Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1A OR 1B, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): Pentacosafluorotridecanoic acid

EC Number(s): 276-745-2

CAS Number(s): 72629-94-8

Submitted by: **BAuA**

Federal Office for Chemicals

Friedrich-Henkel-Weg 1 – 25

44149 Dortmund

Germany

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PREFACE

In four provided dossiers, the intrinsic properties of four perfluorinated carboxylic acids (PFCAs) are assessed: C_{11-14}-PFCAs. Many studies are only available for structurally similar shorter chain PFCAs such as C_8-PFCA and C_9-PFCA. In those cases where studies on the particular substance are missing, studies from either shorter or longer chain PFCAs are used in the provided dossiers by applying read-across. Read-across is based on the structural similarities and on the physicochemical properties, which follow a regular pattern. All PFCAs contain a carboxylic acids group and a perfluorinated carbon chain. The only difference is the number of CF_2-groups in this chain. Details on the read-across approach, i.e. showing the trend of physicochemical properties and the structural similarities are given in Annex I.

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1A OR 1B, PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name(s): Pentacosafluorotridecanoic acid

EC Number(s):276-745-2

CAS Number(s): 72629-94-8

- It is proposed to identify the substance(s) as vPvB according to Article 57 (e).

Summary of how the substance(s) meet(s) the CMR (Cat 1A or 1B), PBT or vPvB criteria, or is/are considered to be (a) substance(s) giving rise to an equivalent level of concern

Degradation studies and BCF experiments on C_{13}-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. C_{8-14}-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF_2-groups.

Comparing the physico-chemical properties of C_{8-14}-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 CF_2-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 carboxylic group in PFCAs alters this persistence of these chemicals. This fact is confirmed by a study which obtained a DT_{50} of >92 years for C_8-PFCA in water. Screening studies of $C_{8,9,12,14}$-PFCA showed no biodegradation within 28 days. Non-standard tests with C_8-PFCA could not detect any degradation products under environmentally relevant conditions. Moreover, a monitoring study showed that C_8-PFCA remained in soil and groundwater, years after application of fire fighting foam which contained PFCAs. Furthermore, screening biodegradation studies on $C_{8,9,12,14}$-PFCAs, one simulation study on aerobic aquatic biodegradation and monitoring studies from contaminated sites on C_8-PFCA in soil and groundwater indicate that these substances may be persistent

Therefore, we conclude that C_{13}-PFCA is not degraded in the environment and thus fulfils the P- and vP-criteria under REACH.

For C_{13}-PFCA, no BCF-value is available. Due to the structural similarity to C_{12}-PFCA and C_{14}-PFCA, they are only one CF_2-group shorter and longer. The BCFs for both substances are well above 5000. Therefore it can be concluded that also C_{13}-PFCA has a BCF larger than 5000, too. This read-across-approach is supported by the increasing trend of BCFs with increasing chain length. A number of BMFs and TMFs are available for C_{13}-PFCA, many of them are >1. This indicates that C_{13}-PFCA has a potential to biomagnify and enriches within the food web.

Hence we conclude that C_{13}-PFCA fulfils the B and the vB-criteria of REACH as well.

In conclusion, C_{13}-PFCA is a vPvB-substance according to Art. 57e) of REACH.

The substance has not yet been registered under REACH.

PART I

JUSTIFICATION

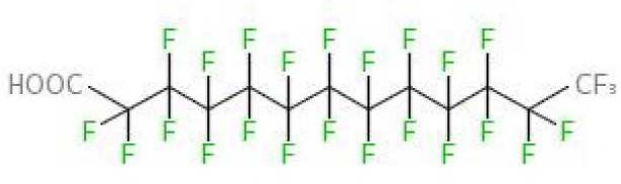
1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	276-745-2
EC name:	Pentacosafluorotridecanoic acid
CAS number (in the EC inventory):	72629-94-8
CAS number:	72629-94-8
CAS name:	Tridecanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-pentacosafluoro-
IUPAC name:	Pentacosafluorotridecanoic acid
Index number in Annex VI of the CLP Regulation	-
Molecular formula:	$C_{13}HF_{25}O_2$
Molecular weight range:	664.1059 g/mol
Synonyms:	C_{13}-PFCA Tridecanoic acid, pentacosafluoro- Perfluorotridecanoic acid

Structural formula:



1.2 Composition of the substance

Name: Pentacosafluorotridecanoic acid

Description: Mono-constituent substance

Degree of purity: Registration dossiers or other information on concentration ranges and on any impurities are not available.

1.3 Physico-chemical properties

No further information regarding the given values or other properties is available.

Table 2: Overview of physicochemical properties

Property	Value	Reference
Physical state at 20°C and 101.3 kPa	solid	According to melting point
Melting/freezing point	112-123 °C 117.5-122°C	Aldrich Handbook of Fine Chemicals and Laboratory Equipmet 2007-2008, Sigma-Aldrich Co.,LTD Kunieda and Shinoda 1976
Boiling point	260.7±35.0 °C, pressure: 760 Torr = 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 3.5E-3 g/L; pH 4 at 25 °C 8.6E-3 g/L; pH 5 at 25 °C 0.0100 g/L; pH 6-10 at 25 °C	Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs)
Adsorption/desorption	logP 10.093±0.901 at 25 °C	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.*
Dissociation constant	pKa 0.52±0.10	Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2012 ACD/Labs)

With increasing chain length the melting and boiling point increase, while no significant change can be found for the vapour pressure and dissociation constant for the C_{11-14}-PFCAs based on the calculations given in Table 2. The water solubility decreases with increasing chain length. This is in agreement with the fact that the polarity of the substances decreases with an increasing chain length. It should be emphasised here that it is not possible to assess the calculated values of C_{11-14}-PFCAs because there are factors like special conformation of the molecules which have an influence on the real values, but which have not been taken into account for the calculation.

However, the calculated values have dimensions which would be theoretically expected for the C_{11-14} PFCAs.

2 HARMONISED CLASSIFICATION AND LABELLING

C_{13}-PFCA is not classified according to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).

3 ENVIRONMENTAL FATE PROPERTIES

3.1 Degradation

3.1.1 Abiotic degradation

3.1.1.1 Hydrolysis

There are no studies on the hydrolysis of C_{13}-PFCA available. Based on the data given in Annex 1, results of studies of structurally similar substances of the same chemical group could be used to evaluate the hydrolysis of C_{11}-PFCA.

Two studies are available on shorter chain lengths PFCAs. Hydrolysis of perfluorinated octanoic acid (C_8-PFCA; PFOA) and its ammonium salt (APFO) (CAS-No: 335-67-1, 3825-26-1) and perfluorinated nonanoic acid (C_9-PFCA; PFNA) (CAS No: 375-95-1) were analyzed. The studies are summarized in the following:

C_8-PFCA is hydrolytically stable under relevant environmental conditions. One study has been discussed in the OECD SIDS Initial Assessment Report for C_8-PFCA (PFOA), which has been copied here in italic letters (OECD, 2006):

The 3M Environmental Laboratory performed a study of the hydrolysis of APFO (3M Co., 2001a) (Realiability = 1). *The study procedures were based on USEPA's OPPTS Guideline Document 835.2110; although the procedures do not fulfil all the requirements of the guideline, they were more than adequate for these studies. Results were based on the observed concentrations of APFO in buffered aqueous solutions as a function of time. The chosen analytical technique was high performance liquid chromatography with mass spectrometry detection (HPLC-MS).*

During the study, samples were prepared and examined at six different pH levels from 1.5 to 11.0 over a period of 109 days. Experiments were performed at 50 °C and the results extrapolated to 25 °C. Data from two of the pH levels (3.0 and 11) failed to meet the data quality objective and were rejected. Also rejected were the data obtained for pH 1.5 because ion pairing led to artificially low concentrations for all the incubation periods. The results for the remaining pH levels (5.0, 7.0, and 9.0) indicated no clear dependence of the degradation rate of PFOA on pH. From the data pooled over the three pH levels, it was estimated that the hydrolytic half-life of PFOA at 25°C is greater than 92 years, with the most likely value of 235 years. From the mean value and precision of PFOA concentrations, it was estimated the hydrolytic half-life of PFOA to be greater than 97 years.

A newer study showed no decomposition of C_{8-9}-PFCAs in hot water in absence of $S_2O_8^{2-}$. After the addition of $S_2O_8^{2-}$ to the reaction system efficient decomposition of PFCAs has been observed at 80 °C. After a reaction time of 6 hours, C_8-PFCA and C_9-PFCA were decomposed completely. The reaction products were mainly F^- and CO_2 at a yield of 77.5 % ((moles of F^- formed)/(moles of fluorine content in initial PFOA)) and 70.2 % ((moles of CO_2 formed)/(moles of carbon content in initial PFOA)), respectively for C_8-PFCA. For C_9-PFCA the reaction products were mainly F^- and CO_2 at a yield of 88.9 % and 75.2 %, respectively.. Short chain PFCAs were a minor reaction product. However, at higher temperatures (150°C) 12.3% of the initial C_8-PFCA remained and the yields of F^- and CO_2 were 24.6 and 37.0 %, respectively (Hori et al., 2008) (Reliabilty = 2).

The water solubility of C_{13}-PFCA is lower than those of $C_{8,9}$-PFCA, which can be explained by the expanded fluorinated carbon chain (Annex 1). However, the stability of the PFCAs is mainly based on the stability of the highly fluorinated carbon chain (Siegemund et al., 2000). Since C_8-PFCA is hydrolytically stable, we estimate a comparable hydrolytically stability also for C_{13}-PFCA.

Based on the read across rationale described in Annex 1, data on C_8-PFCA is used as evidence for C_{13}-PFCA to conclude that it is hydrolytically stable under environmental conditions.

3.1.1.2 Phototransformation/photolysis

Direct photolysis of a carbon fluorine chain is expected to be very slow, with stability expected to be sustained for more than 1000 years (Environment Canada, 2010).

3.1.1.2.1 Phototransformation in air

There are no studies on phototransformation for C_{13}-PFCAs in air available. However, studies on C_8-PFCA exist and are summarized below:

The following information was copied from the OECD SIDS Initial Assessment Report for C_8-PFCA (PFOA) (OECD, 2006):

Hurley et al. determined the rate constants of the reactions of OH radicals with a homologous series of perfluorinated acids (from trifluoroacetic acid to nonafluoropentanoic acid) in 700 Torr of air at 296 K (Hurley et al., 2004). For C_3 to C_5 chain length had no discernible impact on the reactivity of the molecule. The rate constant $k(OH + F(CF_2)_nCOOH) = (1.69±0.22)×10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for n = 2, 3, 4, respectively. Atmospheric lifetimes of $F(CF_2)_nCOOH$ with respect to reaction with OH radicals are estimated to be approximately 230 days for n = 1 and 130 days for n > 1. (Calculation of lifetime by comparison with CH_3CCl3 (half-life 5.99 years, $k = 1.0×10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}). The authors conclude, that the major atmospheric loss mechanism of perfluorinated carboxylic acids is dry and wet (particle mediated) deposition which occur on a time scale which is probably of the order of 10 days. Reaction with OH is a minor atmospheric loss mechanism for perfluorinated carboxylic acids.

3.1.1.2.2 Phototransformation in water

There are no studies on phototransformation in water for C_{13}-PFCAs available. However, studies on C_{8-11}-PFCA exist and are summarized below:

The photochemical decomposition of long-chain PFCAs in water by use of persulfate ion ($S_2O_8^{2-}$) in water (C_9-PFCA) and in an aqueous/liquid CO_2 biphasic system (C_{9-11}-PFCAs) was examined by Hori et al. (Hori et al., 2005b) (Reliability = 2). In water and in the absence of $S_2O_8^{2-}$ (direct photolysis) C_9-PFCA decomposition of 64.5 % was determined. In the presence of $S_2O_8^{2-}$ the decomposition increased to 100%. The decompositions after 12 hours in the biphasic system were 100% for C_9-PFCA and C_{10}-PFCA, and 77.1% for C_{11}-PFCA. The reaction product was mainly F^- (66.2 %, 73.4 % and 46.35 % of (moles of F^- formed)/(moles of fluorine content in initial PFCA)) and the minor reaction products were short-chain PFCAs. Since the conditions in this study are not environmentally relevant, we did not describe this study in detail.

