

# **Draft Ecological Screening Assessment Report**

## **Long-Chain (C9–C20) Perfluorocarboxylic Acids, their Salts and their Precursors**

**Environment Canada**

**October 2010**

## Synopsis

Under the *Canadian Environmental Protection Act, 1999*, the Ministers of the Environment and of Health conducted an ecological screening assessment of Long-Chain (C9-C20) Perfluorocarboxylic Acids, their Salts, and their Precursors which were identified as emerging chemicals of concern. Empirical evidence demonstrated that some perfluorocarboxylic acids are bioaccumulative, persistent, subject to long-range transport (via precursors), widespread and showing a trend toward increasing concentrations in Arctic wildlife. The fact that some of the precursors to the long-chain (C9-C20) perfluorocarboxylic acids are also structurally similar to the four fluorotelomer-based substances prohibited by the Minister of the Environment under the authority of section 84 of the *Canadian Environmental Protection Act, 1999* has contributed to the decision to undertake this ecological screening assessment of the long-chain (C9-C20) perfluorocarboxylic acids. As well, fourteen precursors (listed in Annex 1) were deemed to meet the categorization criteria under Section 73 of the Act.

This ecological assessment focuses on the perfluorocarboxylic acids with carbon chain lengths from 9 to 20 inclusive, their salts and their precursors. Precursors, i.e., substances that could transform or degrade to long-chain (C9-C20) perfluorocarboxylic acids, were considered on the basis of their contribution to the total presence of long-chain (C9-C20) perfluorocarboxylic acids in the environment. This assessment defines precursors as any substances where the perfluorinated alkyl moiety has the formula  $C_nF_{2n+1}$  (where  $8 \leq n \leq 20$ ) and is directly bonded to any chemical moiety other than a fluorine, chlorine or bromine atom.

The presence of long-chain perfluorocarboxylic acids, their salts and their precursors result from anthropogenic activity. In 2000 and 2004, industry surveys by Environment Canada under the authority of section 71 of the *Canadian Environmental Protection Act, 1999* found that long-chain (C9 –C20) perfluorocarboxylic acids were not reported to be manufactured or imported into Canada. However, in both surveys, several precursors to the long-chain (C9-C20) perfluorocarboxylic acids were reported to be imported into Canada.

In traditional toxicity studies, long-chain (C9-C20) perfluorocarboxylic acids were found to be low to moderately toxic, with acute toxicity values ranging from 8.8 to 285 mg/L. There are two studies on the toxicity of long-chain (C9-C20) perfluorocarboxylic acids in terrestrial species. In one study, no adverse effects were observed up to 1.0 mg/kg body weight for male chickens dosed with C10 perfluorocarboxylic acid. In another study, a soil-dwelling nematode showed acute lethality at 306 mg/L and multi-generation effects (decreased fecundity) at 0.000464 mg/L when exposed to C9 perfluorocarboxylic acid.

There are other studies showing the potential for long-chain (C9-C20) perfluorocarboxylic acids to cause other types of effects. For example, although a direct causal relationship has not been demonstrated, liver lesions have been observed in wild polar bears cumulatively exposed to several long-chain perfluorocarboxylic acids. C9 and C10 perfluorocarboxylic acids have been shown to affect the multi-xenobiotic resistance

mechanism in marine mussels at concentrations ranging from 2.23 to 3.65 mg/L. C9 to C12 perfluorocarboxylic acids induced vitellogenesis in rainbow trout at  $2.56 \times 10^{-5}$  to 2 mg/g diet. C9 perfluorocarboxylic acid may cause oxidative stress in the common cormorant. C9 to C11 perfluorocarboxylic acids activated the mammalian peroxisome proliferator-activated receptor  $\alpha$  (PPAR $\alpha$ ) in the livers of Baikal seals. PPAR $\alpha$  plays a critical physiological role as a lipid sensor and a regulator of lipid metabolism. C9-C10 PFCAs are also chemical sensitizers for the marine mussel, *Mytilus californianus*, by allowing normally excluded toxic substances to accumulate in the marine mussel. C12 and C14 PFCAs increased the mitochondrial membrane potential in the freshwater alga, *Scenedesmus obliquus*, indicating damage to the mitochondrial function.

There are no experimental persistence data, under environmentally relevant conditions, available for the long-chain (C9-C20) perfluorocarboxylic acids. However, the carbon-fluorine bond is one of the strongest in nature, making the structure extremely stable and resistant to degradation. The perfluorinated chain provides exceptional resistance to thermal and chemical attack. Thus, due to the strength of the carbon-fluorine bond, it is expected that long-chain (C9-C20) perfluorocarboxylic acids would be persistent. Furthermore, long-chain perfluorocarboxylic acids have been detected in remote areas (e.g., the Canadian Arctic). While mechanisms of transport are not fully understood, certain precursors may undergo long-range transport to remote areas, where subsequent degradation can result in the formation of long-chain (C9-C20) perfluorocarboxylic acids.

A bioaccumulation factor (BAF) or bioconcentration factor (BCF) > 5000 has been demonstrated for C11, C12 and C14 perfluorocarboxylic acids. For C11, C12, and C14 perfluorocarboxylic acids, there is the potential for bioconcentration in fish (BCF > 5000) and some potential for biomagnification in fish and marine mammals. However, there remains a significant potential for biomagnification and/or trophic magnification in water-breathing and air-breathing organisms for all long-chain (C9-C20) perfluorocarboxylic acids. There are no experimental or predicted bioaccumulation data available for long-chain perfluorocarboxylic acids greater than C14, nevertheless, there is the potential that these longer chains could bioaccumulate or biomagnify in marine and/or terrestrial species based on chemical conformations. In addition, C15 perfluorocarboxylic acids have been measured in fish, invertebrates and polar bears.

C9 to C15 perfluorocarboxylic acids were measured in the liver of seals, foxes, fish, polar bears, Greenland shark, narwhals, beluga whales and birds either in the Canadian Arctic or the Great Lakes region. Concentrations ranged from below detection levels to 180 ng/g liver wet weight, with concentrations greatest for polar bears followed by Greenland shark, narwhals and beluga whales. Worldwide, C9 to C15 have been reported in ringed, fur and harbour seals, dolphins (i.e., white-sided, bottlenose, white-beaked, Franciscana, humpback), finless porpoises, glaucous gulls, sperm whale, beavers, Amur tigers, wild rats and several species of birds (little egret, little ringed plover, parrotbills, black-crowned herons). Concentrations ranged from below detection levels to 480 ng/g wet weight, with concentrations highest in the white-beaked dolphin.

From 1980 to 2000, levels of long-chain perfluorocarboxylic acids in ringed seal livers from Greenland increased 3.3 and 6.8% per year for C10 and C11, respectively. From 1992 to 2005, the mean concentrations of C9 and C10 PFCA in the livers of Baikal seals were 1.2 to 1.7-fold higher. From 1972 to 2002, mean doubling times for concentrations in polar bear livers from the Arctic ranged from 5.8 to 9.1 years for C9 to C11. From 1993 to 2004, concentrations in ringed seal liver samples increased, with a doubling time of 4 to 10 years for C9 to C12. In northern fulmar liver samples, C9 to C15 levels increased from 1987 to 1993 and remained steady from 1993 to 2003. Thick-billed murre liver samples showed an increase in C9 to C15 concentrations from 1975 to 2004. Concentrations of C9 to C13 increased significantly in whole eggs of herring gulls in Norway from 1983 to 1993. Male beluga whales from Nunavut showed an annual liver increase of 1.8 ng/g-ww for C9-C12 from 1980-2010.

Long chain (C9-C20) perfluorocarboxylic acids are persistent in the environment and can bioaccumulate and biomagnify in terrestrial and marine mammals. Given these inherent properties, together with environmental concentrations that may approach effect levels (including for vitellogenin induction), increasing temporal trends for several Arctic species (i.e., the polar bear, seals and Arctic birds), their widespread occurrence in biota likely due to the long-range atmospheric or oceanic transport of volatile precursors and/or the acids themselves, and the fact that other perfluorinated compounds and precursors to long-chain perfluorocarboxylic acids may contribute to the overall additive or synergistic impact of long-chain (C9-C20) perfluorocarboxylic acids in biota, it is proposed that long-chain (C9-C20) perfluorocarboxylic acids, their salts and their precursors are entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity.

It is proposed to conclude that long-chain (C9-C20) perfluorocarboxylic acids, their salts, and their precursors meet one or more of the criteria in section 64 of the *Canadian Environmental Protection Act*, 1999.

The presence of long-chain (C9-C20) perfluorocarboxylic acids and their salts results from human activity. In addition, long-chain (C9-C20) perfluorocarboxylic acids and their salts meet the criteria for persistence as set out in the *Persistence and Bioaccumulation Regulations*. While there is scientific evidence that long-chain (C9-C20) perfluorocarboxylic acids and their salts can accumulate and biomagnify in terrestrial and marine mammals, only C11, C12 and C14 perfluorocarboxylic acids and their salts meet the criteria for bioaccumulation as defined in the *Persistence and Bioaccumulation Regulations*.

Where relevant, research and monitoring will support verification of assumptions used during the screening assessment and, where appropriate, the performance of potential control measures identified during the risk management phase.

## Introduction

Under the *Canadian Environmental Protection Act*, 1999 (Canada 1999), the Minister of the Environment has conducted an ecological screening assessment of the long-chain (C9-C20) perfluorocarboxylic acids, their salts and precursors. These were identified as substances of concern as a result of Environment Canada's New Substances notification process and through the Action Plan for the Assessment and Management of Perfluorinated Carboxylic Acids and their Precursors (<http://www.chemicalsubstanceschimiques.gc.ca/fact-fait/pfca-acp-eng.php>). In 2004, Health Canada and Environment Canada assessed four fluorotelomer-based substances under the New Substances provisions of *Canadian Environmental Protection Act*, 1999 (Canada 1999). These substances were suspected of being "toxic" as they contained direct precursors to perfluorocarboxylic acids and were deemed capable of degrading to perfluorocarboxylic acids. Regulations were proposed to maintain the prohibitions on these new sources of perfluorocarboxylic acids. The proposed amendments to the *Prohibition of Certain Toxic Substances Regulations*, 2005 were published in the *Canada Gazette*, Part I, on June 17, 2006.

This ecological assessment focuses on the perfluorocarboxylic acids with carbon chain lengths from 9 to 20 inclusive, their salts and their precursors. Precursors were considered on the basis of their contribution to the total presence of long-chain (C9-C20) perfluorocarboxylic acids in the environment. The precursors, CAS RN 65530-63-4, CAS RN 65530-71-4, CAS RN 65530-72-5, CAS RN 65530-74-7, CAS RN 68391-08-2, CAS RN 68412-68-0, CAS RN 115592-83-1, CAS RN 65530-61-2, CAS RN 70969-47-0, CAS RN 65530-66-7, CAS RN 65605-58-5, CAS RN 65605-70-1, CAS RN 65636-35-3, CAS RN 68239-43-0, and CAS RN 110053-43-5 were found to meet the ecological categorization criteria for persistence, and/or bioaccumulation potential and inherent toxicity to non-human organisms. None of these substances were considered to be a high priority for assessment of potential risks to human health, based upon application of the simple exposure and hazard tools developed by Health Canada for categorization of substances on the Domestic Substances List.

Data relevant to the screening assessment of long-chain (C9-C20) perfluorocarboxylic acids were identified in review and assessment documents, stakeholder research reports and literature searches, up to November 2009. In addition, industry surveys on perfluoroalkyls/fluoroalkyls were conducted for the years 2000 and 2004 through a *Canada Gazette* notice issued pursuant to section 71 of *Canadian Environmental Protection Act*, 1999 (Canada 1999). These surveys collected data on the manufacture, import, and uses of perfluoroalkyls/fluoroalkyls in Canada. Toxicological studies submitted by industry under section 70 of CEPA 1999 were also considered.

Screening assessments focus on information critical to determining whether a substance meets the criteria as set out in section 64 of *Canadian Environmental Protection Act*, 1999 (Canada 1999). The approach taken in this ecological screening assessment was to examine various supporting information and develop conclusions based on multiple lines of evidence such as persistence, bioaccumulation, toxicity, temporal trends, and

widespread occurrence in biota. This screening assessment does not present an exhaustive review of all available data. Instead, it presents the critical studies and lines of evidence supporting the conclusions.

This draft screening assessment was prepared by staff in the Existing Substances program at Environment Canada. This ecological assessment has undergone external written peer review/consultation. Although external comments were taken into consideration, the final content and outcome of the draft screening risk assessment remain the responsibility of Environment Canada.

The critical information and considerations upon which the draft assessment is based are summarized below.

## Substance Identity

This report assesses the long-chain (C9-C20) perfluorocarboxylic acids (PFCAs), their salts and their precursors. The long-chain (C9-C20) PFCAs were grouped and assessed due to greater concerns over the bioaccumulation potential and concentrations of long-chain (C9-C20) PFCAs in the environment and in non-human biota. Perfluorooctanoic acid (PFOA or C8) has been assessed separately.

“Perfluorinated” refers to fluorochemicals in which the hydrogen atoms directly attached to the carbon atoms are all replaced with fluorine atoms. Perfluorocarboxylic acids and their salts are a homologous series of substances with the molecular formula of  $C_nF_{2n+1}CO_2H$  (where  $8 \leq n \leq 20$ ).

