. FKZ 371063415, http://www.bmub.bund.de/fileadmin/Daten_BMU/Pools/Forschungsdatenbank/3710_63_415_stockholm_bf.pdf

Zhang C., Yan H., Li F., Hu X., and Zhou Q. (2013a): Sorption of short- and long-chain perfluoroalkyl surfactants on sewage sludges. J Hazard Mater 260, 689-699. DOI: 10.1016/j.jhazmat.2013.06.022

Zhang S., Lu X., Wang N., and Buck R.C. (2016): Biotransformation potential of 6:2 fluorotelomer sulfonate (6:2 FTSA) in aerobic and anaerobic sediment. Chemosphere 154, 224-230. DOI: 10.1016/j.chemosphere.2016.03.062

Zhang S., Szostek B., McCausland P.K., Wolstenholme B.W., Lu X., Wang N., and Buck R.C. (2013b): 6:2 and 8:2 fluorotelomer alcohol anaerobic biotransformation in digester sludge from a WWTP under methanogenic conditions. Environ Sci Technol 47 (9), 4227-4235. DOI: 10.1021/es4000824

Zhao L., Bian J., Zhang Y., Zhu L., and Liu Z. (2014): Comparison of the sorption behaviors and mechanisms of perfluorosulfonates and perfluorocarboxylic acids on three kinds of clay minerals. Chemosphere 114, 51-58. DOI: http://dx.doi.org/10.1016/j.chemosphere.2014.03.098

Zhao L., Folsom P.W., Wolstenholme B.W., Sun H., Wang N., and Buck R.C. (2013a): 6:2 fluorotelomer alcohol biotransformation in an aerobic river sediment system. Chemosphere 90 (2), 203-209. DOI: 10.1016/j.chemosphere.2012.06.035

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

Zhao S. and Zhu L. (2017): Uptake and metabolism of 10:2 fluorotelomer alcohol in soil-earthworm (Eisenia fetida) and soil-wheat (Triticum aestivum L.) systems. Environmental Pollution 220 (Pt A), 124-131. DOI: 10.1016/j.envpol.2016.09.030

Zhao Z., Xie Z., Moller A., Sturm R., Tang J., Zhang G., and Ebinghaus R. (2012): Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast. Environ Pollut 170, 71-77. DOI: 10.1016/j.envpol.2012.06.004