In addition to the study of Hori et al, further studies are available for C_8-PFCA (PFOA) and its ammonium salt APFO (see table 4).

Table 3: Summary of photodegradation studies for C_8-PFCA and its ammonium salt

Test Substance	Result	Remarks	Reliability	Reference
Ammonium salt of C_8-PFCA	No photodegradation	Direct photolysis	2	(OECD, 2006);(3M Co., 1979)
Ammonium salt of C_8-PFCA	No photodegradation	Direct and indirect (H_2O_2; synthethic humic water, Fe_2O_3) photolysis	1	(OECD, 2006);(3M Co., 2001b)
	Estimated half-life > 349 days	Indirect photolysis (Fe_2O_3)		
C_8-PFCA		Short wave length (<300 nm) used for irradiation → limited relevance for an aqueous environment	2	(Hori et al., 2004)
	44.9% of the initial PFOA was decomposed after 24 hours	Direct photolysis; 0.48 MPa O_2		
	35.5% of the initial PFOA was decomposed after 24 hours	Indirect photolysis (H_2O_2); 0.48 MPa O_2		
	100% of the initial PFOA was decomposed after 24 hours	Indirect photolysis (tungstic heteropolyacid photocatalyst); 0.48 MPa O_2		
C_8-PFCA		Short wave length (<300 nm) used for irradiation → limited relevance for an aqueous environment	2	(Hori et al., 2005a)
	16.8% of the initial PFOA was decomposed after 4 hours	Direct photolysis; 0.48 MPa O_2		
	100% of the initial PFOA was decomposed after 4 hours	Indirect photolysis ($S_2O_8^{2-}$); 0.48 MPa O_2		

The following information was copied from the OECD SIDS Initial Assessment Report for C_8-PFCA (PFOA; APFO is the ammonium salt of C_8-PFCA) (OECD, 2006):

Direct photolysis of APFO was examined in two separate studies (3M Co., 1979; 3M Co., 2001b) and photodegradation was not observed in either study. In the 3M (1979) study, a solution of 50 mg/l APFO in 2.8 litres of distilled water was exposed to simulated sunlight at 22±2 ºC. Spectral energy was characterized from 290-600 nm with a max output at ~360 nm. Direct photolysis of the test substance was not detected.

In the 3M (3M Co., 2001b) study, both direct and indirect photolysis was examined utilizing techniques based on USEPA and OECD guidance documents. To determine the potential for direct photolysis, APFO was dissolved in pH 7 buffered water and exposed to simulated sunlight. For indirect photolysis, APFO was dissolved in 3 separate matrices and exposed to simulated sunlight for periods of time from 69.5 to 164 hours. These exposures tested how each matrix would affect the photodegradation of APFO. One matrix was a pH 7 buffered aqueous solution containing H_2O_2 as a well-characterized source of OH radicals. This tested the propensity of APFO to undergo indirect photolysis. The second matrix contained Fe_2O_3 in water that has been shown to generate hydroxyl radicals via a Fenton-type reaction in the presence of natural and artificial sunlight. The third matrix contained a standard solution of humic material. Neither direct nor indirect photolysis of APFO was observed based on loss of starting material. Predicted degradation products were not detected above their limits of quantification. There was no conclusive evidence of direct or indirect photolysis whose rates of degradation are highly dependent on the experimental conditions. Using the iron oxide (Fe_2O_3) photoinitiator matrix model, the APFO half-life was estimated to be greater than 349 days.

According to Hori et al., aqueous solutions of PFOA absorb light strongly from the deep UV-region to 220 nm (Hori et al., 2004). A weak, broad absorption band reaches from 220 to 270 nm (no absorption coefficient stated). The irradiation of a 1.35 mM PFOA solution (29.6 µmol) in water (under 0.48 MPa of oxygen) with light from a xenon-mercury lamp (no radiant flux stated) for 24 hours resulted in a ca. 44.9 % reduction (13.3 µmol) of PFOA concentration. Concentrations of CO_2 and fluoride increased simultaneously. Small amounts (0.1-5 µmol) of short chain perfluorinated hydrocarbon acids (C_2-C_7) were detected. The addition of the photocatalyst tungsten heteropolyacid ($[PW_{12}O_{40}]^-$) or persulfate ($S_2O_8^{2-}$) (Hori et al., 2005a) *accelerates the reaction rate. Due to the short wave length used for irradiation (< 300 nm) the photodegradation described may be of limited relevance for an aqueous environment but may be used as a technical process.*

3.1.1.2.3 Phototransformation in soil

3.1.1.3 Summary and discussion on abiotic degradation

In general, perfluorinated carboxylic acids are very stable. Since there are no degradation studies on the C_{13}-PFCA available, data from similar substances need to be considered and discussed. Based on the data given in Annex 1, results of studies of structurally similar substances of the same chemical group could be used to evaluate the abiotic degradation of C_{13}-PFCA.

The data on C_8-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days; conclusion by analogy from short-chain perfluorinated acids). Under relevant environmental conditions C_8-PFCA is hydrolytically stable (DT_{50} > 92 years) and does not undergo direct photodegradation in natural waters. The estimated DT_{50} for indirect photolysis is 349 days.

Based on the read across rationale described in Annex 1, data on C_8-PFCA are used as evidence for C_{13}-PFCA to conclude that it is stable under environmental conditions and abiotic degradation is expected to be as low as for the chemically similar substance C_8-PFCA.

3.1.2 Biodegradation

3.1.2.1 Biodegradation in water

3.1.2.1.1 Estimated data

3.1.2.1.2 Screening tests

There are no studies available for the C_{13}-PFCA. Based on the data given in Annex 1, results of studies of structurally similar substances of the same chemical group could be used to evaluate the hydrolysis of C_{13}-PFCA.

Only one study is available for the C_{12} and C_{14} PFCAs, respectively. Moreover, some studies are available on $C_{8,9}$-PFCAs and the ammonium salt of C_8-PFCA. The results are summarized in **Table 4**.

Table 4: Summary of screening tests for $C_{8,9,12,14}$-PFCA and the ammonium salt of C_8-PFCA

Test substance	Method	Result	Reliability	Reference
C_8-PFCA	OECD 301 C	5 % in 28 days	2	(National Institute of Technology and Evaluation, 2007)
Ammonium salt of C_8-PFCA	OECD 301 C	7 % in 28 days	2	(National Institute of Technology and Evaluation, 2007)
C_{12}-PFCA	OECD 301 C	No degradation in 28 days	2	(National Institute of Technology and Evaluation, 2002)
C_{14}-PFCA	OECD 301 C	No degradation in 28 days	2	(National Institute of Technology and Evaluation, 2002)

Ammonium salt of C_8-PFCA	OECD 301 B	13 % in 28 days	2	(OECD, 2007), (DuPont Co., 1997)
C_8-PFCA	OECD 301 F	No biodegradation in 28 days	2	(Stasinakis et al., 2008)
C_9-PFCA	OECD 301 F	No biodegradation in 28 days	2	(Stasinakis et al., 2008)
Ammonium salt of C_8-PFCA	Shake culture test modelled after the Soap and Detergent Association´s presumptive test for degradation	No biodegradation after 2.5 months	2	(OECD, 2006), (3M Co., 1978)

A number of studies for the C_8-PFCA (PFOA) and its ammonium salt APFO were already discussed in the OECD SIDS Assessment Report (OECD, 2006). The following text in italic letters was copied from there:

Using an acclimated sludge inoculum, the biodegradation of APFO was investigated using a shake culture study modeled after the Soap and Detergent Association's presumptive test for degradation (3M Co., 1978). Both thin-layer and liquid chromatography did not detect the presence of any metabolic products over the course of 2 1/2 months indicating that PFOA does not readily undergo biodegradation. In a related study, 2.645 mg/l APFO was not measurably degraded in activated sludge inoculum (Pace Analytical, 2001). Test flasks were prepared using a mineral salts medium, 1 ml methanol, and 50 ml settled sludge. Analysis was conducted with a HPLC/MSD system. Although the results were deemed unreliable due to a lack of description of experimental protocols or indications of a high degree of experimental error, several other studies conducted between 1977-1987 also did not observe APFO biodegradation (Pace Analytical, 1987; 3M Co., 1985; 3M Co., 1980; 3M Co., 1979). In addition, a study conducted by Oakes et al.) . In addition, a study conducted by Oakes et al. indicated little biotic or abiotic degradation of PFOA on a time scale of 35 days, i.e., the PFOA exposure concentrations were stable over time and ranged from 84.5 % to 114.5 % of the initial concentrations (Oakes et al., 2004).

In a 28 day ready biodegradability test (OECD 301 C) using 100 mg/L C_{12}-PFCA, C_{14}-PFCA, C_8-PFCA and its ammonium salt, respectively, and 30 mg/L activated sludge non-biodegradability was demonstrated. Only 5 % (C_8-PFCA) and 7% (ammonium salt of C_8-PFCA) degradation was observed by BOD. For C_{12}-PFCA and C_{14}-PFCA no biodegradation was observed (National Institute of Technology and Evaluation, 2007).

In a further test of ready biodegradability (OECD 301 F) biodegradation of neither C_8-PFCA nor C_9-PFCA was observed in 28 days (Stasinakis et al., 2008).

In summary, on the basis of the available screening tests, $C_{8,9,12,14}$ PFCAs are not readily biodegradable. Based on the read across rationale described in Annex 1, data on $C_{8,9,12,14}$-PFCA are used as evidence to conclude that C_{13}-PFCA is not readily biodegradable.

3.1.2.1.3 Simulation tests

For C_{13}-PFCA no experimental degradation tests are available. Based on the data given in Annex 1, results of studies of structurally similar substances of the same chemical group could be used to evaluate the hydrolysis of C_{13}-PFCA.

Therefore, test results for C_8-PFCA are discussed in the following.

No environmental half-lives for C_8-PFCA have been reported, even in the cases where corresponding tests have been performed (see **Table 5**).

Table 5: Summary of simulations tests of C_8-PFCA (PFOA) and its sodium and ammonium salt (APFO)

Test substance	Method	Result	Reliability	Reference
C_8-PFCA	Closed-loop systems in laboratory scale; Aerobic and anaerobic conditions	No elimination	3	(Meesters and Schroeder, 2004; Schröder, 2003)
Ammonium salt of C_8-PFCA	Biodegradation in mixed bacterial culture and activated sludge Aerobic conditions	< 0.6 % of $^{14}CO_2$ was detected after 28 days	4	(Wang et al., 2005)
Sodium salt of C_8-PFCA	Microcosm study Aerobic conditions	No significant dissipation from water column after 35 days (initial concentration 0.3 mg/L; 1mg/L; 30 mg/L) 32% dissipation in 35 days (initial concentration 100 mg/L)	3	(Hanson et al., 2005)
C_8-PFCA/ ammonium salt of C_8-PFCA	1.Preliminary screening: C_8-PFCA serves as an electron acceptor under anaerobic conditions (in combination with different inocula) 2. Hypothesis refinement: ^{14}C C_8-PFCA serves as an electron acceptor	No significant consumption of the initial C_8-PFCA during 110 – 259 days No loss of ammonium salt of C_8-PFCA No production of	2	(Liou et al., 2010)

	under anaerobic conditions	$^{14}CO_2$ No detection of radiolabel transformation products		

In the OECD SIDS Initial Assessment Report it was concluded that C_8-PFCA (PFOA) is not expected to undergo biodegradation (OECD, 2006). The following text in italic letters was copied from there:

Schroeder (2003), and Meesters and Schroeder (2004) investigated the biochemical degradation of PFOA in sewage sludge in laboratory scale reactors. After 25 days under aerobic conditions PFOA (initial concentration 5 mg/l) was not eliminated by metabolic processes, mineralization processes or by adsorption (Meesters and Schroeder, 2004; Schröder, 2003).