Long-chain (C9-C20) PFCAs are not on the Domestic Substances List (DSL) and were not subject to the categorization provisions of *Canadian Environmental Protection Act, 1999* (Canada 1999). However, some of the 90 identified precursors are present on the DSL and were subject to categorization. This assessment considers any precursor to long-chain (C9-C20) PFCAs which could transform or degrade to a C9–C20 PFCA given similar use applications and similarities in their physical-chemical properties and structures. This assessment defines precursors as any substance where the perfluorinated alkyl moiety has the formula  $C_nF_{2n+1}$  (where  $8 \leq n \leq 20$ ) and is directly bonded to any chemical moiety other than a fluorine, chlorine or bromine atom. While the assessment did not consider the potential additive effects of long-chain (C9-C20) PFCAs and their precursors and their salts, it is recognized that the precursors and salts may contribute to the total presence of long-chain (C9-C20) PFCAs in the environment. The expression, C#, is used to define the carbon chain length of the perfluorocarboxylic acid in question, e.g., C9 is a nine carbon PFCA.

Environment Canada considered some 90 perfluoroalkyl compounds as being long-chain (C9-C20) PFCAs, their salts and their precursors (Appendix II: Long-chain PFCA Precursor Identification). The long-chain (C9-C20) PFCA grouping was defined using expert judgment, chemical structures and the biodegradation estimation modelling, CATABOL (Mekenyan et al. 2002). Using these approaches, structures were analyzed for their potential to degrade to long-chain (C9-C20) PFCAs. CATABOL was trained on the basis of MITI (Ministry of International Trade and Industry, Japan) biodegradation test results and predicts biodegradation over a period of 28 days. It is acknowledged that due to the very limited perfluorinated degradation data in the training set, some degradation products generated by CATABOL may be of limited reliability or relevance in the environment. It should be noted that, for perfluorinated chemistry, the degradation process will be longer but it is difficult to estimate how much longer, especially for high-molecular-weight substances such as oligomers and polymers. The list in Appendix I provides examples of substances in this group and is not considered exhaustive.

In 2000, an industry survey by Environment Canada under the authority of section 71 of *Canadian Environmental Protection Act, 1999* (Canada 1999) identified a total of 256 perfluorinated alkyl compounds in commerce in Canada for the calendar years 1997,

1998, 1999 and 2000 (Environment Canada 2001). The long-chain (C9-C20) PFCAs were not reported to be manufactured or imported in Canada; however, of the approximately 90 identified precursors, several were imported into Canada. The 2004 industry survey of perfluoroalkyl and fluoroalkyl substances (Environment Canada 2005) also found that no long-chain (C9-C20) PFCAs were reported to be manufactured in, or imported into, Canada. However, a number of precursors to long-chain (C9-C20) PFCAs were reported to be imported into Canada.

The Organization for Economic Co-operation and Development (OECD) has prepared a document entitled, *Preliminary Lists of PFOS, PFAS, PFOA and Related Compounds that may Degrade to PFCA* (OECD 2007), which combined information from various member countries, including Canada, to assist the OECD in its risk management activities for perfluorinated compounds. The OECD has gathered a preliminary list of approximately 850 known perfluorinated substances. The majority of the substances on the list can potentially break down to PFCAs. Fluoropolymers such as polytetrafluoroethylene were considered stable and thus not included as a PFCA precursor in the OECD list. Certain PFCAs are used as processing aids in the production of fluoropolymers, and very low concentrations of PFCAs may be present in the finished products, but PFCA is not incorporated into the polymer structure. The long-chain PFCA precursors identified in this assessment can also be found on this OECD list.

**Table 1. Substance identity of C9-C20 long-chain perfluorocarboxylic acids**

Chemical Abstracts Index name	Acronym	Molecular formula	Structural formula	Chemical Abstracts Service Registry Number	Synonyms
Nonanoic acid, heptadecafluoro- (C9 PFCA)	PFNA	C <sub>9</sub> H F <sub>17</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_7-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	375-95-1 (NDSL)	C 1800; Heptadecafluorononanoic acid; Perfluorononanoic acid; Perfluoropelargonic acid
Decanoic acid, nonadecafluoro- (C10 PFCA)	PFDA	C <sub>10</sub> H F <sub>19</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_8-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	335-76-2 (NDSL)	Nonadecafluoro-n-decanoic acid; Nonadecafluorodecanoic acid; Perfluoro-n-decanoic acid; Perfluorocapric acid; Perfluorodecanoic acid
Undecanoic acid, heneicosfluoro- (C11 PFCA)	PFUnDA	C <sub>11</sub> H F <sub>21</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_9-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	2058-94-8 (not listed on NDSL or DSL)	Heneicosfluoroundecanoic acid; Perfluoroundecanoic acid; Perfluoroundecylic acid
Dodecanoic acid, tricosfluoro- (C12 PFCA)	PFDoDA	C <sub>12</sub> H F <sub>23</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{10}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	307-55-1 (NDSL <sup>1</sup> )	Perfluorododecanoic acid; Perfluorolauric acid



Chemical Abstracts Index name	Acronym	Molecular formula	Structural formula	Chemical Abstracts Service Registry Number	Synonyms
Tridecanoic acid, pentacosafuoro- (C13 PFCA)	PFTTrDA	C <sub>13</sub> H F <sub>25</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{11}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	72629-94-8 (not listed on NDSL or DSL)	Perfluorotridecanoic acid
Tetradecanoic acid, heptacosafuoro- (C14 PFCA)	PFTDA	C <sub>14</sub> H F <sub>27</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{12}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	376-06-7 (NDSL)	Perfluoromyristic acid; Perfluorotetradecanoic acid
Pentadecanoic acid, nonacosafuoro- (C15 PFCA)	PFPeDA	C <sub>15</sub> H F <sub>29</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{13}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	141074-63-7 (not listed on NDSL or DSL)	Perfluoropentadecanoic acid
Hexadecanoic acid, hentriacontafuoro- (C16 PFCA)	PFHxDA	C <sub>16</sub> H F <sub>31</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{14}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	67905-19-5 (NDSL)	Perfluoropalmitic acid, perfluorohexadecanoic acid Hexadecanoic acid
Perfluoroheptadecanoic acid (C17 PFCA)	PFHpDA	C <sub>17</sub> H F <sub>33</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{15}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	57475-95-3 (not listed on the NDSL or DSL)	—
Octadecanoic acid, pentatriacontafuoro- (C18 PFCA)	PFODA	C <sub>18</sub> H F <sub>35</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{16}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	16517-11-6 (NDSL)	Perfluorostearic acid Perfluorooctadecanoic acid Octadecanoic acid
Perfluorononadecanoic acid (C19 PFCA)	PFNDA	C <sub>19</sub> H F <sub>37</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{17}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	133921-38-7 (not listed on NDSL or DSL)	—
Perfluoroeicosanoic acid (C20 PFCA)		C <sub>20</sub> H F <sub>39</sub> O <sub>2</sub>	$\begin{array}{c} \text{F} \\   \\ \text{F}-\text{C}-(\text{CF}_2)_{18}-\text{CO}_2\text{H} \\   \\ \text{F} \end{array}$	68310-12-3 (NDSL)	Eicosanoic acid, nonatriacontafuoro- (9CI); Nonatriacontafluoroeico- sanoic acid

NDSL = Non-domestic Substances List

## Physical and Chemical Properties

Information relating to the physical properties of long-chain (C9-C20) PFCAs is limited. Table 2 shows the available physical and chemical data, where available, for C9-C15 long-chain PFCAs. It has been suggested that the carbon-carbon conformation changes as the chain length increases, with longer chains becoming helical (Wang and Ober 1999), resulting in smaller cross-sectional diameter molecules where the chain may fold back on itself or not be completely linear. If so, then this would cause a change in the physical and chemical properties of the longer chain acids relative to the linear PFCAs (i.e., < C8).

**Table 2. Available physical/chemical properties of C9-C15 PFCAs**

Property	Value	Type	Reference
<b>C9 PFCA</b>			
Molecular mass (g/mol)	464.08	–	-
Melting point (°C)	77	Experimental	Fontell and Lindman 1983
	71		Blancou et al. 1976
	71-72		Herbst et al. 1985
	65 (CCl <sub>4</sub> )		Beneficemalouet et al. 1991
	59.3-61.1		Kunieda and Shinoda 1976
	69-71		Ishikawa et al. 1983
Boiling point (°C)	203.4	Calculated	Kaiser et al. 2005
Vapour pressure (Pa) at 25°C	1.3 – 99.97 kPa (99.6 – 203°C)	Calculated	Kaiser et al. 2005
	0.10	Experimental	Arp et al. 2006
Water solubility	<0.2 percent weight at 60°C	Experimental	Fontell and Lindman 1983 <sup>1</sup>
	1.3 g/L (critical micelle concentration)	Experimental	Kunieda and Shinoda 1976 <sup>1</sup>
pK <sub>a</sub> (dimensionless)	<0.8	Calculated	Goss 2008
log K <sub>oc</sub> (dimensionless)	2.3 – 2.48	Experimental	Higgins and Luthy 2006
<b>C10 PFCA</b>			
Molecular mass (g/mol)	514.08	–	-
Melting point (°C)	87.4-88.2 (CCl <sub>4</sub> )	Experimental	Bernett and Zisman 1959
	87.4-88.2 (toluene)		Bernett and Zisman 1959
	83.5-85.5 (CCl <sub>4</sub> , ethanol)		Mukerjee and Handa 1981

Property	Value	Type	Reference
	76.5(CCl4)		Ikawa et al. 1988
	87.4-88.2		Hare et al. 1954
Boiling point (°C)	218	Experimental	Kauck and Diesslin 1951
	219.4	Calculated	Kaiser et al.2005
	203.4	Calculated	Kaiser et al. 2005
	218	Experimental	Sigma Aldrich 2004
Vapour pressure (Pa) at 25°C	3.1 to 99.97 kPa (129.6 to 218.9°C)	Calculated	Kaiser et al.2005
	-0.64	Experimental	Arp et al. 2006
	0.10	Experimental	Arp et al. 2006
Water solubility (g/L)	5.14	Experimental	Kauck and Diesslin 1951
	0.40 (critical micelle concentration)		Bernett and Zisman 1959 <sup>1</sup>
	0.46 (critical micelle concentration at 30°C)		Klevens and Raison 1954 <sup>1</sup>
pKa (dimensionless)	2.57512	Calculated	Moroi et al.2001
log K <sub>oc</sub> (dimesionless)	2.65 – 2.87	Experimental	Higgins and Luthy 2006
<b>C11 PFCA</b>			
Molecular mass (g/mol)	564.1	–	-
Melting point (°C)	112-114	Experimental	Huang et al. 1987
	97.9-100.3		Kunieda and Shinoda 1976
Boiling point (°C)	238.4 at 101.325 kPa	Calculated	Kaiser et al. 2005
Vapour pressure (Pa) at 25°C	0.6 to 99.97 kPa (112 to 237.7°C)	Calculated	Kaiser et al. 2005
	-0.98	Experimental	Arp et al. 2006
log K <sub>oc</sub> (dimesionless)	3.19 – 3.41	Experimental	Higgins and Luthy 2006
<b>C12 PFCA</b>			
Molecular mass (g/mol)	614.1	–	-
Melting point (°C)	112.6 – 114.7 (CCl <sub>4</sub> , toluene)	Experimental	Bernett and Zisman 1959
	112.6-114.7		Hare et al. 1954
	112-114		Huang et al. 1987
Boiling point (°C)	Not available		
Vapour pressure (Pa) at 25°C	0.9 to 99.96 kPa (127.6 to 247.7°C)	Calculated	Kaiser et al. 2005
<b>C13 PFCA</b>			
Molecular mass (g/mol)	664.0989	–	-

Property	Value	Type	Reference
Melting point (°C)	117.5-122	Experimental	Kunieda and Shinoda 1976
<b>C14 PFCA</b>			
Molecular mass (g/mol)	714.12	–	-
Melting point (°C)	130.4 (hexane)	Experimental	Lehmle et al.2001
	130		Kunieda and Shinoda 1976
<b>C15 PFCA</b>			
Molecular mass (g/mol)	764.1129		-

<sup>1</sup> It should be noted that these solubility values refer to an aqueous phase containing a mixture of protonated acid and perfluorocarboxylate anion, at an “autogenous” pH. If the pH is reduced by addition of, for example, a mineral acid, the proportion of protonated acid will increase and the overall solubility will decrease.

Abbreviations: K<sub>oc</sub>, sediment organic carbon coefficient; pK<sub>a</sub>, acid dissociation constant.

## Sources

There are no known natural sources of long-chain (C9-C20) PFCAs, their salts and their precursors (Kissa 1994). Their presence in the environment is due solely to human activity. In 2000, an industry survey by Environment Canada under the authority of section 71 of the *Canadian Environmental Protection Act, 1999* (Canada 1999) identified 256 perfluoroalkyl compounds to be in commerce in Canada for the calendar years 1997, 1998, 1999, and 2000 (Environment Canada 2001). Long-chain (C9-C20) PFCAs were not reported to be manufactured or imported into Canada. In 2004, another industry survey by Environment Canada of perfluoroalkyl and fluoroalkyl substances also found long-chain (C9 –C20) PFCAs were not reported to be manufactured or imported in Canada (Environment Canada 2005). In both surveys, precursors to the long-chain (C9-C20) PFCAs were reported to be imported into Canada.

## Uses

C9 PFCA is used in the production of fluoropolymers, primarily polyvinylidene fluoride (Prevedouros et al. 2006). Based on available information, long-chain (C9-C20) PFCAs are rarely used intentionally in products. Commercially, there are commonly used precursors such as fluorotelomers, e.g., substances derived from fluorotelomer alcohols (FTOHs), or other fluorotelomer-based substances, which can degrade to long-chain (C9-C20) PFCAs. Fluorotelomers are a subgroup of perfluorinated substances that are produced by a process called telomerization, and can occur in a range of fluorocarbon chain lengths. Fluorotelomer alcohols are not fully fluorinated, since they have a 2-carbon hydrocarbon chain linked to the perfluorinated carbon chain. Fluorotelomer epoxides, olefins or alcohols are used as building blocks in the production of fluorotelomer-based substances. These substances provide oil-, grease-, water- and stain-repellent properties to other substrates. Some fluorotelomer-based substances can be further exploited as monomers to generate polymeric fluorotelomer substances with the same characteristic properties.