Wang et al. studied the biodegradation of fluorotelomer alcohols. However, ^{14}C-labelled C_8-PFCA ammonium salt was used as starting material in this study, too. The authors analyzed the headspace of sealed vessels containing mixed bacterial cultures and vessels containing activated sludge from a domestic sewage treatment plant under continuous air flow. The mixed bacterial culture from industrial wastewater treatment sludge was enriched using 8:2 telomere alcohol and ^{14}C-labelled C_8-PFCA ammonium salt, respectively. However, for using C_8-PFCA ammonium salt as a starting material no detailed information are available from the report. The authors describe that potential biodegradation products were separated and quantified by LC/ARC (on-line liquid chromatography/accurate radioisotope counting). Transformation products were identified by quadrupole time of flight mass spectrometry. Only <0.6 % of $^{14}CO_2$ was detected after 28 days. The report contains no graphs or further data to re-evaluate this statement. Although the study seems to be very well documented for ^{14}C labelled 8:2 FTOH, we can only flag the study with a reliability of 4, since details on C_8-PFCA ammonium salt are not available. The documentation for the results obtained with C_8-PFCA is missing in the report. However the result indicates, that C_8-PFCA ammonium salt is not biodegradable within 28 days (Wang et al., 2005).

Hanson et al. performed a microcosm study. Microcosms were approximately 1.2 m deep with a water depth of 1 m, a diameter of 3.9 m, and a surface area of 11.95 m². Each microcosm had a capacity of approximately 12m³ of water. Sediment consisted of a 1:1:1 mixture of sand, loam and organic matter (mainly composted manure). The total carbon content of the sediment was 16.3%. Microcosms were circulated for 2 weeks from a well-fed irrigation pond prior to the experiments. Nominal concentrations of 0.3, 1, 30, and 100 mg/L C_8-PFCA, as the sodium salt, plus controls were added to the microcosms. Each exposure was randomly assigned to three separate microcosms from a total of 15 microcosms. Immediately prior to treatment, water flow into each microcosm from the main irrigation pond ceased, creating a closed system relative to the other microcosms and the irrigation pond.

Water chemistry and PFOA analysis were taken at the same time on a regularly basis. Temperature and dissolved oxygen content were measured daily. Water samples were collected with a metal integrated water column sampler. Integrated subsamples from at least 4 randomly selected locations in each microcosm were collected to a total volume of 4 L. Samples were stored at 4 °C until analysis. Water samples were analyzed by ion chromatography. The mobile phase was 0.5 mM NaOH, 5 % methanol, and 5% acetonitrile with a flow rate of 0.4 mL/min. Injection volumes varied from 5, 10, 75, and 200 µl for the 100, 30, 1 and 0.3 mg/L microcosms, respectively. For each set of samples analyzed five standards and one quality control sample were included at the beginning of

each run and again at the end. Radioactive labelling was not performed. Over a 35-day field study C_8-PFCA showed no significant dissipation from the water column. However, at the highest concentration (100 mg/L) a partitioning from the water column into other compartments is suspected (32% dissipation in 35 days) (Hanson et al., 2005). Since the documentation of the procedure was insufficient in our opinion the study is not reliable (reliability 3).

Liou et al. investigated the anaerobic biodegradability of C_8-PFCA respectively its ammonium salt. In a two-phase experiment (preliminary screening, hypothesis refinement) the use of C_8-PFCA as a physiological electron acceptor (electron donator: acetate, lactate, ethanol or hydrogen gas) was studied. Additionally, the possibility of co-metabolism of C_8-PFCA during reductive dechlorination of trichloroethene and during various physiological conditions (aerobic, nitrate-reducing, iron-reducing, sulfate reducing, and methanogenic) was analyzed. Five different inoculums were used (from a municipal waste-water treatment plant, industrial site sediment, an agricultural soil, and soils from two fire training areas). Environmental samples used as inoculum sources in the biodegradation experiments were aseptically gathered (sterile spatula) placed in 0.5 L sterilized canning jars (filled to the brim), stored on ice in the field, and maintained at 4 °C before being transferred to an anaerobic hood where samples were degassed and dispensed as slurries in biodegradation assays. Soils and sludge were gathered from: the Ithaca sewage treatment plant; a water-saturated drainage ditch adjacent to the DuPont Chambers Works waste treatment facility in Salem County, New Jersey, previously shown to carry out reductive dechlorination (Fung et al., 2009); the Cornell agricultural field station (Collamer silt loam, Ithaca, NY), the Ithaca fire training facility, and the Rochester, NY fire training facility (the latter two sites were chosen due to potential contamination with fluorinated fire retardant chemicals) (Liou et al., 2010).

For the serum bottle –based biodegradation assays treatments occurred in triplicats (160 ml serum bottles with 100 mL of media; live ± C_8-PFCA and abiotic controls, autoclaved for 1 h). For the ^{14}C-PFOA experiments, 15-mL serum bottles were utilized (50% O_2-free N_2 headspace, 50% inoculated anaerobic test medium) with non-radioactive C_8-PFCA and ^{14}C- C_8-PFCA (4.5 Ci/mL test medium) to give a final concentration of 100 mg/L C_8-PFCA medium. For establishing the various terminal electron-accepting processes, a standard anaerobic procedure was used. The anaerobic mineral salts buffer (plus vitamins and trace minerals) was used as diluents for the various inoculums sources (5% wt/volume) with addition of electron donors (10 mM sodium acetate ± 40 mM sodium lactate or 0.6 mM ethanol or 2 atm H_2) or electron acceptors [O_2 as air headspace or O_2- free N_2 headspace in each serum bottle with additions of 30 mM nitrate or 4 mg/mL FeOOH or 10 mM sulfate or 0.4 mM trichloroethene (TCE) or no addition (for the methanogenic treatment)]. Samples (1.0 mL) were periodically removed from each serum bottle, placed in 4-mL glass vials sealed with Al-backed caps, immediately mixed with an equal volume of methanol and stored at _20 °C until analysis. Accumulated batches of samples from serum vials were analyzed for concentrations of PFOA, ^{14}C- C_8-PFCA, fluoride, nitrate, sulfate, and potential C_8-PFCA transformation products. Headspace gases were sampled with a gas-tight syringe (250 mL) and analyzed for TCE, vinyl chloride and methane. In the radiotracer study, dissolved ^{14}C activity in the anaerobic medium and in the 0.4 N KOH solution retrieved from the internal reservoir to trap $^{14}CO_2$ were determined by scintillation counting. To assay potential microbial inhibition by C_8-PFCA, triplicate serum- bottle assays inoculated with 5% Ithaca sewage were prepared, as above. Anaerobic preparations (±100 ppm C_8-PFCA) were assayed for methanogenesis. Aerobic preparations containing 15 ppm naphthalene were sampled as above and analyzed by high-performance liquid chromatography (HPLC). After filtration through nylon acrodisc filters, naphthalene was separated at room temperature. Methanol–water (1:1) was the mobile phase at a flow rate of 1.5 mL/ min. The eluent was monitored by UV VIS at 340 nm. Quantification was done by comparison to authentic standards (Liou et al., 2010). C_8-PFCA

quantification was performed by LC/MS/MS following a standard procedure. Potential C_8-PFCA metabolites were screened by applying LC/MS.

In no combination of the inoculum source, electron donator or physiological conditions a significant percentage of the initial C_8-PFCA (100 ppm and 100 ppb) was consumed (110 - 259 days). In a test with ^{14}C labelled C_8-PFCA ammonium salt (inoculum = sewage), no loss of C_8-PFCA ammonium salt was detected, no $^{14}CO_2$ was produced and no radiolabelled C_8-PFCA ammonium salt transformation product was indicated. Co-metabolism of C_8-PFCA during reductive dechlorination of trichlorethene was suggested by a drop in C_8-PFCA concentration in the 100 ppb treatment after a 65-d incubation. However, extensive analysis failed to determine corroborating transformation products. In summary, under conditions which were examined in this study, C_8-PFCA is environmentally persistent (Liou et al., 2010).

In conclusion, the one non-standard aerobic degradation simulation study and one non-standard anaerobic degradation simulation study on C_8-PFCA demonstrate the high persistence of the compound. Based on the read across rationale described in Annex 1, data on C_8-PFCAs can be used as evidence of persistence for C_{13}-PFCA.

3.1.2.2 Biodegradation in sediments

3.1.2.3 Biodegradation in soil

There are no degradation studies on C_{13}-PFCA available. Based on the data given in Annex 1, results of studies of structurally similar substances of the same chemical group could be used to evaluate the hydrolysis of C_{11}-PFCA.

A number of studies are available for C_8-PFCA (PFOA) which were already discussed in the OECD SIDS Initial Assessment Report. The following text was copied from there (italic letters) (OECD, 2006):

Moody and Field (1999) conducted sampling and analysis of samples taken from groundwater 1 to 3 meters below the soil surface in close proximity to two fire-training areas with a history of aqueous film forming foam use. Perfluorooctanoate was detected at maximum concentrations ranging from 116 to 6750 µg/l at the two sites many years after its use at those sites had been discontinued. These results suggest that PFOA can leach to groundwater (Moody and Field, 1999).

Extensive site specific monitoring of soil and ground water concentrations of PFOA and related substances was conducted by 3M, DuPont Daikin and others. PFOA in soil has been shown to persist for decades and to be a long term source of groundwater and surface water contamination (see for example (DuPont Co., 2003; 3M Co., 2005)).

At the DuPont Washington Works site soil contaminated by perfluorochemical waste has been shown to contain ppm levels of PFOA 3 decades after application ceased. The underlying groundwater also contains ppm levels of PFOA (DuPont Co., 1999).

Extensive field monitoring data generated by 3M at the Decatur, AL site have also shown that PFOA is persistent in soils. Soil samples were collected from a former sludge application area of the 3M Decatur, AL facility also show soil contamination and underlying groundwater contamination up to ppm levels decades after application ceased.

Moody et al. investigated groundwater at a former fire-training area at Wurtsmith Air Force Base which was used between 1950s and 1993. Before sampling, the soil and groundwater in the area has been studied in detail. Groundwater samples were collected from two types of monitoring wells. All samples were collected in high density polypropylene bottles. Samples were shipped on ice without preservation and stored at 4 °C prior to analysis. Perfluorocarboxylate concentrations were measured as described in the following: Strong anion exchange disks were used to extract perfluorocarboxylates (6 to 8 carbons) from groundwater. The perfluorocarboxylates were simultaneously eluted from the disks and derivatized to their methyl esters by treatment with iodomethane for direct analysis by electron impact gas chromatography-mass spectrometry (GC-MS). A single analysis was conducted for each groundwater sample. The detection limit (defined as a signal-to-noise ratio greater than 3) and quantification limit (defined as a signal-to-noise ratio greater than 10) for perfluorocarboxylates were 3 and 13 mg/L, respectively, using 2-chlorolepidine as the internal standard. Additionally, electron capture negative chemical ionization GC-MS was employed to confirm the identity of PFOA, in groundwater samples (Moody et al., 2003). Depending on the location of sampling, the concentrations of C_8-PFCA were between 8 and 105 µg/L in groundwater. The authors estimated that perfluorinated surfactants had been in the groundwater for at least five years and possibly for as long as 15 years. This showed that C_8-PFCA did not degrade under the environmental conditions at this site (for both soil and groundwater) (Reliability = 2) (Moody et al., 2003).

The anaerobic biodegradability of C_8-PFCA and its ammonium salt, respectively, in soil from two fire training areas was investigated by Liou et al. (see above 3.1.2.1.3 Simulation tests). No significant amount of the initial PFOA was dissipated after 259 days.

In conclusion, the available data on C_8-PFCA demonstrate the high persistence of the compound. Based on the read across rationale described in Annex 1, data on C_8-PFCAs can be used as evidence of persistence for C_{13}-PFCA.

3.1.2.4 Summary and discussion on biodegradation

Screening studies for C_{13}-PFCA are not available. However, results from screening studies of $C_{8,9,12,14}$-PFCAs used for read across approach as described in Annex1 indicate that structurally similar compounds are not readily biodegradable. The results of one non-standard aerobic biodegradation simulation test, one non-standard anaerobic biodegradation simulation test and field monitoring data on C_8-PFCA from contaminated sites provide evidence that biodegradation in water, soil and sediment occurs. Since the stability of PFCAs is in general mainly based on the stability of the fluorinated carbon chain it can be concluded that also for C_{13}-PFCA no biodegradation in water, soil and sediment can be expected. Thus, it can be assumed that C_{13}-PFCA is persistent as well.

3.1.3 Summary and discussion on degradation

For C_{13}-PFCA no experimental data on degradation are available. Therefore, data from chemically similar compounds should be considered in a read-across approach (please see Annex 1 for further details). The degradation potential of substances differing only in the number of carbons in the fluorinated carbon chain has been analyzed in some studies. Generally, it is known that the bond between carbon and fluorine is one of the most stable ones in organic chemistry.

A number of studies for the shorter chain C_8-PFCA show that this substance is very persistent and does not undergo abiotic or biotic degradation at all under relevant environmental conditions.

Abiotic degradation

The data on C_8-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days). The hydrolytic half-life of C_8-PFCA at 25°C is greater than 92 years, with the most likely value of 235 years under relevant environmental conditions *(3M Co., 2001a)*. No photodegradation of C_8-PFCA has been observed in studies conducted under relevant environmental conditions. The estimated DT_{50} for indirect photolysis is 349 days.

Biotic degradation

Standard screening tests are available for $C_{8,9,12,14}$-PFCAs. No biodegradation at all has been observed for $C_{9,12,14}$-PFCAs within 28 days. For C_8-PFCA test results differ from "no biodegradation" to 13% biodegradation of the ammonium salt. Thus, it can be concluded that $C_{8,9,12,14}$-PFCAs are not readily biodegradable.

For C_8-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

PFCAs are synthetic compounds which contain a structural feature: a perfluorinated carbon chain combined with a carboxylic group. 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).

Based on their molecular properties it is, thus, not surprising, that researchers could not measure degradation of the intensively studied C_8-PFCA or its salts. Considering the organic chemistry of this substance group it seems to be very likely that a carbon chain being some CF_2-groups longer is as persistent as a shorter chain C_8-PFCAs. We therefore conclude that $C_{9\text{-}14}$-PFCAs are as resistant to degradation as it has been shown for C_8-PFCA.

In summary, using the described read-across approach, we conclude that C_{13}-PFCA is a very persistent synthetic compound which is resistant to abiotic and biotic degradation.

3.2 Environmental distribution

3.2.1 Adsorption/desorption

Not relevant for this dossier.

3.2.2 Volatilisation

Not relevant for this dossier.

3.2.3 Distribution modelling

Not relevant for this dossier.

3.3 Bioaccumulation

3.3.1 Aquatic bioaccumulation

3.3.1.1 Bioconcentration factor BCF

Bioconcentration is the process by which a chemical is accumulated by an organism as a result of exposure to the chemical in water – it often refers to a condition usually achieved under laboratory and steady state conditions. The BCF is typically calculated as the ratio of the measured concentrations of the chemical in the organism and the water once a steady state has been achieved:

$$BCF = \frac{c_{Biota}}{c_{Water}}$$

The BFC can alternatively be determined kinetically by using the uptake rate k_1 and the depuration rate k_2:

$$BCF = \frac{k_1}{k_2}$$

There are no studies available which determined the BCFs of C_{13}-PFCA. However, two studies are available where the BCFs for $C_{11,12,14}$-PFCAs have been analyzed. These studies are discussed below:

In the first study carp were exposed to $C_{11,12,14}$-PFCAs (National Institute of Technology and Evaluation, 2007). The test was conducted in accordance with the OECD 305 guideline this means the test was conducted in a flow through test system, the concentration of the test substance was analytically checked and the pH was within the range 6.0 to 8.5. The uptake period was 60 days. The depuration period was 45 days. Steady state BCFs (whole body) were in the range from 2300 - 3700, 10000 - 16000 and 16000-17000 for C_{11}-PFCA, C_{12}-PFCA and C_{14}-PFCA, respectively (Table 7 and Figure 1). This laboratory study is reliable (reliability 2).

In the second study rainbow trout were exposed in a flow-through system for 12 days followed by a depuration time of 33 days in fresh water to determine tissue distribution and bioconcentration (Martin et al., 2003a). For determination of bioconcentration, juvenile fish (5-10g) were exposed simultaneously to PFCAs of varying chain length. No adverse effects were observable based on fish mortality, growth and liver somatic index. The exposure concentration of each PFCA was analytically checked. PFCA concentrations were stable throughout the uptake phase. There was an initial decrease between 0.25 h and 24 h which is considered to be caused by the rapid uptake of the PFCAs. The mean waterborne concentrations were 0.48 µg/L for C_{11}-PFCA, 0.20 µg/L for C_{12}-

PFCA and 0.014 µg/L for C_{14}-PFCA. The concentration was relatively stable. A direct analysis was possible as the concentration was above the limit of detection. At 7 occasions during uptake period and 9 occasions during depuration phase, three fish from the exposure tank and one fish from the control were removed to determine the kinetics of uptake and depuration. The BCFs (carcass, blood and liver) were determined on the basis of the uptake and depuration kinetics and results are given in Table 7 and Figure 1. All tissue concentrations were corrected for growth dilution. Additionally, for the tissue distribution study, four immature trout (30 – 48 g) were exposed in separate tanks but under the same uptake conditions (Martin et al., 2003a).

This tissue distribution study showed that unlike lipophilic organic compounds PFCAs did not preferentially accumulate in adipose tissue. Hence a lipid-normalisation of the BCFs would not be reasonable. C_{11}-C_{14}-PFCA concentrations were highest in blood, kidney, liver and gall bladder and low in the gonads, adipose and muscle tissue. Within the blood, the plasma contained between 94 – 99 % of PFCA, with only a minor fraction detectable in the cellular fraction. Recovery from hearts and spleen was low (<10%). Based on high blood, liver and gall bladder concentrations and slow depuration the authors assume that PFCA enter the enterohepatic recirculation in fish. That means the compounds are continuously transferred between the different organs (Martin et al., 2003a).

BCFs were calculated for different body compartments. Though, bioaccumulation should preferably be based on whole body. According to the authors carcass BCFs closely approximate the whole-body BCF. However, compartment-specific BCFs can be more relevant if there is a potential for direct organ-specific toxicity. PFCAs cause hepatomegaly in rodents (Kudo et al., 2000) which is an indicator for hepatotoxicity. Thus, from a toxicological perspective, BCFs based on concentrations in individual organs, such as the liver, may be more relevant when the potential for direct organ-specific toxicity (i.e., liver toxicity) is being predicted. No statistically significant difference was found between the liver somatic index of exposed and control fish. However, bioaccumulation tests are not designed for showing toxic effects. The calculated kinetic BCFs are summarized in Table 6 and Figure 1.

In a recent study, BCFs have been calculated on the basis of BMF data (Inoue et al., 2012). A recently published comparison of BCFs and biomagnification factors (BMFs) investigated 9 substances in a laboratory fish feeding study with carp (Inoue et al. 2012). Five substances showed BCFs larger than 5000 but only two of these substances were likely to biomagnify. Based on linear regression conducted with their data the authors suggest that a BMF of 0.31 indicates a high bioaccumulation potential. Therefore, we used this approach in a similar way to calculated further BCFs based on BMFs of a study by Martin et al (Martin et al., 2003b) (please find details of the study in section 3.3.1.2).

The calculated BCFs from BMFs of the fish feeding study (Martin et al., 2003b) deviate from the measured BCF, whereby they are still in a similar order of magnitude (Martin et al., 2003a). Deviations may be due to an erroneous regression. Though, according to the authors the results of the study are highly suggestive. More data would be necessary to support their findings. On the other hand the elimination rates were different in the two studies of Martin et al. (Martin et al., 2003a; Martin et al., 2003b), which may be due to the different fish size and may explain the differences.

There are also other mechanistic models available to roughly estimate a kinetic bioconcentration factor (BCF_{Kin}) from data generated in the dietary study. These models depend on physical-chemical input parameters such as the log K_{OW}. As this parameter cannot be sufficiently estimated for the PFCAs these approaches should not be used (Weisbrod et al., 2009).

Table 6 Bioconcentration factors (BCF) of $C_{11,12,14}$ –PFCAs.

Substance	Species/foodweb	BCF	Reliability	Reference
C_{11}-PFCA	Rainbow trout (carcass)	2700 ± 400	2	(Martin et al., 2003a)
	Rainbow trout (blood)	11000 ± 1400		
	Rainbow trout (liver)	4900 ± 770		
	Carp (whole)	2300 - 3700	2	(National Institute of Technology and Evaluation, 2007)
	Juvenile rainbow trout (Carcass)	4044-5132*	3	(Inoue et al., 2012; Martin et al., 2003b)
C_{12}-PFCA	Rainbow trout (carcass)	18000 ± 2700	2	(Martin et al., 2003a)
	Rainbow trout (blood)	40000 ± 4500		
	Rainbow trout (liver)	18000 ± 2900		
	Carp (whole)	10000-16000	2	(National Institute of Technology and Evaluation, 2007)
	Juvenile rainbow trout (Carcass)	5761-7327*	3	(Inoue et al., 2012; Martin et al., 2003b)
C_{14}-PFCA	Rainbow trout (carcass)	23000 ± 5300	2	(Martin et al., 2003a)
	Rainbow trout (blood)	30000 ± 4200		
	Rainbow trout (liver)	30000 ± 6000		
	Carp (whole)	16000 - 17000	2	(National Institute of Technology and Evaluation, 2007)
	Juvenile rainbow trout (Carcass)	10388-15857*	3	(Inoue et al., 2012; Martin et al., 2003b)

* Calculated BCFs based on BMF values for C_{11}-PFCA (0.28±0.04), C_{12}-PFCA (0.43±0.062) and C_{14}-PFCA (1.0±0.25). The BMFs were measured by Martin et al. 2003b (please find details of the study in section 3.3.1.2) and the calculation was done as suggested by (Inoue et al., 2012).

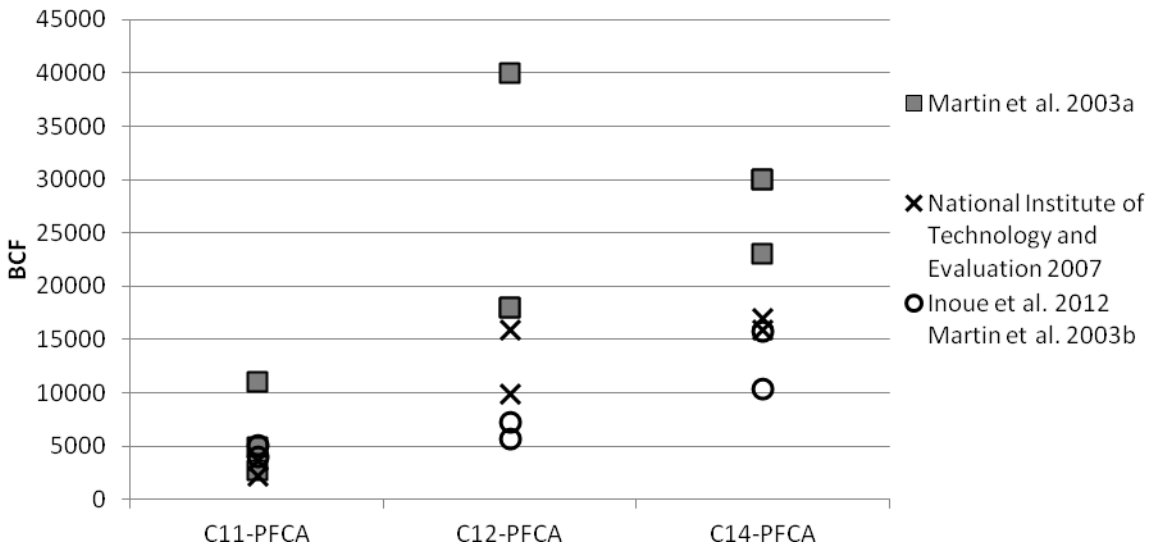


Figure 1: BCFs for $C_{11,12,14}$-PFCAs. For National Institute of Technology and Evaluation 2007, Martin et al 20003a, Inoue et al. 2012 and Martin et al. 2003b reported minimum and maximum data are shown.