## Releases to the Environment

### *Direct Releases*

There are no available data on the direct release of long-chain (C9-C20) PFCAs to the Canadian environment.

### *Indirect Releases*

There is empirical evidence available regarding the degradation of fluorotelomer-based polymers into long-chain (C9-C20) PFCAs. Fluorotelomer alcohols (FTOHs) with  $x$  number of carbons produces intermediates such as fluorotelomer unsaturated carboxylates ( $x$ :2 FTUCA) where  $x$  equals the number of carbons and fluorotelomer carboxylic acids ( $x$ :2 FTCA) that can further degrade to a long-chain (C9-C20) PFCAs. FTOHs can be biodegraded or metabolized to long-chain (C9-C20) PFCAs as shown in studies by Hagen et al. 1981, Lange 2002, Dinglasan et al. 2004, Kudo et al. 2005, Martin et al. 2005, Wang et al. 2005a, 2005b; Fasano et al. 2006, 2008; Liu et al. 2007, and Nabb et al. 2007. Further evidence that FTUCAs and FTCAs are formed as intermediates in the biodegradation or metabolism of FTOHs is provided by Kudo et al. (2005), Martin et al. (2005) and Liu et al. (2007).

Recognition of FTOHs as potential sources of long-chain (C9-C20) PFCAs came from the detection of FTOH metabolites in biota (Smithwick et al. 2006; Butt et al. 2008; Powley et al. 2008; Furdui et al. 2007). Metabolism of FTOHs is expected to result in the formation of intermediates such as FTCAs and FTUCAs (Dinglasan et al. 2004; Wang et al. 2005a, 2005b). Houde et al. (2005) reported levels of 8:2 and 10:2 FTUCAs in plasma of bottlenose dolphins sampled from the region of the Gulf of Mexico along the Eastern coast of the Atlantic. FTCAs were not detected. A temporal trend study by Butt et al. (2008) also reported levels of FTUCAs in all ringed seal liver samples from the Canadian Arctic. Furdui et al. (2007) reported 8:2 FTUCA and 10:2 FTUCA in 52% and in 40% of all samples of lake trout from the Great Lakes, respectively. The presence of FTCAs and FTUCAs in animal biota is also reported in a number of studies such as Taniyasu et al. 2005, Verreault et al. 2005, Powley et al. 2008, Smithwick et al. 2006, Butt et al. 2007a, 2007b, 2008; and Furdui et al. 2007. Dinglasan and Mabury (2005) showed that 8:2 FTOH, 8:2 FTCA and 8:2 FTUCA are formed through the degradation of an 8:2 telomer methacrylate monomer that is used in building polymers. Although the rate of degradation was not determined, the aerobic sewage treatment plant inoculum was able to significantly degrade the monomer over the ~73-day test.

The relative abundance of linear vs. branched forms of PFCAs can provide some indication of their potential source. For example, DeSilva and Mabury (2004) showed that liver samples had at least 99% linear PFCA isomers in polar bears from southeastern Hudson Bay and eastern Greenland. Linear PFCAs reflect degradation largely from linear FTOHs and indicate that the source of PFCAs originates from telomerization rather than electrochemical fluorination (a process that would produce about 20% branched isomers). Additional indications for FTOHs as a source of PFCAs come from the odd-chain length and even-chain length patterns from PFCAs detected in tissue samples. It can be

expected that the degradation of a given FTOH would result in the formation of an equal number of adjacent odd-chain length and even-chain length PFCAs via atmospheric oxidation. FTOH has been shown to degrade to a relatively equal concentration of even-chain length and odd-chain length PFCAs (Ellis et al. 2004b) and therefore, the exposure to each should be the same in lower-trophic-level biota. The odd-chain length PFCAs would be expected to be found at slightly higher levels in higher-trophic-level biota (Martin et al. 2004a). Such a pattern is seen in observations in polar bear sampling by Kannan et al. (2005) and Smithwick et al. (2005b). The correlated odd-chain length and even-chain length PFCAs tend to indicate a single uniform source (Smithwick et al. 2005b; van de Vijver et al. 2005) and could, therefore, be reflective of the manufacture of fluorotelomer alcohols. FTOHs appear to be available to biota in the environment and are being metabolized, in vivo, to intermediates (other PFCA precursors) which may ultimately yield long-chain PFCAs. Furdui et al. (2008) detected branched C11 PFCA and C13 PFCA isomers in lake trout from Lake Ontario that declined from 1993 to 2004 and then linear isomers increased in more recent samples (up to year 2004) suggesting that current PFCA sources to Lake Ontario result from the telomerization process.

The levels of residual FTOHs in polymers were measured in a study by Dinglasan-Panlilio and Mabury (2006) where several products containing fluorinated polymers or related fluorochemicals were analyzed. FTOHs (4:2 to 12:2) were found in products at levels between 0.11 and 3.8% on a dry weight basis. Extraction solvent was ethyl acetate of 2 x 5 ml aliquots which were subsequently combined. The concentration of the ethyl acetate was not provided. Although the actual levels of FTOHs present as residual<sup>1</sup> or present as part of product formulations could not be distinguished, their presence provides some indication that fluorotelomer-based polymers could be a source of FTOHs to the environment.

The levels of long-chain (C9-C20) PFCAs measured in Canadian urban aquatic compartments suggest indirect input sources, e.g., wastewater treatment plants (WWTPs) (Boulanger et al. 2005a; Simcik and Dorweiler 2005; Crozier et al. 2005). C9 to C12 PFCAs have been detected in WWTP sludge in a number of studies (Boulanger et al. 2005b; Higgins et al. 2005; Sinclair and Kannan 2006; Crozier et al. 2005). Higgins et al. (2005) indicated higher levels of even-chained-length PFCAs (C8 to C12) in aerobically digested sludge from a WWTP and in sediment from the San Francisco Bay area. Sinclair and Kannan (2006) reported a pattern of higher even-chained-length PFCAs over odd-chained-length PFCAs in WWTP effluent waters in plants in New York State.

WWTPs with simple primary treatment did not have releases of long-chain (C9-C20) PFCAs. However, WWTPs that included secondary treatment increased the presence of long-chain (C9-C20) PFCAs (Sinclair and Kannan 2006), suggesting rapid biological or chemical degradation of precursors during secondary treatment. Precursors such as FTCAs and FTOH degradation products have been measured in influent and primary treatment samples, but not in secondary treatment waters (Sinclair and Kannan 2006). As the FTCAs are only found in primary treatment samples, this suggests that the conversion

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<sup>1</sup> A residual is PFOA, a long-chain PFCA or a precursor that is not deliberately added as an ingredient in a product. A residual includes impurities, un-reacted monomers and other un-reacted reactants.

of FTOHs to long-chain (C9-C20) PFCAs is incomplete, whereas the absence of FTCAs and presence of C9 to C11 PFCAs in secondary samples suggests complete conversion. Crozier et al. (2005) measured levels of C9 and C10 PFCAs in effluent waters (concentrations ranging from 3 – 6 ng/L) and biosolids (concentrations ranging from 0.4 – 5.2 ng/g) from Ontario sewage treatment plants. C11 and C12 PFCAs were not detected (detection limit 2 ng/L). Crozier et al. (2005) also noted that C10 PFCA which was not detected in the influent of one sewage treatment plant but was detected in the effluent at 4 ng/L indicating that C10 PFCA was formed during the sewage treatment plant process whereas C9 PFCA was detected at 4 ng/L in both the influent and effluent of the sewage treatment plant, suggesting no removal of the compound.

De Silva et al. (2009) suggested that the biodegradation and/or metabolism of polyfluorophosphoric acids (diesters equals diPAPs) such as 10:2 diPAP can yield C10 PFCAs. diPAPs were measured at 50 -100 ng/g in wastewater treatment plant (WWTP) sludge.

Guo et al. (2009) detected C9 to C12 PFCAs in typical American homes with carpeted floors, pre-treated carpet, and commercial carpet-care liquids. Floor waxes and stone/tile/wood sealants that contain fluorotelomer products are potential sources of C9 to C12 PFCAs in homes containing these materials. Other potential sources include treated home textile, upholstery and apparel and household carpet/fabric care liquids and foams (Guo et al. 2009). The release of PFCA precursors from household products is shown by several studies in which indoor air in houses was sampled. Archived U.S. house dust samples collected between 2000 and 2001 from Ohio and North Carolina were analyzed for FTOHs (6:2, 8:2 and 10:2) and PFCAs (C9–C12) (Strynar and Lindstrom 2005). Mean concentrations were 0.5–0.804 µg/g of dust for C9–C12 PFCAs. Mean 6:2, 8:2, and 10:2 FTOH levels ranged from 0.4 to 1.0 µg/g dust. The mean values between the two locations did not differ significantly, suggesting similar sources such as treated carpets or textiles. Shoeib et al. (2005) reported levels of 6:2, 8:2 and 10:2 FTOH in indoor dust collected from vacuum cleaners from randomly selected homes in Ottawa, with mean concentrations of 0.035, 0.055 and 0.035 µg/g of dust, respectively. Air samples for FTOH analysis were not collected due to technical difficulties. FTOHs have also been found in all-weather clothing (Berger and Herzke 2006) and as emissions from non-stick frying pans (Sinclair et al. 2007). PFCAs themselves (and in some cases, FTCAs and FTUCAs) may also be released from products, including all-weather clothing, cookware, commercial fabric protector and food contact materials (Begley et al. 2005; Boulanger et al. 2005b; Mawn et al. 2005; Washburn et al. 2005; Bradley et al. 2007; Sinclair et al. 2007).

## **Environmental Fate**

Environmental modeling of long-chain (C9-C20) PFCAs cannot be conducted using widely accepted models as they cannot be applied to ionizable surfactants.  $K_{ow}$  (octanol-water partition coefficient) is a problematic parameter for surfactants because they tend to aggregate at the interface of a liquid-liquid system and therefore cannot be measured directly.

Long-chain (C9-C20) PFCAs and/or their salts are expected to partition primarily to the aqueous medium as a result of their high water solubility and low volatility. The presence of the acid functional group imparts a large proportion of the nature and character of the long-chain (C9-C20) PFCAs. The acid functional group is hydrophilic and is completely dissociated in the aqueous phase (Ellis et al. 2004a). Substances containing a perfluoroalkyl moiety may have surfactant properties due to the combined properties of oleophobicity, hydrophobicity and hydrophilicity over portions of a particular molecule, whereas unsubstituted hydrocarbon chains are oleophilic and hydrophobic (Key et al. 1997). Furthermore, a functional group attached to the perfluorinated chain (e.g., a charged moiety such as a carboxylate anion) can impart hydrophilicity to part of the molecule. However, as the length of the perfluorinated chain increases, the PFCA molecule will likely become more hydrophobic and its water solubility diminishes (Ellis et al. 2004a).

### **Persistence and Bioaccumulation Potential**

The information below was considered in evaluating whether long-chain (C9-C20) perfluorocarboxylic acids, their salts and their precursors meet the criteria for persistence and bioaccumulation as defined under the *Persistence and Bioaccumulation Regulations* (Canada 2000). Persistence criteria are half-lives of greater than or equal to 2 days in air, 182 days in water, 365 days in sediment, or 182 days in soil, or evidence of long-range transport to remote areas. Bioaccumulation criteria are bioaccumulation factors (BAFs) or bioconcentration factors (BCFs) of greater than or equal to 5000 or a log  $K_{ow}$  of greater than or equal to 5.0.

#### *Persistence*

A small amount of C9 PFCA was produced through a photo-induced hydrogen peroxide system, demonstrating rapid degradation of 10 and 100 µg/M solutions of 8:2 FTOH within minutes to hours via the formation of 8:2 FTAL (fluorotelomer aldehyde), 8:2 FTCA and 8:2 FTUCA (Gauthier and Mabury 2005). However, this is an aqueous photolysis reaction that may not significantly contribute to long-chain (C9-C20) PFCAs in the environment given the low aqueous solubility and large Henry's Law constant of FTOHs.

Hori et al. (2005a) have reported C9 PFCA decomposition where the concentration of C9 was 1.51 mg/L. Hori et al (2005b) also examined the degradation of C9, C10 and C11 PFCA with persulfate ion ( $S_2O_8^{2-}$ ) in an aqueous/liquid  $CO_2$  biphasic system. C9 PFCA was degraded to fluoride ions and carbon dioxide in a solution containing  $S_2O_8^{2-}$  heated to 80°C for 6 hours (Hori et al. 2008). However, the conditions in these studies are not environmentally relevant.

Hurley et al. (2004) have shown that atmospheric degradation lifetime of gas phase short-chain PFCAs (C3–C5), under artificial smog conditions, is expected to be on the order of 130 days due to OH radical reactions, with a lifetime of the order of 10 days due to wet/dry deposition (particle mediated). Direct gas phase photolysis of the acids was not



observed. Hurley et al. (2004) also stated that it is unlikely that these values will significantly change as the chain length of the acid is increased. The degradation pathway initiated by the reaction  $C_nF_{2n+1}COOH + OH \rightarrow H_2O + C_nF_{2n+1}COO$  (followed by  $C_nF_{2n+1}COO \rightarrow C_nF_{2n+1} + CO_2$ , etc.) is not believed to be particularly efficient, given that the lifetime for this process (130 d) is considerably greater than that estimated for removal of PFCAs from the atmosphere by wet/dry deposition (~ 10 d). In other words, even if PFCAs are formed in the atmosphere from FTOHs, they will not remain there long enough to be degraded.