Conclusion:

In general, all the BCFs reported indicate a high bioaccumulation potential of the $C_{11,12,14}$-PFCAs.

There are no studies available reporting a BCF for C_{13}-PFCA. For the structural analogues C_{12}-PFCA which is a CF_2-group shorter than C_{13}-PFCA and C_{14}-PFCA which is CF_2-group longer BCFs higher than 5000 were shown (Martin et al., 2003a; Martin et al., 2003b; National Institute of Technology and Evaluation, 2007). As the BCFs for both substances are well above 5000 it can be concluded that also C_{13}-PFCA has a BCF larger than 5000, too. This approach is supported by the increasing trend of BCFs with increasing chain length as can be seen from Figure 1.

3.3.1.2 Biomagnification factors (BMFs)

Besides bioconcentration also biomagnification describes the potential of a chemical to bioaccumulate. Biomagnification factors (BMFs) can be measured in the laboratory in a fashion similar to that used in the OECD and US-EPA bioconcentration test protocols. Organisms are exposed to a chemical preliminary via diet. The BMF test typically includes an uptake phase, where levels of chemicals are followed over time, ideally until the chemical concentration in the organism no longer changes with time (i.e., reaching the steady-state). If a steady-state cannot be reached in the experiment, the uptake phase is followed by a depuration phase where organisms are exposed to uncontaminated food. The rate of decline in chemical concentration over time measured in the depuration phase can then be used to derive the chemical uptake rate from which a hypothetical steady-state concentration can be estimated (Conder et al., 2011).

The laboratory-derived dietary BMF is calculated using the ratio of the chemical concentrations in the test animals at steady-state and their diet:

$$BMF_{(diet)} = \frac{C_{biota}}{C_{diet}}$$

where chemical concentration in the organism (C_{biota}) and its diet (C_{diet}) are appropriately normalized, if needed, (e.g., lipid- or protein-normalized) (Conder et al., 2011).

BMF values based on field studies are based on the ratio of the concentration in the predator and the prey:

$$BMF_{(field)} = \frac{C_{predator}}{C_{prey}}$$

Problems arise with increasing body size of predators because analysis is based on tissue or serum samples. Whole-body analysis is not feasible for ethical reasons, i.e. a whole whale would be needed, and due to the challenging logistics with respect to sampling and laboratory constraints. Therefore, some of the derived BMF-values are restricted to certain tissue samples rather than whole body samples. BMF values based on liver samples may be over estimative. From a toxicological perspective concentrations in individual organs, such as the liver, may be more relevant when the potential for direct organ-specific toxicity (i.e., liver toxicity) is being predicted. Whole body values may be estimated if the tissue mass fraction is known for the organism regarded. There may however be some uncertainties due to inter individual and geographical differences (Houde et al., 2006).

Butt et al. conducted a study in the Canadian Arctic. Ringed seal liver samples were provided by local hunters from 11 different locations. The age of the animals was determined via tooth aging and for a few samples the age was estimated using length-age correlations. Stable isotope analysis was done with ^{15}N to ^{14}N and ^{13}C to ^{12}C. Based on liver samples from polar bears obtained from another study and ringed seal data measured in this study BMFs were calculated (see Figure 2 and Table 8). The polar bear sample sites were associated with ringed seal populations. However, the sample collection year for ringed seal populations varied from 2002 to 2005, and it is possible that interpretation of spatial trends may be confounded by temporal variations of PFCA concentration within seal populations (Butt et al., 2008).

Martin et al. examined PFCA contents in the food web from Lake Ontario in Canada (Martin et al., 2004). Adult lake trouts (top predator) were collected at various years and locations in Lake Ontario. Samples of prey fish (sculpins, smelts and alewifes) and macroinvertebrates (*Mysis sp.*, *Diporeia sp.*) were collected at one location in October 2002. Lake trout samples analyzed represented individual whole fish homogenates. The other species were processed as composites of whole individuals. Data are shown in Table 7.

Table 7: Biomagnification factors (BMF) for C_{13} PFCA ; if not indicated otherwise BMFs refer to whole body

Substance	Location	Species/foodweb	BMF	Reference	Relaibility
C13 PFCA	Canadian Arctic	Polar bear (liver)/ ringed seal (liver)	1.6-3.4	Butt et al. 2008	2
	Lake Ontario	Lake trout/alewife	3.1	Martin et al. 2004	2
	Lake Ontario	Lake trout/smelt	1.2		
	Lake Ontario	Lake trout/sculpin	0.35		
	Lake Ontario	Lake trout/prey (weighted)	2.5		

The following studies investigated BMFs of structurally related PFCAs :

Martin et al. (2003b) exposed juvenile rainbow trout (*Oncorhynchus mykiss*) for 34 days to PFCAs in the diet, followed by a 41 day depuration period. Though, the authors describe their results as BAF the results of this study should rather be assigned as BMFs according to the above mentioned definition as uptake only derived from the diet. During the uptake period, animals were daily fed with spiked food at a rate of 1.5 % food per body weight. Spiked food concentrations were 0.57 µg/g for C_{11}-PFCA, 1.1 µg/g for C_{12}-PFCA and 1.2 µg/g for C_{14}-PFCA. Water samples collected before and after feeding revealed no traces of PFCAs in water. At 6 occasions during uptake period and during depuration period, fish were removed to determine the kinetics of uptake and depuration. The authors estimated the steady state to less than 34 days. Carcass and liver concentrations were determined by using liquid chromatography-tandem mass spectrometry, and kinetic rates were calculated to determine bioaccumulation parameters. Bioaccumulation (carcass) increased with increasing chain length but was with the exception of C_{14}-PFCA not larger than one: 0.28 ± 0.04 for C_{11}-PFCA; 0.43 ± 0.062 for C_{12}-PFCA and 1.0 ± 0.25 for C_{14}-PFCA (see also Figure 2). This indicates that a dietary exposure will not result in biomagnification in juvenile trout. The authors assume that the lack of observed biomagnification was likely due to the small size of fish used in the study, resulting in more rapid chemical elimination to water, relative to body size and and that their natural feeding rate is too low. This more rapid chemical elimination would reduce the BMF stronger than what would be observed for larger species or size classes (Martin et al., 2003b).

Furthermore BMFs were estimated from field studies. Studies are described below and results are shown in Figure 2.

Transfer of PFCAs was elucidated in Lake Ontario including one 4-membered pelagic food chain (Martin et al., 2004). Whole body samples were collected. Two macroinvertebrates (*Diporeia* and *Mysis*) were considered as primary prey whereas rainbow trout inhabited the top predator´s position.

Due to the inherent uncertainties correlated with constitution of diet 4 individual combinations of rainbow trout and its prey were regarded. As this study was conducted with fish uptake of PFCAs may not have occurred exclusively over diet but also over the gills. Thus, the factors may be more accurately addressed as BAF. A striking finding of this study was the unexpectedly high content of PFCAs in the benthic invertebrate *Diporeia* occupying the lowest trophic level. The mechanism leading to this exceptional accumulation still needs to be unravelled. The author's hypothesis is that sediments are a major source for PFCAs. Results are given in Figure 2.

Tomy et al. also investigated liver samples of the beluga whale, ringed seal, fish pelagic and whole body samples of amphipod and arctic copepod of the Western Canadian Arctic. As the authors state themselves differences in sampling years may influence the interpretation of the food web transfer. On the other hand the Arctic as a remote area may be less prone to temporal changes and the existence of point sources there is unlikely. The derived BMF-values (see Figure 2) are restricted to the liver and the resulting BMF and may be over estimative. From a toxicological perspective concentrations in individual organs, such as the liver, may be more relevant when the potential for direct organ-specific toxicity (i.e., liver toxicity) is being predicted (Tomy et al., 2009).

Houde et al. examined PFCA serum concentrations in bottlenose dolphins at two different habitats. The authors claim that utilization of serum or liver concentrations of dolphins will overestimate the BMF by a factor of 10 - 30. Whole body concentrations were estimated on the basis of tissue distribution. Samples were collected between 2002 and 2004. Unfortunately, concentrations in other representative fish species originated from different years, thus, entailing additional uncertainty when assessing BMF through the food chain. On the other hand it may be assumed that media and biota were continuously exposed to PFCA in this area throughout the years. The results are summarized in Figure 2 (Houde et al., 2006).

Various predator prey relationships in the Westerschelde (Netherlands) were investigated by van Heuvel-Greve and co-workers. Samples of harbour seal plasma and whole body samples of herring, sea bass and flounder as well as zooplankton were collected in 2007 and 2008. The trophic level was estimated based on stable isotope (^{15}N) analysis. BMFs were considerable for harbour seal as well as for the sediment dwelling flounder (see Figure 2) (Environment Canada Health Canada, 2010; van den Heuvel-Greve et al., 2009).

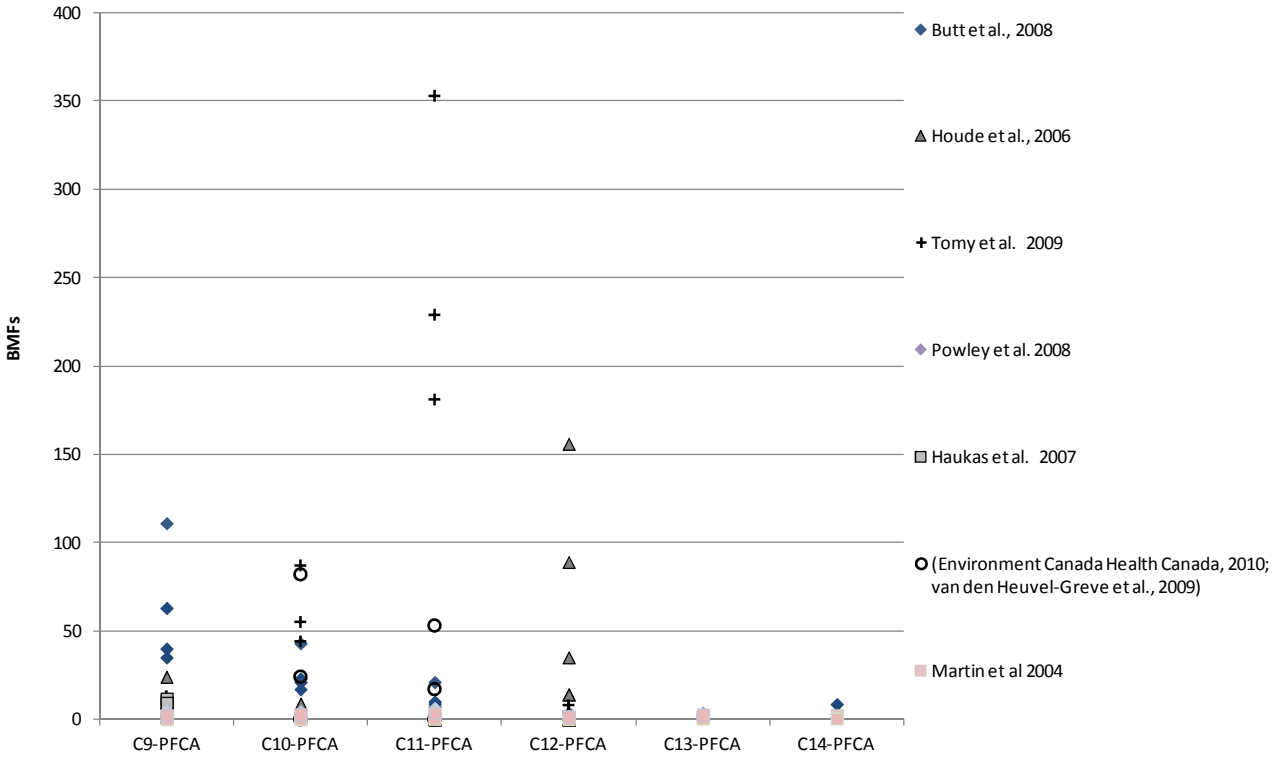


Figure 2: Biomagnification factors (BMFs) for $C_{9\text{-}14}$-PFCA.

Conclusion:

For C_{13}-PFCA two studies are available which reported bioaccumulation factors (BAFs). For BMFs for lake trout in Lake Ontario samples, 3 out of 4 values were above 1, indicating bioaccumulation of this compound. BMFs for polar bear were also above 1. Hence, C_{13}-PFCA shows the potential to biomagnify.

The biomagnification potential of $C_{11,12,14}$-PFCAs was investigated in several field studies and one laboratory study. Field studies, investigating the biomagnifications potential between different predator/prey-relationships, showed BMFs well above one indicating biomagnification. Biomagnification was greater in homeotherms than in poikilotherms. Especially for dolphin, walrus, narwhal, polar bear, arctic cod and harbour seal, BMFs greater than one have been reported. These findings substantiate the biomagnifying potential of the structural similar substance C_{13}-PFCA.

3.3.1.3 Trophic magnification factors (TMFs)

The trophic magnification factor (TMF) is a measure to evaluate biomagnification occurring in food webs. In the Guidance Document on Information Requirements, Chapter R.7.10.1.1, TMF is defined as the concentration increase in organisms with an increase of one trophic level. Again, a TMF greater than one indicates accumulation within the food chain. As already discussed in the BMF chapter sample collection is often restricted to tissue or serum samples with increasing body size of predators due to ethical reasons and due to the challenging logistics with respect to sampling and laboratory constraints.

Martin et al. examined PFCA contents in the food web from Lake Ontario in Canada (Martin et al., 2004). Adult lake trouts (top predator) were collected at various years and locations in Lake Ontario. Samples of prey fish (sculpins, smelts and alewifes) and macroinvertebrates (*Mysis sp.*, *Diporeia sp.*) were collected at one location in October 2002. Lake trout samples analyzed represented individual whole fish homogenates. The other species were processed as composites of whole individuals. TMFs are shown in Table 8 and Figure 3.

Table 8: Trophic Magnification Factors (TMF) of C_{13}-PFCA; if not indicated otherwise TMFs refer to whole body.

Location	Species/foodweb	TMF	Reference	Reliability
Lake Ontario	Diporeia/slimy sculpin	No significant association with trophic level	Martin et al. 2004	2
	Mysis/alewife/rainbow smelt/lake trout	2.45		

In the studies described below structurally similar substances $C_{11,12,14}$-PFCAs, were analyzed according to their trophic magnification potential:

Houde et al. investigated the food web of bottlenose dolphins. The authors sampled different biota, i.e. croaker, pinfish, spotfish, spotted seatrout, striped mullet and samples from bottlenose dolphins, as well as water and surface sediment. Sample collection was conducted between 2002 and 2004. Based on stable isotope (15N) analysis the trophic level of each biota sample was determined. PFCAs were analysed in plasma and liver of dolphins and afterwards a whole body burden was

calculated. For prey whole body homogenates were analysed for PFCA (Houde et al., 2006). For results see Figure 3.

Kelly et al. measured PFCAs in the Canadian Arctic marine food web. The authors used concentrations in sediment and in different organisms (lichens, macroalgae, bivalves, fish, seaducks, and marine mammals) to calculate TMFs. Sample collection was conducted between 1999 and 2003. PFCAs were measured in different tissues/fluids of the beluga whale including blood, muscle liver, milk and also in foetuses. The authors could show that PFCAs especially accumulate in protein rich compartments such as blood and liver and that the TMF of PFCAs correlates with the partitioning behaviour between protein and water and protein and air. Comparisons of different food webs show that the TMF is below one in the case of piscivorous food webs if air breathing organisms are excluded but becomes larger than one if air breathing organisms are taken into account (see Figure 3) (Kelly et al., 2009).

Loi et al. investigated a subtropical pelagic food web in a nature reserve including phytoplankton, zooplankton, gastropod, worm and shrimp, and liver samples of fish and water bird. Samples were collected between 2008 and 2010. Surface water and sediment samples were collected concurrently with the biota samples. BSAF were calculated based on the assumption that sediment was the major exposure pathway for worms. The study investigated PFCAs with different chain length. Longer chained PFCAs i.e. C_{12}-PFCA and C_{14}-PFCA were detected in sediment only (Loi et al., 2011) (see Figure 3).

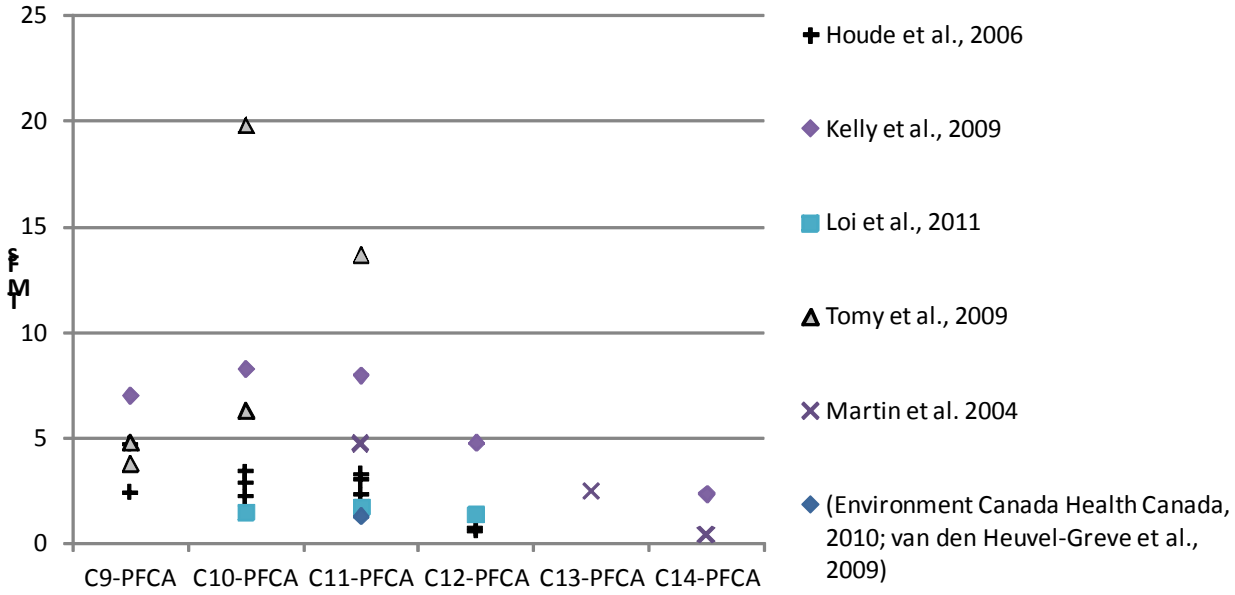


Figure 3: Trophic Magnification Factors (TMF) of C_{9-14}-PFCAs.

Conclusion:

Only one study was available reporting the trophic magnification of C_{13}-PFCA. For the food web mysis/alewife/rainbow smelt/lake trout a TMF greater than 1 has been reported, indicating a potential to magnify within the food chain.

A number of field studies are available, which analyzed the trophic magnification potential of structurally similar compounds - $C_{11,12,14}$ PFCAs. For food chains of dolphin, beluga whale, and harbour seal, TMFs greater than one have been reported, indicating trophic biomagnification. Trophical magnification was greater if the food chain contained homeotherms. TMFs were smaller in the case of piscovorous food webs and if air breathing organisms are excluded but became larger if air breathing organisms were taken into account (Kelly et al., 2009).

3.3.2 Terrestrial bioaccumulation

Müller et al. conducted a terrestrial food web study consisting of lichen and plants aswell as tissue samples (liver muscle and kidney) from caribou and wolves from two remote northern areas in Canada. Some samples are not from the same season. This food web is considered as relatively well documented example (Kelly and Gobas, 2003). The study illustrates a considerable carry over between plants and caribou. Caribou are a major human food source in numerous arctic communities. This food-chain may also be considered comparable to the pasture-cow food-chain in temperate regions. The results of the study, BMFs as well as TMFs are shown in Table 9. Tissue concentrations and whole body concentrations were used for calculations. Tissue based BMFs differ considerably. Therefore it is concluded that BMFs based on whole body concentrations are more appropriate (Müller et al., 2011).

Table 9: BMF and TMF values for C_{13}-PFCA for a terrestrial food chain (Müller et al., 2011).

	Food chain	**Location**	
		Porcupine	**Bathurst**
BMF	Caribou (whole) / lichen	2.4	6.9
BMF	Caribou (whole)/ lichen	7.1	9.0
BMF	Wolf (whole)/caribou (whole)	0.8	3.2
TMF	Wolf (whole)/ caribou (whole)/ lichen	1.4	2.0
TMF	Wolf (whole)/ caribou (whole) / vegetation	1.4	1.8

Conclusion:

The terrestrial BMF and TMF of C_{13}-PFCA are greater than one for the remote Arctic food chain lichen – caribou – wolf, indicating trophic biomagnification.

3.3.3 Summary and discussion of bioaccumulation

In table 10 data describing the bioaccumulation potential of the C_{11-14}-PFCAs are summarized.

Table 10: Summary of the BCFs, BMFs and TMFs available for C_{11-14}-PFCAs. The data were taken from the studies discussed in Section 3.3.

	C_{11}-PFCA	**C_{12}-PFCA**	**C_{13}-PFCA**	**C_{14}-PFCA**
BCF	2700 – 5132	>5000	-	>5000
BMF	0.21 - 353	0.1 – 156	0.35 – 9	0.33 – 8.5
TMF	0.75 – 31.2	0.6 – 3.76	1.4 – 2.45	0.23 – 2.6

There are no studies available which report a BCF for C_{13}-PFCA. Based on the data given in Annex 1, results of studies of structurally similar substances of the same chemical group could be used to evaluate the bioaccumulation of C_{13}-PFCA.

For the structural analogues C_{12}-PFCA, which is one CF_2-group shorter than C_{13}-PFCA, and C_{14}-PFCA, which is one CF_2-group longer, BCFs higher than 5000 were shown. Applying the read-across approach, as the BCFs for both substances are well above 5000 it can be concluded that the BCF of C_{13}-PFCA is very likely larger than 5000, too.

Moreover, two studies derived BMFs > 1 indicating biomagnification. The data are comparable to those of the C_{12} and C_{14}-PFCAs. Hence, we conclude, that C_{13}-PFCA is a very bioaccumulative substance according to REACH Annex XIII.

4 HUMAN HEALTH HAZARD ASSESSMENT

Not relevant for this dossier.

5 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant for this dossier.

6 CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

6.1.1 Assessment of PBT/vPvB properties – comparison with the criteria of Annex XIII

6.1.1.1 Persistence

For C_{13}-PFCA no experimental data on degradation are available. Therefore, data from chemically similar compounds are considered in a read-across approach (please see Annex 1 for further details). 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.

Abiotic degradation

The data on $_8$-PFCA indicate that abiotic degradation in the atmosphere is expected to be slow (atmospheric lifetime = 130 days). The hydrolytic half-life of C_8-PFCA at 25°C is greater than 92 years, with the most likely value of 235 years under relevant environmental conditions *(3M Co., 2001a)*. No photodegradation of C_8-PFCA has been observed in studies conducted under relevant environmental conditions. The estimated DT_{50} for indirect photolysis is 349 days.

Biotic degradation

Standard screening tests are available for $C_{8,9,12,14}$-PFCAs. No biodegradation at all has been detected for $C_{9,12,14}$-PFCAs within 28 days. For C_8-PFCA test results differ from "no biodegratation" to 13% biodegradation of the ammonium salt. Thus, it can be concluded that $C_{8,9,12,14}$-PFCAs are not readily biodegradable.

For C_8-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

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 C_{8-14}-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 CF_2-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_{13}-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.

6.1.1.2 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.