The presence of long-chain PFCAs in the Canadian Arctic (Martin et al. 2004a) indicates the long-range transport either of long-chain (C9-C20) PFCAs (e.g., via ocean currents) (Wania 2007; Prevedouros et al. 2006) or of volatile precursors to long-chain (C9-C20) PFCAs such as FTOHs (e.g., via atmospheric transport) or both (Wallington et al. 2006, Stock et al. 2007). C9 to C11 PFCAs were measured in polar ice caps from three areas in the High Arctic in the spring of 2005 and 2006 (Melville ice cap, Northwest Territories; Agassiz ice cap, Nunavut; and Devon ice cap, Nunavut) (Young et al. 2007). C9 PFCA concentrations ranged from 0.005 to 0.246 ng/L. C10 PFCA concentrations ranged from below detection to 0.022 ng/L. C11 PFCA concentrations ranged from below detection to 0.027 ng/L. Between 1996 and 2005, concentrations were increasing for C9 and C10 PFCAs (Young et al. 2007). Fluxes were calculated using the density corrected concentration, multiplied by the yearly accumulation. Fluxes calculated to each of the ice caps were multiplied by the area of the Arctic to yield a flux of C9, C10, and C11 PFCAs to the area north of 65°N. These fluxes are estimates and may not be representative of actual deposition in this region due to wide variations in precipitation rates. In 2005, C9 showed a flux ranging from 73- 860 kg/year; C10 PFCA showed a flux ranging from 16 – 84 kg/year and C11 PFCA showed a flux ranging from 26-62 kg/year (Young et al. 2007).

A suggested hypothesis for the presence of long-chain (C9-C20) PFCAs in biota in remote regions is that a precursor (e.g., FTOHs) is emitted to the atmosphere and ultimately degrades to yield long-chain (C9-C20) PFCAs through biotic and abiotic degradation. Ellis et al. (2004a) showed that the atmospheric lifetime of short-chain FTOHs, as determined by their reaction with hydroxy radicals, was approximately 20 days. Shoeib et al. (2006) collected air samples during a crossing of the North Atlantic and Canadian Archipelago in July 2005 to investigate concentrations of FTOHs. The highest concentrations were for 8:2 FTOH at 5.8–26 pg/m<sup>3</sup>, followed by 10:2 FTOH at 1.9–17 pg/m<sup>3</sup> and then 6:2 FTOH at below detection limit to 6.0 pg/m<sup>3</sup>. The surfactant properties of PFCAs have been examined for their influence on the potential formation of perfluorinated aerosols over the marine environment (Waterland et al. 2005) and may suggest a mechanism for long-range transport to remote regions via oceanic routes. However, available research suggests that the presence of long-chain (C9-C20) PFCAs in remote regions may be a result of the degradation of volatile fluoroalkyl precursor substances such as FTOHs. Young et al. (2007) suggested that the presence of C9, C10 and C11 PFCAs on Canadian High Arctic ice caps is indicative of atmospheric oxidation of volatile precursors as a source. High Arctic ice caps receive contamination from atmospheric sources and have the potential to provide long-term temporal trends of

atmospheric concentrations. The ratios of these PFCAs to sodium concentrations were variable, indicating that PFCA concentrations on the ice cap are unrelated to marine chemistry. By examining the concentrations of PFCAs in ice caps, atmospheric fluxes were determined by considering the area of each ice cap. Fluxes of PFCAs were estimated for the area north of 65°N for 2005 to be 73–860 kg/year for C9, 16–84 kg/year for C10 and 26–62 kg/year for C11.

The carbon-fluorine bond is one of the strongest in nature (~110 kcal/mol), making the bond extremely stable and generally resistant to degradation. Fluorine has the highest electronegativity of all elements in the periodic table. This contributes to a high ionization potential and low polarizability. It also results in low inter- and intra-molecular interactions and extremely low surface tension. Direct photolysis of a carbon-fluorine chain is also expected to be very slow, with stability to such energy expected to be sustained for more than 1000 years (Environment Canada and Health Canada 2006). PFCAs, in general, have surfactant properties due to the combined properties of oleophobicity, hydrophobicity, and hydrophilicity over portions of a particular molecule. The nature of PFCAs, e.g., their strong tendency to ionize, would likely lead to them to be more prevalent in the aqueous phase, and they are not expected to partition significantly to the atmosphere (Ellis et al. 2004a). It is unlikely that these acids will degrade under environmentally relevant conditions in any medium, including water and/or sediment.

#### *Bioaccumulation*

Regulatory criteria (BCFs and BAFs) have been developed under the *Canadian Environmental Protection Act, 1999* (Canada 1999) to determine whether or not a substance is to be considered bioaccumulative. However, these threshold criteria are based on historical experience with neutral, non-metabolized organic substances. These criteria, based on the Federal Toxic Substances Management Policy (TSMP) persistence and bioaccumulation criteria, were developed in the mid-1990s and formally published in 1995 (Canada 1995). These criteria were intended to identify lipophilic substances with the potential to bioaccumulate primarily in aquatic systems. Thus, substances that meet the criteria, i.e., BAF or BCF > 5000 or  $\log K_{ow} \geq 5$ , have significant potential for bioaccumulation at the organism level and biomagnification through the food web. It should be noted, however, that information on BAFs, BCFs or  $\log K_{ow}$ s is but one part of the overall weight of evidence in determining the bioaccumulation potential of a given substance. Furthermore, a substance may be deemed to be sufficiently bioaccumulative to cause concern, even if regulatory criteria are not met.

Additional measures of bioaccumulation which directly address the potential for chemicals to biomagnify include biomagnification factors (BMFs) and trophic magnification factors (TMFs; sometimes referred to as food-web biomagnification factors). The BMF represents the ratio of the chemical concentration in a predator to that in its food or prey. A BMF greater than 1 may be considered cause for concern, as it suggests that biomagnification is occurring. The BMF measured relative to a food item in the laboratory is sometimes referred to as a “dietary BAF.” An important uncertainty in BMF measurements is associated with determining the actual trophic status of a predator

and its prey, given that most organisms are omnivores (Gray 2002). A TMF may be thought of as the average ratio of the concentration of a substance in predator and prey across an entire or partial food web. As with BMF, a TMF value exceeding 1 may also be cause for concern, since it indicates that food web biomagnification is occurring. BMFs and TMFs are most often measured in the field, although laboratory feeding studies can also be used to estimate BMFs (or “dietary BAFs”). Generally, chemical concentrations are lipid-normalized prior to making BMF and TMF determinations; however, lipid-normalizing concentrations of perfluorinated substances may not be appropriate, since these substances appear to preferentially bind to proteins in liver, kidney and plasma rather than partition to lipids (Houde et al. 2006b; Martin et al. 2003a). The lack of a normalization method for substances that associate with protein/plasma introduces a source of uncertainty when evaluating BMFs and TMFs of PFCAs.

PFCAs have the combined properties of oleophobicity, hydrophobicity, and hydrophilicity over different portions of these molecules. Furthermore, the carboxylate functional group attached to the perfluorinated chain imparts polarity to the molecule. Due to these properties, the normal assumption that the hydrophobic and lipophilic interactions between compound and substrate are the main mechanisms governing partitioning may not be applicable for long-chain (C9-C20) PFCAs. Long-chain (C9-C20) PFCAs are considered to be “model-difficult” (i.e., most models use  $\log K_{ow}$  which is not applicable to perfluorinated substances due to their partitioning preference to proteins) with respect to bioaccumulation, and standard measures of bioaccumulation should be applied cautiously for these substances. There are no reported  $K_{ow}$  measurements for any long-chain (C9-C20) PFCA, and the use of this physical property for estimation of bioaccumulation potential is unlikely to be useful because these substances can sit at the interphase between organic and aqueous phases rather than partition between the two phases (Houde et al. 2006b).

It has been suggested that an additional assumption of the BAF/BCF/ $\log K_{ow}$  approach is that bioaccumulation occurs by the same mechanisms for all chemicals in both water-breathing animals (e.g., fish and aquatic invertebrates) and air-breathing animals (e.g., terrestrial mammals, birds and marine mammals), resulting in a similar bioaccumulation potential between these organism classes for a particular substance (Kelly et al. 2004; Mackay and Fraser 2000). As described by Kelly et al. (2004), organic chemicals can be grouped according to polarity (as indicated by a  $\log K_{ow}$  that decreases with increasing polarity due to expected changes in aqueous solubility), and volatility (as indicated by a  $\log K_{oa}$  (octanol-air partition coefficient) that decreases with increasing volatility). In general, non-polar, non-volatile (NPNV) chemicals such as PCBs are expected to have low elimination rates to both water and air, resulting in a similarly high bioaccumulation potential for both air-breathing and water-breathing organisms. The polar nature of polar, non-volatile (PNV) chemicals and the potential ionization of PFCAs in particular, will cause their water solubility to increase relative to NPNVs. For water-breathing organisms, this potentially results in more rapid elimination of PNVs to the water phase and a reduction in bioaccumulation potential. However, because bioaccumulation potential in air-breathing organisms is driven primarily by volatility rather than polarity, the non-volatile nature of PNVs such as PFCAs results in their relatively slow

elimination to air, resulting in higher bioaccumulation potential in air breathers (Stevenson 2006b).

Although the general assumption is that chemical properties and partitioning behaviour are the primary processes governing uptake and elimination, in many cases metabolic transformation of a particular chemical allows for rapid elimination and lower bioaccumulation potential (Kelly et al. 2004). However, studies have not been performed on the metabolic transformation and elimination of PFCAs or precursors in air-breathing organisms.

An additional complication relating to bioaccumulation assessment for long-chain (C9-C20) PFCAs is that BCFs, BAFs, BMFs and TMFs are often based on concentrations in individual organs, as opposed to whole-body burdens. From a toxicological perspective, BCFs, BAFs, BMFs and TMFs for individual organs, such as the liver, may be more relevant when predicting potential for direct organ-specific toxicity (e.g. liver toxicity). Conder et al. (2008) suggest that, as bioaccumulation is expressed on a whole-body mass-basis, the concentrations of perfluorinated acids in tissues such as liver are not appropriate for use in assessing the bioaccumulation potential of these compounds. Due to the small proportion of the body mass that is composed of liver tissue and blood and the magnitude of the differences in concentrations between these compartments and other tissues, the concentration of perfluorinated acids on a whole-body mass-basis has been estimated to be 10 times lower than concentrations of perfluorinated acids in plasma in dolphins, narwhal and beluga whale and 2–10 times lower than the concentrations of perfluorinated acids in blood and liver of trout (Conder et al. 2008).

However, measures of bioaccumulation (BCFs, BAFs, BMFs) may be used as indicators of either direct toxicity to organisms that have accumulated long-chain (C9-C20) PFCAs or of indirect toxicity to organisms that consume prey containing long-chain (C9-C20) PFCAs (via food chain transfer). Concerning the potential to cause direct toxicity, the critical body burden is the minimum concentration of a substance in an organism that causes an adverse effect. From a physiological perspective, it is the concentration of a substance at the site of toxic action within the organism that determines whether a response is observed, regardless of the external concentration. In the case of long-chain (C9-C20) PFCAs, the site of toxic action is often considered to be the liver. Concerning the potential for toxicity to consumer organisms, it is the concentration in the whole body of a prey that is of interest since the prey is often completely consumed by the predator—including individual tissues and organs, such as the liver and blood. Given the partitioning into liver and blood, most field measurements for perfluorinated substances have been performed for those individual organs and tissues especially for higher-trophic-level organisms (e.g., polar bear) where whole-body analysis is not feasible due to either sampling or laboratory processing constraints. While it is feasible to measure whole-body BAFs on smaller, lower-trophic-level species, the lower trophic status of the organism would mean that, for perfluorinated substances, the estimated overall BAFs may be underestimated due to their trophic status. Thus, from a toxicological perspective, BCFs, BAFs and BMFs based on concentrations in individual organs, such as the liver, may be more relevant when predicting potential for direct organ-specific toxicity (i.e.,

liver toxicity). BCFs and particularly BMFs based on concentrations in whole organisms may provide a useful measure of overall potential for food chain transfer. Conder et al. (2008) suggested that BMF values are relevant for bioaccumulation potential in higher-trophic-level biota, as extrapolating BCF/BAF data for fish and invertebrates is difficult due to the biological differences between the higher and lower trophic levels.

#### *Bioaccumulation/Bioconcentration/Biomagnification Studies*

Bioaccumulation of C9 to C12 PFCAs from laboratory-spiked and contaminated field sediments was assessed using the freshwater oligochaete, *Lumbriculus variegatus*, a deposit feeder that can serve as an entry point for sediment-bound contaminants into food webs (Higgins et al. 2007). Semi-static batch experiments were conducted over 56 days. It should be noted that the sediment concentrations in the laboratory-spiked systems decreased slightly over time, whereas the sediment concentrations for nearly all the long-chain PFCAs in the contaminated field sediment remained essentially constant. The biota-sediment accumulation factors (BSAF), wet weight (ww), were as follows: C9 (0.64–1.60), C10 (0.59–1.02), C11 (0.42–0.62) and C12 (0.42–0.55). The authors suggest that the long-chain PFCAs may not have reached steady-state.