There are no studies available which report a BCF for C_{13}-PFCA. For the structural analogues C_{12}-PFCA, which is one CF_2-group shorter than C_{13}-PFCA, and C_{14}-PFCA, which is one CF_2-group longer, BCFs higher than 5000 were shown. As the BCFs for both substances are well above 5000 it can be concluded that the BCF of C_{13}-PFCA is larger than 5000, too (see Annex I).

Moreover, two studies derived BMFs > 1 indicating biomagnification. The data are comparable to those of the C_{12} and C_{14}-PFCAs. Hence, we conclude, that C_{13}-PFCA is a very bioaccumulative substance according to REACH Annex XIII.

6.1.1.3 Toxicity

Not relevant for this dossier.

6.1.2 Summary and overall conclusions on the PBT, vPvB properties

Degradation studies on C_{13}-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. $C_{8,9-14}$-PFCAs contain a highly similar chemical structure, a perfluorinated carbon chain and a carboxylic acid group. The compounds differ only in the number of CF_2-groups.

Comparing the physico-chemical properties of C_{8-14}-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 CF_2-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 DT_{50} of >92 years for C_8-PFCA in water. Screening studies of $C_{8,9,12,14}$-PFCA showed no biodegradation within 28 days. Non-standard tests with C_8-PFCA could not detect any degradation products under environmentally relevant conditions. Moreover, a monitoring study showed that C_8-

PFCA remained in soil and groundwater, years after application of fire fighting foam which contained PFCAs.

Therefore, we conclude that C_{13}-PFCA is - like C_8-PFCA - not degraded in the environment and thus fulfils the P- and vP-criteria under REACH.

For C_{13}-PFCA, no BCF-value is available. The available BCF-values of $C_{12,14}$-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 C_{13}-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 C_{13}-PFCA fulfils the B and the vB-criteria of REACH as well.

In conclusion, C_{13}-PFCA is a vPvB-substance according to Art. 57e) of REACH.

6.2 CMR assessment

Not relevant for this dossier.

6.3 Substances of equivalent level of concern assessment.

Not relevant for this dossier.

PART II

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES –CONCLUSIONS ON EXPOSURE

Information on environmental exposure of the environment with C11-14-PFCAs can be seen from time trends of concentrations in monitoring studies. It has to be kept in mind that concentrations of PFCAs in different environmental media can be caused by degradation of precursors as well. Nevertheless, concentration trends give a hint on the relevance of PFCAs.

A study determined PFCAs in livers of melon-headed whales (*Peponocephala electra*) collected along the coast of Japan, from three mass strandings that occurred during the past 25 years (Hart et al., 2008). Whereas in 1982 C11,12-PFCAs were below the limit of detection, they were detected in 2006.

Concentrations of PFCAs were determined in liver of harbour seals (n = 68) collected from the northwest Atlantic between 2000 and 2007 showed an increasing trend (Shaw et al., 2009).

The temporal trends of PFCAs were determined in lake trout collected between 1979 and 2004 from Lake Ontario. From 1998 on concentrations show an increasing trend for C_{11-14}-PFCAs (Furdui et al., 2008).

Significant annual increases for $C_{11,12,13}$-PFCAs (5.9%, 8.5% and 5.2%, respectively) were found in polar bears (*Ursus maritimus*) within the period 1984 – 2006 (Dietz et al., 2008).

These increasing trends outside of Europe are supported by two studies performed with samples from the German Specimen Bank. An increasing trend of concentrations of C_{11-14}-PFCAs was found in fish samples within the years 1995 – 2010. Fish samples originated from different location and the increasing trend was found for all locations (Theobald et al., 2011). This increasing trend is supported by data from a biomonitoring study with human sera samples from two German cities. These data are not yet published and are therefore confidential. Serum samples cover the period from 1982 – 2009 and an increasing trend of concentrations was found for $C_{11,12}$-PFCAs. This trend is also supported by concentrations in serum samples from a Norwegian study (Haug et al., 2009).

There is evidence that C11-14-PFCAs are in use and that exposure of the environment is taking place. Furthermore PFOA and long chain PFCA are used in the production of fluoropolymers and fluorotelomers and as additives and components in consumer and industrial products (Environment Canada Health Canada. 2010b).

CURRENT KNOWLEDGE ON ALTERNATIVES

Only little information is available on substitutes. It can be assumed that some substitutes for C_8-PFCA might also be usable for C_{11-14}-PFCAs.

In general, PFCAs with eight carbon atoms can be replaced with shorter chain fluorinated chemicals containing six or less carbon atoms. Non-fluorinated alternatives are available as well, i.e. propylated aromatics (naphthalene or biphenyls) and aliphatic alcohols (sulphosuccinate and fatty alcohol ethoxylates) (Danish Ministry of the Environment, 2005; van der Putte et al., 2010; Walters and Santillo, 2006). In the table below known C_8-PFCA alternatives are summarized.

Table 11: Alternative compounds, their product names, company and use for C_8-PFCA and its salts.

Alternative compound	Product name	Company	Used for /Used in	Ref.
PFBS or based on different C_4-perfluoro-compounds	Novec®	3M	Paint and coatings industry. Electronic coating, industrial and commercial cleaning, cleaner for solder flux residue, degreasing applications	(Poulsen et al., 2005; van der Putte et al., 2010; Walters and Santillo, 2006)
Dodecafluoro-2-methylpentan-3-one(CF_3-CF_2-C(O)-$CF(CF_3)_2$)	Novec®	3M	Fire-fighting fluid	(Poulsen et al., 2005; Walters and Santillo, 2006)
C6-fluorocompounds	Forafac®	DuPont	Fire-fighting foam	(Poulsen et al., 2005)
CF_3 or C_2F_5 pendant fluoroalkyl polyethers	PolyFox®	OMNOVA Solutions Inc.	Surfactant and flow, level and wetting additive for coating formulations. Also used in floor polish	(Poulsen et al., 2005)
Propylated aromatics (naphthalenes or biphenyls)	Ruetasolv®	Rütgers Kurehe Solvents GmbH	Water repelling agents for rust protection systems, marine paints, coatings, etc.	(Poulsen et al., 2005; Walters and Santillo, 2006)
Aliphatic alcohols (sulphosuccinate and fatty alcohol	Emulphor®, Lutensit®	BASF	Levelling and wetting agents	(Poulsen et al., 2005)

ethoxylates)				
Sulfosuccinates	EDAPLAN® LA451	Münzing Chemie	Paint and coatings industry: Wetting agents for water based applications, e.g. wood primers	(Poulsen et al., 2005)
Sulfosuccinate	Hydropalat®875	Cognis	Paint and coating industry: Weting and dispersing agents	(Poulsen et al., 2005)
Silicone Polymers	WorléeAdd®	Welrée-Chemie	Wetting agents in paint and ink industry	(Poulsen et al., 2005)
Branched fluoro ethers			Can be applied for all products	(van der Putte et al., 2010)
Short-chain fluorinated technologies (six or less carbons)	Capstone	DuPont	Commercially available in home furnishings, fire fighting foam, fluorosurfactants, paper packaging, textiles, stone and tile, and leather end uses	[1]
Ammonium 4,8-dioxa-3H-perfluorononanoate	ADONA	3M	Emulsifier used in the aqueous emulsion polymerization of fluoropolymers made from tetrafluoroethylene (TFE)	(Gordon, 2011)

[1] http://www.oecd.org/document/34/0,3746,en_21571361_44787844_44799586_1_1_1_1,00.html

ANNEX I - READ-ACROSS APPROACH

In general, the read-across approach can be applied if substances whose physicochemical and/or toxicological and/or ecotoxicological properties are likely to be similar or follow a regular pattern as a result of structural similarity. Those substances may be considered as a group or a category of substances. According to ECHA`s practical guide 6 "How to report read-across and categories" similarities may be due to a common functional group, common precursor or breakdown products, constant pattern in changing potency or common constituents or chemical class.

Structural similarities of C8-14 PFCAs and some salts

In Table 12 the chemicals structures of the C8-14-PFCAs are displayed. All PFCAs contain a carboxylic acids group and a perfluorinated carbon chain. The compounds differ only in the number of carbon atoms within the fluorinated carbon chain. Thus, we conclude, that all the C8-14-PFCAs belong to the same chemical class and contain not only a common functional group but are highly similar according to their chemical structure.

Table 12: CAS-Numbers and similarity of chemical structures of long chain PFCAs.

Name	Abbreviation	CAS-No	IUPAC Name	Chemical structure
PFOA	C_8-PFCA	335-67-1	Octanoic acid, pentadecafluoro-	$CF_3(CF_2)_6$-COOH
PFNA	C_9-PFCA	375-95-1	Nonanoic acid, heptadecafluoro-	$CF_3(CF_2)_7$-COOH
PFDA	C_{10}-PFCA	335-76-2	Decanoic acid, nonadecafluoro-	$CF_3(CF_2)_8$-COOH
PFUnDA	C_{11}-PFCA	2058-94-8	Undecanoic acid, heneicosafluoro-	$CF_3(CF_2)_9$-COOH
PFDoDA	C_{12}-PFCA	307-55-1	Dodecanoic acid, tricosafluoro-	$CF_3(CF_2)_{10}$-COOH
PFTrDA	C_{13}-PFCA	72629-94-8	Tridecanoic acid, pentacosafluoro-	$CF_3(CF_2)_{11}$-COOH
PFTeDA	C_{14}-PFCA	376-06-7	Tetradecanoic acid, heptacosafluoro-	$CF_3(CF_2)_{12}$-COOH

Dissociation of $C_{8\text{-}14}$-PFCAs and its 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 (pK_a) 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 pK_a 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.

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

Physicochemical properties and partition coefficients of C_{8-14}-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. Nevertheless, there are models available, i.e. COSMOtherm calculating partitioning coefficients of neutral PFCAs. 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 13** below, Wang et al., 2011). This can be explained by the increasing molecular volume with each additional CF_2-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., 2010) (see **Table 13**).

Table 13: Basic substance information and physical chemical properties relevant to justify read across in the PBT assessment.