Martin et al. (2003a,b) used juvenile rainbow trout (*Oncorhynchus mykiss*), dietary exposure and a flow-through aqueous exposure using C9-C14 PFCAs. BCFs for rainbow trout increased as perfluoroalkyl chain lengths increased, with reported whole-body values from 450 L/kg for C10 PFCA to 23 000 L/kg for C14 PFCA (Martin et al. 2003b). No experimental data were available for C9 PFCA because it was used as an internal standard in these studies. For the juvenile rainbow trout dietary exposure study, Martin et al. (2003a,b) also report “dietary BAFs.” However, based on an examination of the accumulation equation and given that exposure was via the diet rather than water, it can be concluded that the measurements were actually equivalent to BMFs. The lab-measured BMFs for rainbow trout showed an increasing trend approaching 1 for C14 PFCA. The authors speculated that the lack of observed biomagnification (i.e., no BMFs exceeded 1) 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, than would be observed for larger species or size classes. This more rapid chemical elimination would reduce the BMF.

Martin et al. (2004b) also conducted a field study of the biomagnification of C9 to C14 PFCAs in the pelagic food web of Lake Ontario and determined lake trout (*Salvelinus namaycush*) BMFs for a variety of prey species (alewife – *Alosa pseudoharengus*; rainbow smelt – *Osmerus mordax*; and slimy sculpin – *Cottus cognatus*), as well as overall TMFs for the pelagic food web. Lake trout / alewife BMFs exceeded 1 for all long-chain PFCAs measured in the study (C9-C14); lake trout / smelt BMFs ranged from 0.6 (C9) to 2.2 (C14); and lake trout/sculpin BMFs ranged from 0.1 (C9) to 0.4 (C13). The authors report that alewife comprise 90% of lake trout prey, suggesting that lake trout/alewife results provide the best BMF estimates. Given that the other prey species comprised a much lower proportion of the diet of lake trout (7% for smelt and 2% for sculpin), the lake trout BMF estimates for these prey are likely to be less reliable. In particular, the authors cautioned that the low dietary proportion of sculpin for lake trout and the position of sculpin in the benthic rather than pelagic food web could explain the low BMFs observed for lake trout/sculpin. To address differences in dietary composition,

the authors also calculated lake trout/prey BMFs that weighted the concentration in each prey species with the proportion of each prey species in the diet. The resulting BMFs were above 1 for all of the C9–C14 PFCA, indicating biomagnification from consumed prey for the lake trout of Lake Ontario.

Trophic magnification factors (TMFs) measured in the pelagic aquatic food web of Lake Ontario by Martin et al. (2004b) suggest trophic magnification for some long-chain PFCA over the whole food web. Concentrations of C10, C11 and C13 PFCA increased significantly within the pelagic food web, resulting in TMFs greater than 1 for C10, C11 and C13. Trophic magnification was greatest for C11 PFCA (4.7) and decreased for longer and shorter PFCA alike. TMFs equal to 1 for C9, C12 and C14 PFCA indicated either no biomagnification or that the results were too variable to detect a statistically significant trend in concentration with trophic status for this food web.

Gulkowska et al. (2005) analyzed avian and fish blood samples and water samples from the Gulf of Gdansk for C9 PFCA. Sixty-five blood samples were collected during winter 2002–2003 from five species of waterfowl—razorbill (*Alca torda*), red-throated loon (*Gavia stellata*), black scoter (*Melanitta nigra*), long-tailed duck (*Clangula hyemalis*) and common eider (*Somateria molissima*)—while 18 blood samples were collected from cod (*Gadus morhua*). The mean concentration of C9 PFCA in avian blood samples ranged from 0.3 ng/ml in razorbill to 1.1 ng/ml in red-throated loon. The mean concentration of C9 PFCA in cod blood samples was 1.2 ng/ml. The authors reported a blood:water “BCF” for C9 PFCA in cod of approximately 3000. However, given that this measurement was field-based, where the cod would be exposed via water and the diet, the reported BCF is analogous to a BAF. The bird/cod BMFs ranged from 0.25 to 0.92, but the authors cautioned that all bird species sampled were migratory and it is unclear whether they included a large proportion of cod in their diet. There is also uncertainty as to whether the blood-based BMFs would be similar to whole-body BMFs.

Haukås et al. (2007) determined C9 PFCA BMFs for a Barents Sea (east of Svalbard) ice edge food web comprising of the ice-associated amphipod (*Gammarus wilkitzkii*), polar cod (*Boreogadus saida*), black guillemot (*Cepphus grylle*), and glaucous gull (*Larus hyperboreus*). BMFs were not calculated for the amphipod as C9 PFCA was not quantifiable. However, the BMF for the black guillemot/polar cod was calculated to be 8.76; the BMF for the glaucous gull/polar cod was 11.6; and the BMF for the glaucous gull/black guillemot was 9.34.

Tomy et al. (2009c) determined TMFs for C9 – C11 PFCA for a marine food web in the western Canadian Arctic (Hendrickson Island and Holman Island) comprising of the Beaufort Sea beluga whale (*Delphinapterus leucas*), ringed seal (*Phoca hispida*), Arctic cod (*Boreogadus saida*), Pacific herring (*Clupea pallasii*), Arctic cisco (*Coregonus autumnalis*), a pelagic amphipod (*Themisto libellula*), and a Arctic copepod (*Calanus hyperboreus*). TMFs ranged from 0.1 (C10, Arctic cod/*Themisto libellula*) to 353 (C11, beluga whale/Pacific herring).

Houde et al. (2006a) conducted field studies of the bottlenose dolphin food web in Charleston, South Carolina, and Sarasota Bay, Florida. C9 to C12 PFCA were measured in seawater, marine sediment, zooplankton (Sarasota Bay only; species not identified) and a variety of fish species: Atlantic croaker (*Micropogonias undulatus*), pinfish (*Lagodon rhomboids*), red drum (*Sciaenops ocellatus*), spotfish (*Leiostomus xanthurus*), spotted seatrout (*Cynoscion nebulosus*), striped mullet (*Mugil cephalus*) and bottlenose dolphin (*Tursiops truncatus*). It should be noted that for this particular study, samples were collected over a series of years, and prey and predator species may have been collected in different years/seasons, which may impact the BMFs and TMFs reported. Fish were captured from 2002 to 2004. Zooplankton samples were collected in 2004. Dolphin plasma, skin and teeth were collected from both locations in summer 2004. Recently deceased bottlenose dolphins from 2002 and 2003 were also used. Dolphin samples included plasma from a catch-and-release study and multiple whole-body samples from recently deceased or stranded dolphins, facilitating an examination of trophic magnification in terms of both dolphin plasma and whole body. BMFs were reported for whole-body concentrations only. For Charleston, marine fish BMFs (sea trout/pinfish) ranged from 0.1 (C12) to 3.7 (C10), with no clear trend with chain length. Dolphin BMFs were reported for whole-body samples and a wide range of prey fish species. BMFs exceeded 1 for all dolphin/prey combinations for C9, C10 and C11 PFCA. For C12 PFCA, the dolphin/prey BMFs ranged from 0.1 to 1.8. In Sarasota Bay, BMFs were reported for C12 PFCA only and ranged from 0.2 to 156 for fish/prey (multiple species) and measured 0.1 for dolphin/striped mullet. TMFs for the dolphin food web were only reported for Charleston. For C9–11 PFCA, both whole-body- and plasma-based TMFs exceeded 1, while for C12 PFCA neither the plasma nor the whole-body TMF exceeded 1. Dolphin BMFs exceeding 1 for C9–C11 PFCA suggest that these PFCA are biomagnifying from fish to dolphins in this food web. For C12 PFCA, the range in BMFs makes it difficult to draw conclusions regarding biomagnification without knowledge of the feeding preferences of bottlenose dolphins. The evidence for fish-to-fish biomagnification is mixed; however, biomagnification might be expected to be lower in fish than in dolphins given that PFCA may be eliminated more rapidly to water than to air. The TMF results integrate the findings for the whole food web. Despite the expected lower biomagnification potential in fish, TMFs for C9–C11 PFCA exceeded 1 for the dolphin food web, indicating that trophic magnification is occurring.

van den Heuvel-Greve et al. (2009) determined C11 PFCA BMFs in the harbour seal (*Phoca vitulina*) food web in the Westerschelde, an estuary in the southwest of the Netherlands. The BMFs ranged from 1.9 (herring:zooplankton) to 53 (harbour seal:herring) with a TMF of 1.3.

Katz et al. (2009) showed that C9-C12 PFCA were bioaccumulating in the vegetation (plants and lichens)-barren ground caribou (*Rangifer tarandus groenlandicus*)-wolf (*Canis lupus*) terrestrial food chain in northern Yukon, Canada. Lichens reflect direct atmospheric input of long-chain PFCA as they lack roots and receive their nutrients from the atmosphere. Lichen is large part of the caribou diet. Caribou are the staple prey of wolves – the top predator in the ecosystem. C9 PFCA was dominant in wolf liver at 6.8 ng/g ww followed by C10 PFCA at 3.1 ng/g ww and C11 PFCA at 3.4 ng/g ww. C12

and C13 PFCAs were also measured with average concentrations < 0.6 ng/g ww. BAFs or BMFs were not calculated. However, the results of the carbon and nitrogen stable isotope analyses of the vegetation, caribou muscle and wolf muscle showed that the caribou were primarily feeding on the lichen and that the wolves were feeding primarily on the caribou.

Powley et al. (2008) determined C10-C12 PFCA bioaccumulation factors for a western Canadian Arctic (Banks Island on the eastern edge of the Beaufort Sea in the Northwest Territories) food web comprising of three different species of zooplankton (*Calanus hyperboreus*, *Themisto libellula*, and *Chaetognatha*), Arctic cod (*Boreogadus saida*), ringed seal (*Phoca hispida*), and bearded seal (*Erignathus barbatus*). C11 PFCA had the highest concentration at 10.8 ng/g. Bioaccumulation factors ranged from 0.3 to 3.1.

Multiple investigations (Martin et al. 2004a; Kannan et al. 2005; Smithwick et al. 2005a) have also found concentrations of C9 (108–230 ng/g-ww), C10 (35–76 ng/kg-ww), C11 (56–78 ng/g-ww), C12 (4.7–8.2 ng/kg-ww), C13 (7.5–14 ng/g-ww), and C14 (< 0.5–1.1 ng/kg-ww) in polar bear livers located in the Canadian Arctic and sub-Arctic regions. Butt et al. (2008) calculated regionally-based for ringed seal liver –polar bear liver BMFs for C9 to C15 PFCAs by grouping 11 populations of ringed seals to correspondingly, similarly located polar bear populations. BMF geometric means ranged from 2.2 (C13 PFCA) to 56 (C9 PFCA).

There are no bioaccumulation studies for long-chain PFCAs greater than C14. However, there is the potential that long-chain PFCAs greater than C14 could bioaccumulate or biomagnify in marine and/or terrestrial species. It has been suggested the carbon-carbon conformation changes as the chain length increases, with longer chains becoming helical (Wang and Ober 1999), resulting in smaller cross-sectional diameter molecules with the ability to accumulate in organisms. C14 and C15 have been found in fish, invertebrates, dolphin and polar bears (e.g., Martin et al. 2004b; Smithwick et al. 2005a, 2005b, 2006; Houde et al. 2005). Conder et al. (2008) highlighted, based on available research on the bioaccumulation of perfluorinated acids, five key points:

- A) Bioconcentration and bioaccumulation of perfluorinated acids are directly related to the length of each compound's fluorinated carbon chain
- B) Perfluorosulfonic acids are more bioaccumulative than PFCAs of the same fluorinated carbon chain length.
- C) PFCAs with seven fluorinated carbons or less (perfluorooctanoate (PFO) and shorter PFCAs) are not considered bioaccumulative according to the range of international promulgated bioaccumulation regulatory criteria of 1000–5000 L/kg.
- D) PFCAs with seven fluorinated carbons or less have low biomagnification potential in food webs.
- E) More research is necessary to fully characterize the bioaccumulation potential of PFCAs with longer fluorinated carbon chains (> 7 fluorinated carbons), as PFCAs with longer fluorinated carbon chains may exhibit partitioning behavior similar to or greater than PFOS.