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	NaPFO	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
IUPAC Name	**Octanoic acid, pentadecafluoro-**	**ammonium pentadeca-fluoro-octanoate**	**pentadeca octanoic acid sodium salt**	**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	CF3(CF2)6-COOH	CF3(CF2)6-COO-$NH4^+$	CF3(CF2)6-COO-Na^+	CF3(CF2)7-COOH	CF3(CF2)8-COOH	CF3(CF2)9-COOH	CF3(CF2)10-COOH	CF3(CF2)11-COOH	CF3(CF2)12-COOH
CAS No	335-67-1	3825-26-1	335-95-5	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	414.09	431.1		464.08	514.08	564.0909	614.0984	664.1059	714.11
Partitioning Coefficient logKow				2.3 – 2.48 (exp)	2.65 – 2.87 (exp)	3.19 – 3.41	logP 9.363±0.888 at 25°C (calc)	logP 10.093±0.901 at 25 °C (calc)	logP 10.823±0.914 at 25 °C (calc)
	5.30 (calc., COSMOtherm, Wang et al., 2011)			5.9 (calc., COSMOtherm, Wang et al., 2011)	6.5 (calc., COSMOtherm, Wang et al., 2011)	7.2 (calc., COSMOtherm, Wang et al., 2011)	7.8 (calc., COSMOtherm, Wang et al., 2011)	8.25 (calc., COSMOtherm, Wang et al., 2011)	8.90 (calc., COSMOtherm, Wang et al., 2011)
log K_{OA}	7.23 (calc., COSMOtherm, Wang et al., 2011)			7.50 (calc., COSMOtherm, Wang et al., 2011)	7.77 (calc., COSMOtherm, Wang et al., 2011)	8.08 (calc., COSMOtherm, Wang et al., 2011)	8.36 (calc., COSMOtherm, Wang et al., 2011)	8.63 (calc., COSMOtherm, Wang et al., 2011)	8.87 (calc., COSMOtherm, Wang et al., 2011)
log K_{AW}	-1.93 (calc., COSMOtherm, Wang et al., 2011)			-1.58 (calc., COSMOtherm, Wang et al., 2011)	-1.27 (calc., COSMOtherm, Wang et al., 2011)	-0.92 (calc., COSMOtherm, Wang et al., 2011)	-0.58 (calc., COSMOtherm, Wang et al., 2011)	-0.38 (calc., COSMOtherm, Wang et al., 2011)	0.03 (calc., COSMOtherm, Wang et al., 2011)
Dissociation constant	2.5 2.8 in 50% aqueous ethanol 1.5 - 2.8					0.52±0.10; (calculated)	0.52±0.10 (calculated)	0.52±0.10; (calculated)	0.52±0.10; (calculated)
Partition coefficients log Kd (sediment and overlapping	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_8-PFCA**			**C_9-PFCA**	**C_{10}-PFCA**	**C_{11}-PFCA**	**C_{12}-PFCA**	**C_{13}-PFCA**	**C_{14}-PFCA**
Acronym	PFOA	APFO	NaPFO	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
dissolved phase)									
Log Koc (sediment organic carbon-normalized distribution coefficient)	2.06 (Higgins and Luthy, 2006)# 1.09 (Ahrens et al., 2010) *			2.39 (Higgins and Luthy, 2006) # 2.4 (Ahrens et al., 2010) *	2.76 (Higgins and Luthy, 2006) # 3.6 (Ahrens et al., 2010) *	3.3 (Higgins and Luthy, 2006) # 4.8 (Ahrens et al., 2010) *			
Water solubility	9.5 g/L (25° C) 4.14 g/L (22°C)	0.033 mol/L, 14.2 g/L at 2.5 °C (Nielsen 2012)	0.036 mol/L at 8.0 °C at critical micelle concentration (Nielsen 2012)			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)	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 (calculated)	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 3.5E-3 g/L; pH 4 at 25 °C 8.6E-3 g/L; pH 5 at 25 °C 0.0100 g/L; pH 6-10 at 25 °C (calculated)	1.9E-6 g/L; pH 1 at 25°C 1.4E-5 g/L; pH 2 at 25°C 1.3E-4 g/L; pH 3 at 25°C 9.3E-4 g/L; pH 4 at 25°C 2.2E-3 g/L; pH 5 at 25°C 2.6E-3 g/L; pH 6-10 at 25°C (calculated)
Vapour pressure	4.2 Pa (25 °C) for PFOA extrapolated from measured data 2.3Pa (20 °C) for PFOA extrapolated from measured data 128 Pa (59.3 °C) for PFOA measured	0.0081 Pa at 20 °C, calculated from measured data <0.1 hPa at 20 °C 0.012 Pa at 25 °C 0.0028 Pa at 25 °C (Nielsen 2012)				0.6 to 99.97 kPa (112 to 237.7°C) (calculated)	9.40E-3 Torr at 25°C(calculated)	3.59E-3 Torr at 25°C (calculated)	1.37E-3 Torr at 25 °C (calculated)

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	NaPFO	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA
	Stability								
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 (S2O82-) in water	No photodegradation tested under relevant env. Conditions 100 % after 12 h by use of persulfate ion (S2O82-) in water	No photodegradation tested under relevant env. Conditions 77% after 12 h by use of persulfate ion (S2O82-) in water			
Hydrolysis DT50	>97 yr								
Direct photolysis		No photo-degradation							
indirect photolysis		No photo-degradation (H2O2; synthethic humic water, Fe2O3) estimated half-life > 349 days (Fe2O3)							
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								

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

Table 14 : Information on BCF, BMF and TMF of C_{9-14} PFCAs relevant to justify read across in the B assessment.

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
IUPAC Name	Nonanoic acid, heptadecafluoro-	Decanoic acid, nonadecafluoro-	Undecanoic acid, heneicosafluoro-	Dodecanoic acid, tricosafluoro-	Tridecanoic acid, pentacosafluoro-	Tetradecanoic acid, heptacosafluoro-
Chemical Structure	CF3(CF2)7-COOH	CF3(CF2)8-COOH	CF3(CF2)9-COOH	CF3(CF2)10-COOH	CF3(CF2)11-COOH	CF3(CF2)12-COOH
CAS No	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	464.08	514.08	564.0909	614.0984	664.1059	714.11
Partitioning Coefficient log K_{OW}	2.3 – 2.48 (exp)	2.65 – 2.87 (exp)		logP 9.363±0.888 at 25°C (calc)	logP 10.093±0.901 at 25 °C (calc)	logP 10.823±0.914 at 25 °C (calc)
	5.9 (calc., COSMOtherm, Wang et al., 2011)	6.5 (calc., COSMOtherm, Wang et al., 2011)	7.2 (calc., COSMOtherm, Wang et al., 2011)	7.8 (calc., COSMOtherm, Wang et al., 2011)	8.25 (calc., COSMOtherm, Wang et al., 2011)	8.90 (calc., COSMOtherm, Wang et al., 2011)
log K_{OA}	7.50 (calc., COSMOtherm, Wang et al., 2011)	7.77 (calc., COSMOtherm, Wang et al., 2011)	8.08 (calc., COSMOtherm, Wang et al., 2011)	8.36 (calc., COSMOtherm, Wang et al., 2011)	8.63 (calc., COSMOtherm, Wang et al., 2011)	8.87 (calc., COSMOtherm, Wang et al., 2011)
log K_{AW}	-1.58 (calc., COSMOtherm, Wang et al., 2011)	-1.27 (calc., COSMOtherm, Wang et al., 2011)	-0.92 (calc., COSMOtherm, Wang et al., 2011)	-0.58 (calc., COSMOtherm, Wang et al., 2011)	-0.38 (calc., COSMOtherm, Wang et al., 2011)	0.03 (calc., COSMOtherm, Wang et al., 2011)
BCF						
MITI (fish)			2300 - 3700	10000 - 16000		16000 - 17000
Lumbriculus variegatus / sediment	0.64 ± 0.05	0.06 ± 0.04				
Rainbow trout (carcass)			2700 ± 400	18000 ± 2700		23000 ± 5300
Rainbow trout (blood)		2700±350	11000 ± 1400	40000 ± 4500		30000 ± 4200
Rainbow trout (liver)		1100 ± 180	4900 ± 770	18000 ± 2900		30000 ± 6000
Carp (whole)			2300 - 3700	10000-16000		16000 - 17000
Juvenile rainbow trout (carcass)		450 ± 6 62	4044-5132*	5761-7327*		10388-15857*
BMF	0.13-111	0.21-87	0.21 - 353	0.1 – 156	0.35 – 9	0.33 – 8.5
TMF	1.9-7.0	1.5-20	0.75 – 31.2	0.6 – 3.76	1.4 – 2.45	0.23 – 2.6

* Calculated BCFs based on BMF values for C_{11}-PFCA (0.28 ± 0.04), C_{12}-PFCA (0.43 ± 0.062) and C_{14}-PFCA (1.0 ± 0.25).

pH of sediment analysed: 5.7 to 7.6

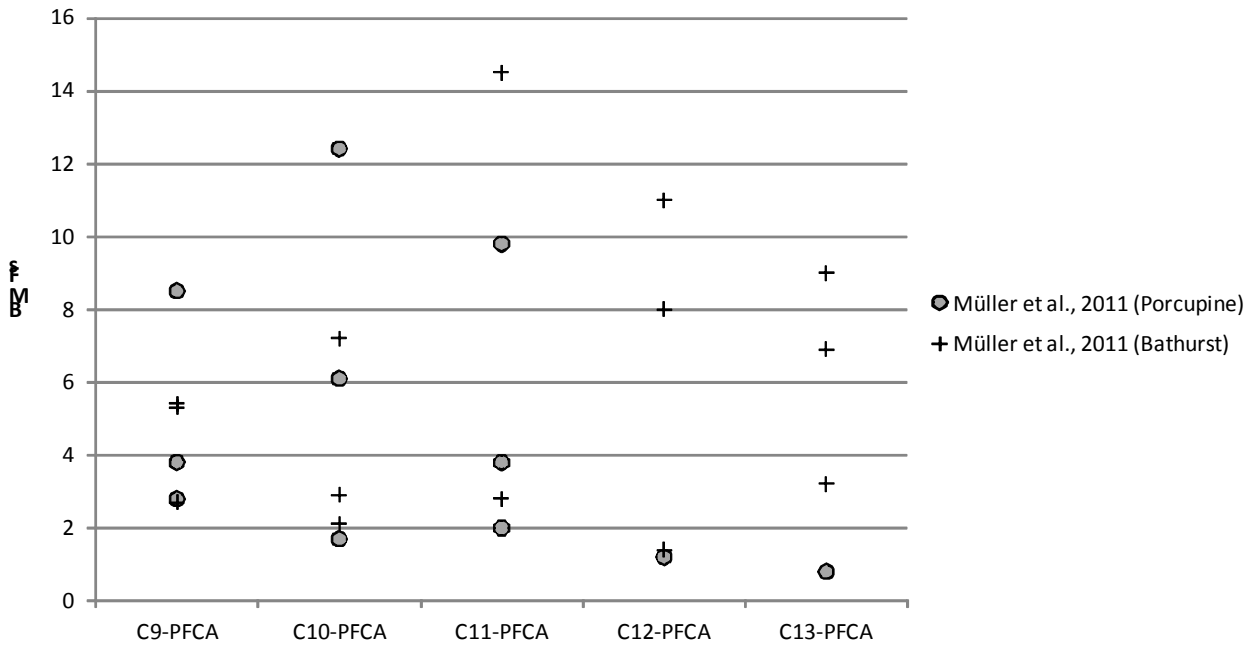


Figure 4: BMFs for C_{11-13}-PFCAs in a remote terrestrial food chain from two different locations (whole body, Müller et al., 2011). The study is reliable (reliability 2).

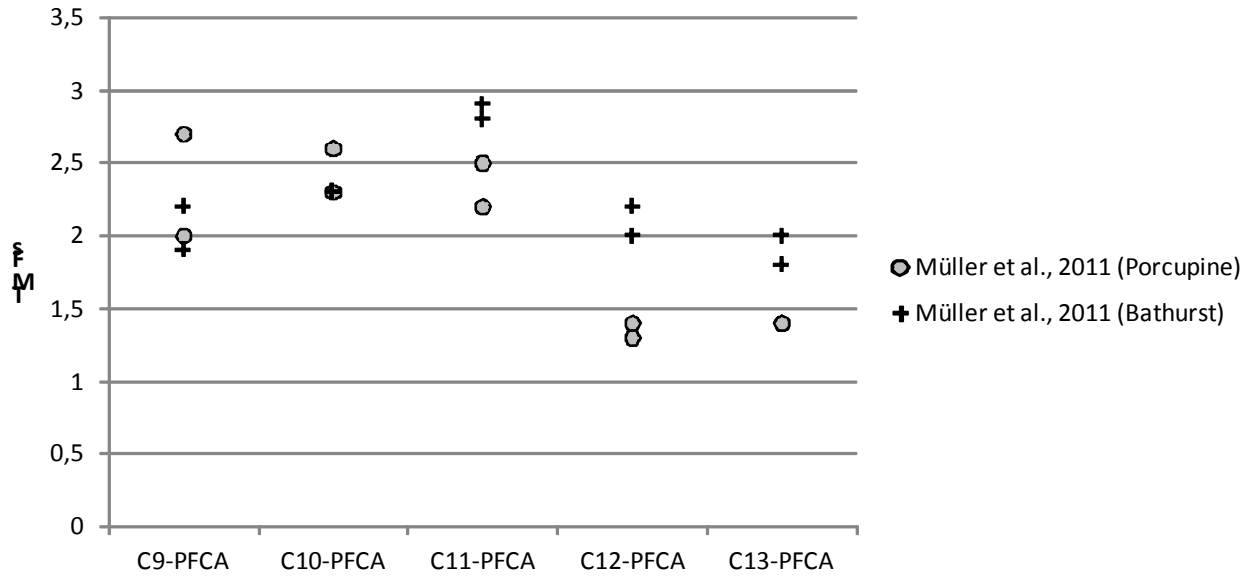


Figure 5: TMFs for C_{11-13}-PFCAs in a remote terrestrial food chain from two different locations (whole-body, Müller et al., 2011). The study is reliable (reliability 2).

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