**Table 3. Summary of Bioaccumulation Data for Long-Chain (C9-C20) PFCAs**  
 (Italics and bold indicate values that exceed the persistence and bioaccumulation criteria, and shaded areas indicate values for BMF or TMF > 1)

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
<b>C9 PFCAs</b>					
<i>L. variegatus</i>	Lab/field	California, downstream WWTP	BSAF ww	0.64– 1.60	Higgins et al. 2007
Juvenile rainbow trout (carcass)	Lab	NA	BCF	39 L/kg	Martin et al. 2003b
Juvenile rainbow trout (carcass)	Lab	NA	BMF <sup>1</sup>	0.089	Martin et al. 2003a
Lake trout / alewife (whole)	Field	Lake Ontario	BMF	5.3	Martin et al. 2004b
Lake trout / smelt (whole)	Field	Lake Ontario	BMF	0.6	Martin et al. 2004b
Lake trout / sculpin (whole)	Field	Lake Ontario	BMF	0.1	Martin et al. 2004b
Lake trout / prey (weighted average)	Field	Lake Ontario	BMF	2.3	Martin et al. 2004b
Seatrout/pinfish (whole)	Field	Charleston, SC	BMF	1.5	Houde et al. 2006a
Dolphin/striped mullet (whole)	Field	Charleston, SC	BMF	5	Houde et al. 2006a
Dolphin/pinfish (whole)	Field	Charleston, SC	BMF	3.2	Houde et al. 2006a
Dolphin/red drum (whole)	Field	Charleston, SC	BMF	1.4	Houde et al. 2006a
Dolphin/Atlantic croaker (whole)	Field	Charleston, SC	BMF	24	Houde et al. 2006a
Dolphin/spotfish (whole)	Field	Charleston, SC	BMF	4.6	Houde et al. 2006a
Dolphin/seatrout (whole)	Field	Charleston, SC	BMF	2.1	Houde et al. 2006a
Pelagic food web <sup>3</sup>	Field	Lake Ontario	TMF	1 <sup>2</sup>	Martin et al. 2004b
Bottlenose dolphin food web (dolphin plasma) <sup>4</sup>	Field	Charleston, SC	TMF	4.7	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) <sup>4</sup>	Field	Charleston, SC	TMF	2.4	Houde et al. 2006a
Cod (blood)	Field	Gulf of Gdansk, Poland	BAF <sup>5</sup>	3000	Gulkowska et al. 2005
Common scoter / cod (blood)	Field	Gulf of Gdansk, Poland	BMF	0.83	Gulkowska et al. 2005

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Eider duck (blood)	Field	Gulf of Gdansk, Poland	BMF	0.33	Gulkowska et al. 2005
Red-throated loon (blood)	Field	Gulf of Gdansk, Poland	BMF	0.92	Gulkowska et al. 2005
Razorbill (blood)	Field	Gulf of Gdansk, Poland	BMF	0.25	Gulkowska et al. 2005
Long-tailed duck (blood)	Field	Gulf of Gdansk, Poland	BMF	0.50	Gulkowska et al. 2005
Black guillemot / polar cod	Field	Barents Sea ice edge	BMF	8.76	Haukås et al. 2007
Glaucous gull / polar cod	Field	Barents Sea ice edge	BMF	11.6	Haukås et al. 2007
Glaucous gull / polar cod	Field	Barents Sea ice edge	BMF	9.34	Haukås et al. 2007
Ringed seal/polar bear (liver)	Field	Canadian Arctic	BMF	56	Butt et al.2008
Ringed seal/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	1.2	Tomy et al. 2009c
Beluga/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	12.9	Tomy et al. 2009c
Beluga/ Pacific herring (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	5.8	Tomy et al. 2009c
Beluga/ Arctic cisco (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	2.9	Tomy et al. 2009c
Cod (liver)/ <i>Calanus hyperboreus</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.7	Tomy et al. 2009c
Cod (liver)/ <i>Themisto libellula</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.3	Tomy et al. 2009c
<b>C10 PFCA</b>					
<i>L. variegatus</i>	Lab/field	California, downstream WWTP	BSAF ww	0.59– 1.02	Higgins et al. 2007
Juvenile rainbow trout (carcass)	Lab	NA	BCF	450	Martin et al.

<b>Species, predator/prey, food web (tissue in brackets)</b>	<b>Study type</b>	<b>Location</b>	<b>Endpoint</b>	<b>Result</b>	<b>Reference</b>
				L/kg	2003b
Juvenile rainbow trout (blood)	Lab	NA	BCF	2700 L/kg	Martin et al. 2003b
Juvenile rainbow trout (liver)	Lab	NA	BCF	1100 L/kg	Martin et al. 2003b
Juvenile rainbow trout (carcass)	Lab	NA	BMF <sup>1</sup>	0.23	Martin et al. 2003a
Lake trout/water concentration from each Great Lake (whole)	Field	All of the Great Lakes	BAF	3.9	Furdui et al. 2007
Lake trout / alewife (whole)	Field	Lake Ontario	BMF	4.4	Martin et al. 2004b
Lake trout / smelt (whole)	Field	Lake Ontario	BMF	1	Martin et al. 2004b
Lake trout / sculpin (whole)	Field	Lake Ontario	BMF	0.2	Martin et al. 2004b
Zooplankton/arctic cod	Field	Western Canadian Arctic	BAF	0.5	Powley et al. 2008
Arctic cod/seal (blood)	Field	Western Canadian Arctic	BAF	1.4	Powley et al. 2008
Lake trout / prey (weighted average)	Field	Lake Ontario	BMF	2.7	Martin et al. 2004b
Seatrout/pinfish (whole)	Field	Charleston, SC	BMF	3.7	Houde et al. 2006a
Dolphin/striped mullet (whole)	Field	Charleston, SC	BMF	2.9	Houde et al. 2006a
Dolphin/pinfish (whole)	Field	Charleston, SC	BMF	8.8	Houde et al. 2006a
Dolphin/red drum (whole)	Field	Charleston, SC	BMF	2.4	Houde et al. 2006a
Dolphin/Atlantic croaker (whole)	Field	Charleston, SC	BMF	2.5	Houde et al. 2006a
Dolphin/spotfish (whole)	Field	Charleston, SC	BMF	2.8	Houde et al. 2006a
Dolphin/seatrout (whole)	Field	Charleston, SC	BMF	2.4	Houde et al. 2006a
Pelagic food web <sup>3</sup>	Field	Lake Ontario	TMF	3.7	Martin et al. 2004b
Bottlenose dolphin food web (dolphin plasma) <sup>4</sup>	Field	Charleston, SC	TMF	3.4	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) <sup>4</sup>	Field	Charleston, SC	TMF	22	Houde et al. 2006a
Ringed seal/polar bear (liver)	Field	Canadian Arctic	BMF	2.3	Butt et al.2008

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Ringed seal/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	2.5	Tomy et al. 2009b
Beluga/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	55	Tomy et al. 2009b
Beluga/ Pacific herring (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	87	Tomy et al. 2009b
Beluga/ Arctic cisco (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	44	Tomy et al. 2009b
Cod (liver)/ <i>Calanus hyperboreus</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.4	Tomy et al. 2009b
Cod (liver)/ <i>Themisto libellula</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.1	Tomy et al. 2009b
<b>C11 PFCA</b>					
<i>L. variegatus</i>	Lab/field	California, downstream WWTP	BSAF ww	0.42– 0.62	Higgins et al. 2007
Juvenile rainbow trout (carcass)	Lab	NA	BCF	2700 L/kg	Martin et al. 2003b
<b>Juvenile rainbow trout (blood)</b>	<b>Lab</b>	<b>NA</b>	<b>BCF</b>	<b>11 000 L/kg</b>	<b>Martin et al. 2003b</b>
Juvenile rainbow trout (liver)	Lab	NA	BCF	4900 L/kg	Martin et al. 2003b
Juvenile rainbow trout (carcass)	Lab	NA	BMF <sup>1</sup>	0.28	Martin et al. 2003a
Lake trout / alewife (whole)	Field	Lake Ontario	BMF	6.4	Martin et al. 2004b
Lake trout / smelt (whole)	Field	Lake Ontario	BMF	1.2	Martin et al. 2004b
Lake trout / sculpin (whole)	Field	Lake Ontario	BMF	0.2	Martin et al. 2004b
Lake trout / prey (weighted average)	Field	Lake Ontario	BMF	3.4	Martin et al. 2004b
Arctic cod/seal (blood)	Field	Western Canadian Arctic	BAF	3.1	Powley et al. 2008
Seatrout/pinfish (whole)	Field	Charleston, SC	BMF	0.9	Houde et al.

<b>Species, predator/prey, food web (tissue in brackets)</b>	<b>Study type</b>	<b>Location</b>	<b>Endpoint</b>	<b>Result</b>	<b>Reference</b>
					2006a
Dolphin/striped mullet (whole)	Field	Charleston, SC	BMF	1.9	Houde et al. 2006a
Dolphin/pinfish (whole)	Field	Charleston, SC	BMF	2.4	Houde et al. 2006a
Dolphin/red drum (whole)	Field	Charleston, SC	BMF	3.2	Houde et al. 2006a
Dolphin/Atlantic croaker (whole)	Field	Charleston, SC	BMF	2.1	Houde et al. 2006a
Dolphin/spotfish (whole)	Field	Charleston, SC	BMF	3.9	Houde et al. 2006a
Dolphin/seatrout (whole)	Field	Charleston, SC	BMF	2.5	Houde et al. 2006a
Pelagic food web <sup>3</sup>	Field	Lake Ontario	TMF	4.7	Martin et al., 2004b
Bottlenose dolphin food web (dolphin plasma) <sup>4</sup>	Field	Charleston, SC	TMF	3	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) <sup>4</sup>	Field	Charleston, SC	TMF	2.3	Houde et al. 2006a
Ringed seal/polar bear (liver)	Field	Canadian Arctic	BMF	11	Butt et al.2008
Herring/zooplankton	Field	The Westerschelde, Netherlands	BMF	1.9	van den Heuvel- Greve et al. 2009
Sea bass/Herring	Field	The Westerschelde, Netherlands	BMF	3.2	van den Heuvel- Greve et al. 2009
Harbour seal/herring	Field	The Westerschelde, Netherlands	BMF	53	van den Heuvel- Greve et al. 2009
Harbour seal/sea bass	Field	The Westerschelde, Netherlands	BMF	17	van den Heuvel- Greve et al. 2009
Flounder/peppery furrow shell	Field	The Westerschelde, Netherlands	BMF	10	van den Heuvel- Greve et al. 2009
Flounder/lugworm	Field	The Westerschelde, Netherlands	BMF	25	van den Heuvel- Greve et al. 2009
Harbour seal/flounder	Field	The Westerschelde, Netherlands	BMF	9	van den Heuvel- Greve et al. 2009
Ringed seal/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	6.6	Tomy et al. 2009b
Beluga/Arctic cod (liver)	Field	Western	BMF	229	Tomy et al.

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
		Canadian Arctic	(trophic level adjusted)		2009b
Beluga/ Pacific herring (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	353	Tomy et al. 2009b
Beluga/ Arctic cisco (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	181	Tomy et al. 2009b
Cod (liver)/ <i>Calanus hyperboreus</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.3	Tomy et al. 2009b
Cod (liver)/ <i>Themisto libellula</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.3	Tomy et al. 2009b
<b>C12 PFCA</b>					
<i>L. variegatus</i>	Lab/field	California, downstream WWTP	BSAF ww	0.42 - 0.55	Higgins et al. 2007
<i>Juvenile rainbow trout (carcass)</i>	<b>Lab</b>	<b>NA</b>	<b>BCF</b>	<b>18 000 L/kg</b>	<b>Martin et al. 2003b</b>
<i>Juvenile rainbow trout (blood)</i>	<b>Lab</b>	<b>NA</b>	<b>BCF</b>	<b>40 000 L/kg</b>	<b>Martin et al 2003b</b>
<i>Juvenile rainbow trout (liver)</i>	<b>Lab</b>	<b>NA</b>	<b>BCF</b>	<b>18 000 L/kg</b>	<b>Martin et al. 2003b</b>
Juvenile rainbow trout (carcass)	Lab	NA	BMF <sup>1</sup>	0.43	Martin et al 2003a
Lake trout / alewife (whole)	Field	Lake Ontario	BMF	1.9	Martin et al. 2004b
Lake trout / smelt (whole)	Field	Lake Ontario	BMF	1	Martin et al. 2004b
Lake trout / sculpin (whole)	Field	Lake Ontario	BMF	0.3	Martin et al. 2004b
Lake trout / prey (weighted average)	Field	Lake Ontario	BMF	1.6	Martin et al. 2004b
Seatrout/pinfish (whole)	Field	Charleston, SC	BMF	0.1	Houde et al. 2006a
Dolphin/striped mullet (whole)	Field	Charleston, SC	BMF	0.2	Houde et al. 2006a
Dolphin/pinfish (whole)	Field	Charleston, SC	BMF	0.1	Houde et al. 2006a
Dolphin/red drum (whole)	Field	Charleston, SC	BMF	0.4	Houde et al. 2006a

<b>Species, predator/prey, food web (tissue in brackets)</b>	<b>Study type</b>	<b>Location</b>	<b>Endpoint</b>	<b>Result</b>	<b>Reference</b>
Dolphin/Atlantic croaker (whole)	Field	Charleston, SC	BMF	1.8	Houde et al. 2006a
Dolphin/spotfish (whole)	Field	Charleston, SC	BMF	0.6	Houde et al. 2006a
Dolphin/seatrout (whole)	Field	Charleston, SC	BMF	0.6	Houde et al. 2006a
Striped mullet / zooplankton (whole)	Field	Sarasota Bay, FL	BMF	89	Houde et al. 2006a
Pigfish/zooplankton (whole)	Field	Sarasota Bay, FL	BMF	2.5	Houde et al. 2006a
Sheephead/zooplankton (whole)	Field	Sarasota Bay, FL	BMF	156	Houde et al. 2006a
Pinfish/zooplankton (whole)	Field	Sarasota Bay, FL	BMF	2.5	Houde et al. 2006a
Seatrout/zooplankton (whole)	Field	Sarasota Bay, FL	BMF	35	Houde et al. 2006a
Seatrout/striped mullet (whole)	Field	Sarasota Bay, FL	BMF	0.4	Houde et al. 2006a
Seatrout/pigfish (whole)	Field	Sarasota Bay, FL	BMF	14	Houde et al. 2006a
Seatrout/sheephead (whole)	Field	Sarasota Bay, FL	BMF	0.2	Houde et al. 2006a
Seatrout/pinfish (whole)	Field	Sarasota Bay, FL	BMF	14	Houde et al. 2006a
Dolphin/striped mullet (whole)	Field	Sarasota Bay, FL	BMF	0.1	Houde et al. 2006a
Pelagic food web <sup>3</sup>	Field	Lake Ontario	TMF	1 <sup>2</sup>	Martin et al. 2004b
Bottlenose dolphin food web (dolphin plasma) <sup>4</sup>	Field	Charleston, SC	TMF	0.7	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) <sup>4</sup>	Field	Charleston, SC	TMF	0.6	Houde et al. 2006a
Zooplankton/Arctic cod	Field	Western Canadian Arctic	BAF	0.3	Powley et al. 2008
Arctic cod / Seal (blood)	Field	Western Canadian Arctic	BAF	0.8	Powley et al. 2008
Ringed seal/polar bear (liver)	Field	Canadian Arctic	BMF	2.8	Butt et al.2008
Ringed seal/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.1	Tomy et al. 2009b

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Beluga/Arctic cod (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	3.2	Tomy et al. 2009b
Beluga/ Pacific herring (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	7.9	Tomy et al. 2009b
Beluga/ Arctic cisco (liver)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	4.0	Tomy et al. 2009b
Cod (liver)/ <i>Calanus hyperboreus</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	1.2	Tomy et al. 2009b
Cod (liver)/ <i>Themisto libellula</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	1.3	Tomy et al. 2009b
<b>C13 PFCA</b>					
Lake trout / alewife (whole)	Field	Lake Ontario	BMF	3.1	Martin et al. 2004b
Lake trout / smelt (whole)	Field	Lake Ontario	BMF	1.2	Martin et al. 2004b
Lake trout / sculpin (whole)	Field	Lake Ontario	BMF	0.4	Martin et al. 2004b
Lake trout / prey (weighted average)	Field	Lake Ontario	BMF	2.5	Martin et al. 2004b
Pelagic food web <sup>3</sup>	Field	Lake Ontario	TMF	2.5	Martin et al. 2004b
Ringed seal/polar bear (liver)	Field	Canadian Arctic	BMF	3.8	Butt et al.2008
<b>C14 PFCA</b>					
<i>Juvenile rainbow trout (carcass)</i>	<i>Lab</i>	<i>NA</i>	<i>BCF</i>	<i>23 000 L/kg</i>	<i>Martin et al. 2003b</i>
<i>Juvenile rainbow trout (blood)</i>	<i>Lab</i>	<i>NA</i>	<i>BCF</i>	<i>30 000 L/kg</i>	<i>Martin et al. 2003b</i>
<i>Juvenile rainbow trout (liver)</i>	<i>Lab</i>	<i>NA</i>	<i>BCF</i>	<i>30 000 L/kg</i>	<i>Martin et al. 2003b</i>
Juvenile rainbow trout (carcass)	Lab	NA	BMF <sup>1</sup>	1	Martin et al. 2003a
Lake trout / alewife (whole)	Field	Lake Ontario	BMF	> 2.6	Martin et al. 2004b
Lake trout / smelt (whole)	Field	Lake Ontario	BMF	2.2	Martin et al. 2004b



Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Lake trout / sculpin (whole)	Field	Lake Ontario	BMF	0.3	Martin et al. 2004b
Lake trout / prey (weighted average)	Field	Lake Ontario	BMF	> 2.3	Martin et al. 2004b
Ringed seal/polar bear (liver)	Field	Canadian Arctic	BMF	5.5	Butt et al. 2008
Pelagic food web <sup>3</sup>	Field	Lake Ontario	TMF	1 <sup>2</sup>	Martin et al. 2004b

<sup>1</sup>Martin et al. (2003a) report their result as a “BAF;” however, through examination of their accumulation equation and given that exposure was via the diet rather than water, it can be concluded that the measurements were actually “dietary BAFs” (i.e., the concentration ratio of fish to diet), analogous to BMFs.

<sup>2</sup>Slope of PFCA concentration vs.  $\delta^{15}\text{N}$  concentration not significantly different from 1.

<sup>3</sup>Organisms included mysid shrimp, alewife, rainbow smelt and lake trout.

<sup>4</sup>Organisms included striped mullet, pinfish, red drum, Atlantic croaker, spotfish, spotted seatrout and bottlenose dolphin.

<sup>5</sup>The authors report this value as a BCF. However, given that it was determined in the field where the cod would be exposed via water and diet, it is analogous to a BAF.

## Potential to Cause Ecological Harm

### Ecological Exposure Assessment

#### Atmosphere

Loewen et al. (2008) studied atmospheric concentrations and lake water concentrations of FTOHs over an altitudinal transect in western Canada. Lake water samples were collected at Cedar Lake (a small lake near Golden, British Columbia), at Bow Lake in Banff National Park (Banff, Alberta) and at another unnamed small lake in Banff National Park (Banff, Alberta). Passive air samplers were deployed on altitudinal transects (800–2740 above sea level) from Golden, British Columbia, to Banff National Park. Loewen et al. (2008) noted that the amount of 8:2 and 10:2 FTOHs (<2.0 ng/sampler) increased with increasing altitude. C10 PFCA lake water concentrations were below 0.2 ng/L.

Stock et al. (2007) took atmospheric particle/gas phase samples on Cornwallis Island, Nunavut where mean values of total concentrations of FTOHs ranged from 2.8 (10:2 FTOH) and 14  $\text{pg}/\text{m}^3$  (8:2 FTOH). The 8:2 and 10:2 FTUCAs were measured at mean concentrations of 0.06–0.07  $\text{pg}/\text{m}^3$ . C9 and C10 PFCAs were measured at mean concentrations of 0.4  $\text{pg}/\text{m}^3$  while C11, C13 and C14 PFCAs were measured at mean concentrations ranging from 0.02 to 0.06  $\text{pg}/\text{m}^3$ . Shoeib et al. (2006) took twenty high-volume air samples during a crossing of the North Atlantic and Canadian Archipelago in July 2005 (Gothenburg, Sweden to Barrow, Alaska via the North Atlantic and Canadian Archipelago). The highest concentrations (sum of gas- and particle-phases) of FTOHs were for 8:2 FTOH at 5.8–26  $\text{pg}/\text{m}^3$ , followed by 10:2 FTOH at 1.9–17  $\text{pg}/\text{m}^3$  and 6:2 FTOH at below detection to 6.0  $\text{pg}/\text{m}^3$ . For comparison purposes, Shoeib et al. (2006) also collected air samples at a semi-urban site in Toronto in March 2006 where the mean 8:2 FTOH concentration in Toronto was 41  $\text{pg}/\text{m}^3$ . Studies from Toronto measured

levels of 4:2, 6:2, 8:2 and 10:2 FTOHs from non-detect (ND) to 650 pg/m<sup>3</sup> over a two-year period, with 8:2 FTOH dominating in the first half of the period and 10:2 FTOH dominating in the later half (Stock et al. 2005). Dreyer et al. (2009) conducted high volume air sampling in the Atlantic Ocean, the Southern Ocean and the Baltic Sea. C9 PFCA, C10 PFCA, C11 PFCA, C12 PFCA and C13 PFCA were all detected in the particle fraction (< 1 pg/m<sup>3</sup>). 6:2 FTOH and 8:2 FTOH were dominant in the gas-phase fraction. The concentrations of 8:2 FTOH were between 1.8 and 130 pg/m<sup>3</sup>. The sum of all the FTOHs (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH and 12:2 FTOH) ranged between 0.3–47 pg/m<sup>3</sup>.

As previously discussed, FTOHs may degrade to long-chain (C9-C20) PFCAs; therefore, levels of FTOHs in the atmosphere may contribute to levels of long-chain (C9-C20) PFCAs in the environment, including the Canadian Arctic. Atmospheric degradation of FTOH is expected to produce relatively equal quantities of adjacent odd-and even-chained perfluorinated PFCAs (Ellis et al. 2004b), whereas aerobic biodegradation of FTOH tends to yield predominantly even-chain-length PFCAs (Dinglasan et al. 2004).

#### *Water*

Long-chain (C9-C20) PFCAs have been measured in precipitation from 1998 to 1999 in Canadian remote areas in Saturna Island (British Columbia), Algoma (Ontario) and Kejimikujik (Nova Scotia) (Scott et al. 2006b). Scott et al. (2006b) measured C9 PFCA concentrations ranging from < 1 to 7.6 ng/L, with Algoma, Ontario, having the highest concentration, at 7.6 ng/L. In urban areas (Egbert and north Toronto, Ontario), C9 PFCA concentrations ranged from 0.4 to 9.7 ng/L. C9 to C12 PFCAs were detected in urban areas only, at concentrations ranging from < 0.07 to 5.2 ng/L. The authors also detected 8:2 and 10:2 FTCAs and FTUCAs at two urban sites in Canada (Egbert and north Toronto, Ontario) at concentrations ranging from < 0.07 to 8.6 ng/L. Loewen et al. (2005) also measured C10 and C12 FTCAs and FTUCAs in rainwater samples in Winnipeg, Manitoba.

Simcik and Dorweiler (2005) measured levels of long-chain (C9-C20) PFCAs in remote areas (Tettegouche and Nipisiquit) located along the north shore of Lake Superior and Voyageurs National Park along the U.S.-Canada border (Loiten and Little Trout lakes). These four remote lakes are all hike-in lakes (no roads) and have no surface inflow. Only C9 PFCA was found at a concentration greater than 1 ng/L, in Nipisiquit. Scott et al. (2006a, 2003) measured C9 PFCAs in the Great Lakes (lakes Ontario, Erie, Superior and Huron) at concentrations ranging from <0.5 to 0.11 ng/L. Three connected urban lakes in Minneapolis, Minnesota (Lake of the Isles, Lake Calhoun and Lake Harriet), and the Minnesota River, a major tributary to the Mississippi River, were studied (Simcik and Dorweiler, 2005). C9 PFCA was found in Lake Calhoun (< 1 ng/L) and Minnesota River (< 10 ng/L). C10 PFCA was found in Lake Calhoun (< 1 ng/L).

Stock et al. (2007) measured concentrations of C9, C10, C11 and C12 PFCAs in lake water samples from three remote Arctic Lakes (Resolute, Char, and Amituk) on Cornwallis Island, Nunavut in 2003. C9 PFCA mean concentrations ranged from 0.3 – 4.1 ng/L. C10 PFCA mean concentrations ranged from 1.1 – 19 ng/L and C11 PFCA

concentrations ranged from 0.3 – 4.9 ng/L. C12 PFCA mean concentrations ranged from 0.2 – 0.8 ng/L. 8:2 FTUCA and 10:2 FTUCA were measured in all three lakes at concentrations ranging from 1.1 to 6.4 ng/L.

Ahrens et al. (2009) analyzed surface water samples from the Atlantic Ocean along the longitudinal gradient from Las Palmas (Spain) to St. John's (Canada) and along the latitudinal gradient from the Bay of Biscay to the South Atlantic Ocean, in 2007. No long-chain (C9-C20) PFCAs were detected in the particulate phase and in the two deep water samples at 200 m and 3800 m. C9 PFCA was detected in concentrations ranging from < 0.0051 to 0.107 ng/L, and C12 PFCA was not detected generally above 0.0014 ng/L. Del Vento et al. (2009) measured up to 0.13 ng/L C9 PFCA in seawater in eastern part of the Beaufort Sea near Banks Island. Del Vento et al. (2009) also measured snow concentrations in the Amundsen Gulf for C9 – C11 PFCAs ranging from 0.035 – 1.3 ng/L. C9 PFCA was measured in Asian seawaters at ng/L levels, with values reported three times higher and with higher variability in coastal regions than in open oceans (So et al. 2004; Yamashita et al. 2004, 2005).

### *Sediments*

Stock et al. (2007) measured concentrations of C9, C10, C11, and C12 PFCAs in sediment core samples taken from three remote Arctic lakes—Resolute, Char, and Amituk Lakes on Cornwallis Island, Nunavut in 2003. Concentrations of the PFCAs decreased with depth and sediment age. C9 –C12 PFCAs were present in Amituk Lake. C9 -C11 PFCAs were measured in Char Lake at 0.6 – 3.3 ng/g. In Resolute Lake, C9 PFCA was measured up to 3.2 ng/g while C10, C11 and C12 PFCAs were at the limit of detection of 0.5 ng/g. 10:2 FTUCA was measured in Amituk and Char Lakes at concentrations ranging from 0.5 to 2 ng/g.

### *Biota*

Levels of long-chain (C9–C20) PFCAs have been reported in a number of freshwater and marine animals in North America and Greenland, including polar bear (De Silva and Mabury 2004; Kannan et al. 2005; Smithwick et al. 2005a,b; Smithwick et al. 2006; Dietz et al. 2008), ringed seal (Bossi et al. 2005; Butt et al. 2008), bottlenose dolphins (Houde et al. 2005), animals from a Lake Ontario food web (Martin et al. 2004b), lake trout (Furdui et al. 2007, 2008), northern fulmar and thick-billed murre (Butt et al. 2007a).

Martin et al. (2004b) measured C9–C15 in whole homogenate samples from a variety of fish from Lake Ontario. Concentrations ranged from < 0.5 ng/g-ww (detection limit of 0.5 ng/g) to 39 µg/kg-ww (sculpin; C11). In an accidental spill situation at Etobicoke Creek (Ontario) of aqueous fire-fighting foam, Moody et al. (2002) showed the presence of C10, C11, and C13 PFCAs in the livers of common shiner fish (*Notropus cornutus*). It should be noted that the level of biota concentrations may not necessarily be all associated with the spill. Concentrations ranged from 8.8 to 390 ng/g-ww, with the highest concentration observed for the C10 PFCA.

Martin et al. (2004a) have shown the presence of C9 through C15 PFCAs in the liver of a variety of species including seals, foxes, fish, polar bears and birds sampled between

1993 and 2002 in the Canadian Arctic. Liver concentrations in all species ranged from non-detect to 180 ng/g-ww (detection limit = 0.5 ng/g). Liver concentrations were greatest for polar bears (*Ursus maritimus*; maximum 180 ng/g-ww, C9) and decreased as the chain length increased. Stern (2009) measured C9 – C11 PFCA concentrations in burbot liver from the Mackenzie River at Fort Good Hope, Northwest Territories. Thirty-seven burbot were sampled with mean concentrations ranging from 0.89 – 7.97 ng/g-ww for C9, 1.2 – 36.85 ng/g-ww for C10, and 7 – 2.25 ng/g-ww for C11. Butt et al. (2007a) noted a predominance of C11 to C15 PFCA concentrations in Arctic seabirds, although the PFCA detected in most wildlife, e.g., ringed seals, is often C8 to C11 PFCA. Powley et al. (2008) detected C9 to C12 PFCA concentrations in a variety of organisms from Banks Island (eastern edge of the Beaufort Sea in the Northwest Territories). Concentrations in zooplankton (*Calanus hyperboreus*, *Themisto libellula*, Chaetognatha) ranged from non-detect to 1.1 ng/g-ww. In Arctic cod (*Boreogadus saida*), concentrations ranged from non-detect to 0.6 ng/g-ww. In ringed seal (*Phoca hispida*), concentrations in blubber ranged from non-detect to 0.2 ng/g-ww, concentrations in blood ranged from 1 to 2.5 ng/g, and concentrations in liver ranged from 1 to 6.9 ng/g-ww. Concentrations were not detected in bearded seal (*Erignathus barbatus*) blubber, blood or liver. It should be noted that the sample sizes were small, ranging from 1 to 5. Tomy et al. (2009b) measured C8-C12 PFCA concentrations in the liver of various top trophic level mammals in an eastern Arctic marine food web from Cumberland Sound, Nunavut in 2007. Liver-based concentrations in beluga ranged from 38.07 – 47.6 ng/g-ww; narwhal liver-based concentrations ranged from 11.71 – 50.78 ng/g-ww; harp seal liver-based concentrations ranged from 2.93- 12.78 ng/g-ww; ringed seal liver-based concentrations ranged from 2.18 – 23.4 ng/g-ww; and Greenland shark liver-based concentrations ranged from 17.76 - 110.79 ng/g-ww. In general, C11 PFCA concentrations were dominant except in the Greenland shark where C12 PFCA dominated.

Houde et al (2006c) assessed the concentrations of C9 to C12 PFCA, and C14 PFCA in plasma, milk and urine of bottlenose dolphins residing in and around Sarasota Bay, Florida, USA. During the past 35 years, the year-round resident population (approx. 160 animals) has been the subject of a long-term monitoring project. Houde et al (2006c) investigated the relationships between PFCA concentrations and known biological parameters (age, gender, reproductive history and morphometrics). The dominant PFCA detected was C11. C9 PFCA concentrations in plasma ranged from 11.7 to 24.5 ng/g-ww, the concentration in milk was 2.2 ng/g-ww, and the concentration in urine was below detection limit. C10 PFCA concentrations in plasma ranged from 15.8 to 35.7 ng/g-ww, the concentration in milk was 2.4 ng/g, and the concentration in urine was below detection limit. C11 PFCA plasma concentrations ranged from 31.4 to 64.7 ng/g-ww, 3 ng/g ww in milk, and 0.06 ng/g in urine. C12 PFCA concentrations in plasma ranged from 2.7 to 8.2 ng/g-ww, the concentration in milk was 2.9 ng/g, and the concentration in urine was below detection limit. C14 PFCA plasma concentrations ranged from 1.1 to 3.4 ng/g-ww, and no analyses were made for milk or urine. No significant differences were found between dolphins inhabiting the northern end of Sarasota Bay and those frequenting the southern part. Sarasota Bay is a semi-enclosed environment surrounded by a highly residential urban area, which may explain the relatively high concentrations detected in resident dolphins. Temporal trend analyses showed that PFC concentrations in

plasma were not significantly greater in dolphins captured in the summer of 2003 and winter 2004 compared to other sampling seasons. Results showed significant negative correlations between C9–C12 PFCA and age of the dolphins. No significant relations were found for gender. Concentrations were found to decrease with age for both male and female dolphins.

Worldwide, a number of studies have reported levels of long-chain (C9–C20) PFCA in biota, including porpoises (van der Vijver et al. 2004, 2007), harbour seals (van der Vijver et al. 2005) and glaucous gulls (Verreault et al. 2005). van der Vijver et al. (2007) collected liver samples from harbour porpoises (*Phocena phocena relict*) along the Ukrainian coast of the Black Sea. Concentrations ranged from 1.4 to 19 ng/g-ww with C10 PFCA having the highest concentration. van der Vijver et al. (2003) also has shown the presence of C9–C11 PFCA in the livers of several mammals taken from the North Sea coast, including a sperm whale, a white-sided dolphin and white-beaked dolphins. Concentrations ranged from non-detection to 480 ng/g-ww for all four species (detection limit 30–90 ng/g). Concentrations were highest in the white-beaked dolphin (*Lagenorhynchus albirostris*). Leonel et al. (2008) measured C9–C12 PFCA in Franciscana dolphin (*Pontoporia blainvillei*) collected from southern Brazil. Liver concentrations ranged from < 0.1 to 0.46 ng/g-ww with C11 PFCA having the highest concentration. Leonel et al. (2008) also measured C9–C12 PFCA in Subantarctic fur seal (*Arctocephalus tropicalis*) also collected from southern Brazil. Liver concentrations ranged from <0.1 to 0.74 ng/g-ww – again C11 PFCA had the highest concentration. C9–C12 PFCA were measured in liver of the Indo-Pacific humpback dolphins (*Sousa chinensis*) and finless porpoises (*Neophocaena phocaenoides*) in Hong Kong (Yeung et al. 2009c). C9–C12 PFCA concentrations in the humpback dolphins ranged from 0.243 to 120 ng/g-ww. C9–C12 PFCA were detected in finless porpoises at concentrations ranging 0.522 to 34.3 ng/g-ww.

Tseng et al (2006) found C10 PFCA in oysters (*Crassostrea gigas*), in tilapia (*Oreochromis* sp.) and Japanese seaperch (*Lateolabrax japonicus*) in Taiwan. C10 PFCA concentrations in the oysters ranged from 140 – 320 ng/g-ww. Liver and fish muscle concentrations of C10 PFCA in tilapia was 390 and 250 ng/g-ww, respectively. C10 PFCA concentration in the Japanese seaperch was 480 ng/g-ww.

Concentrations of C9–C12 PFCA were measured in egg yolks of three species of birds—the little egret (*Egretta garzetta*), little ringed plover (*Charadrius dubius*) and vinous-throated parrotbill (*Paradoxornis webbiana*)—collected around Lake Shihwa, Korea (Yoo et al. 2008). C9–C12 PFCA concentrations ranged from 5.7 to 675 ng/g-ww. The highest concentration was found in the little ringed plover with a C11 PFCA concentration of 675 ng/g ww. C9 PFCA was not detected in the liver of the northern fulmar (*Fulmarus glacialis*) along the coast of Svalbard and Bjørnøya in the Barents Sea (Norwegian Arctic) (Knudsen et al. 2007). However, Holmstrom and Berger (2008) measured C9 – C16 PFCA in common guillemot (*Uria aalge*). C16 PFCA was below the detection limit. However C9 – C15 PFCA were measured in concentrations ranging from 0.17 to 32 ng/g-ww. Wang et al. (2008) measured concentrations of C9 – C12 PFCA in waterbird eggs in South China. C9–C12 PFCA concentrations in egg samples

from black-crowned night herons (*Nycticorax nycticorax*) ranged from 0.072 to 41.3 ng/g-ww, concentrations in great egrets (*Ardea alba*) ranged from 0.225 to 5.79 ng/g-ww and concentrations in little egrets (*Egretta garzetta*) ranged from 0.77 to 39.4 ng/g-ww.

C9 – C12 PFCA was detected in beaver liver collected from Poland at concentrations ranging from < 0.04 to 4.46 ng/g-ww with C9 PFCA having the highest concentration (Taniyasu et al. 2005). Male wild rats (*Rattus norvegicus*) were collected from eight sites in Japan (i.e., a WWTP, a port, two industrial areas, a seafood market, a marketplace, two landfill sites and a seafood port)(Yeung et al. 2009b). Whole-blood samples were analyzed for C9 to C12 PFCA with mean concentrations ranging from 0.792 to 7.3 ng/mL. C9 and C10 PFCAs were measured in serum of the Chinese Amur tiger (*Panthera tigris altaica*) (Li et al. 2008) found in northeastern China, far eastern Russia and North Korea. C9 PFCA at concentrations of 0.13–0.89 ng/mL was found to be one of the most prevalent perfluorinated compounds in the serum of the Amur tigers. C10 PFCAs was found at a mean concentrations of 0.1 – 0.15 ng/mL. Gender differences were found for C9 and C10 PFCA accumulation where concentrations were slightly higher in females than in males.

#### *Temporal and Spatial Trends*

A temporal study over a 22-year period between 1980 and 2002 examined suspended sediment in Niagara River discharge where reported PFCA levels generally increased over time (Lucaciu et al. 2004). Myers et al. (2009) examined spatial distribution and temporal trends of perfluorinated compounds in Great Lakes sediment and surface waters. It was found that spatial distributions of PFCAs (C7 – C12 PFCAs) indicated that urban and industrial activities influenced concentrations in Great Lakes sediment and water. In Lake Ontario surface water, tributary samples showed the highest C7-C12 PFCA concentrations relative to near-shore and open lake samples; however, for sediment, open lake samples showed the highest concentrations. Myers et al. (2009) also noted that C7-C12 PFCA sediment concentrations are increasing in Lake Ontario. However, an observed increase and levelling –off was observed in Lake Superior sediments which may reflect atmospheric transport in C7-C12 PFCAs.

Furdui et al. (2007) determined the spatial trends of long chain PFCAs in lake trout (*Salvelinus namaycush*, age class equal to 4 years) collected from the Great Lakes in 2001. C9 to C15 PFCAs were detected in concentrations ranging from 0.37 to 4.9 ng/g ww. The highest concentrations were observed in Lake Erie, followed by Lake Huron, Lake Ontario, Lake Michigan and Lake Superior. No significant correlation was determined between concentrations and fish weight. The temporal trends of long chain PFCAs were determined in lake trout collected between 1979 and 2004 from Lake Ontario (Furdui et al. 2008). PFCA concentrations were generally low (non-detect to 3 ng/g) with C11 PFCA, C12 PFCA and C13 PFCA having the greatest concentrations. Most PFCA concentrations in 1988 and/or 1993 were generally higher than in 1979 followed by a levelling or decrease in concentrations. Regression analyses for individual PFCAs were not of sufficient significance to indicate declines in recent years since the peaks in 1998 and/or 1993.

An investigation of the temporal trends in liver of northern fulmar (*Fulmarus glacialis*) and thick-billed murre (*Uria lomvia*) from the Canadian Arctic reported overall increases in PFCAs over time for both species (Butt et al. 2007a). The geometric mean concentrations for the  $\Sigma$ PFCAs in thick-billed murres and northern fulmars were 23.9 ng/g and 12.4 ng/g, respectively. C13 PFCA was the predominant compound followed by C11 and C14 PFCA. Thick-billed murres showed increasing concentrations of PFCAs through 1975-2004 with doubling times ranging from 2.3 years for C15 PFCA to 9.9 years for C12. Doubling times for northern fulmars ranged from 2.5 years for C15 PFCA and 11.7 years for C12 PFCA. However, in the case of the northern fulmars, most PFCAs showed maximum concentrations in 1993 or statistically similar concentrations between 1987, 1993, and 2003. This may be the result of differing migratory patterns in bird species (Butt et al 2007a). Gebbink et al. (2009a) determined the spatial distribution, trends and sources of C9 – C15 PFCAs in 16 colonies of gull species sampled from eastern (Nova Scotia, New Brunswick, Newfoundland), central (Quebec, Ontario, Manitoba) to western Canada (Alberta, British Columbia). The four species are glaucous-winged gull (*Larus glaucescens*), California gull (*Larus californicus*), ring-billed gull (*Larus delawarensis*), and herring gull (*Larus argentatus*). The authors noted that the  $\Sigma$ PFCAs were greatest in the herring gull eggs collected in southern Ontario and western Quebec colonies close to urban sources. C11 and C13 PFCAs were generally dominant for most of the colonies although differences were observed among colonies. Overall, the spatial distribution of PFCAs in gull eggs across Canada was considered to be primarily influenced by location and proximity to local sources as opposed to diet. Gebbink et al (2009b) collected herring gull (*Larus argentatus*) eggs from 15 colonies located at Canadian and some American sites across the Laurentian Great Lakes. PFCAs ranging from C9 to C15 were detected with C11 and C13 PFCAs as the most dominant. C9 PFCA was more abundant in Lake Superior and Lake Michigan colonies and C11 PFCA was more abundant in the Lake Erie and Lake Ontario colonies. The highest  $\Sigma$ PFCAs were found in Lake Huron at 113 ng/g-ww followed by colonies in Lake Erie and Ontario. 8:2 and 10:2 FTOHs were not detected in any herring gull eggs.

Verreault et al. (2007) showed temporal trends for whole eggs of herring gulls (*Larus argentatus*) from two geographically isolated colonies (Hornøya and Røst) in northern Norway. These colonies encompassed the southern and northern distribution range of herring gulls breeding in northern Norway. The dominant long chain PFCA in the herring gull eggs was C11 PFCA (4.2 ng/g ww, Hornøya), followed by C13 (2.8 ng/g-ww, Røst). C9 to C13 PFCAs for both colonies showed significant increases between 1983–1993 followed either by an increase post-1993 (i.e., C9, C10 and C11 PFCAs) or a leveling off (i.e., C12 and C13 PFCAs). Spatial trends between the two colonies were not different with the exception of C9 PFCA which was highest in the Røst colony. The eggs from the Røst colony collected in 1993 also had higher proportions of the C14 and C15 PFCAs compared to the Hornøya colony and other sampling years. Verreault et al. (2007) suggested that the direct and indirect local-sources and/or remote-sources of long chain PFCAs may have changed over the last two decades in northern Norway. Alternately, there might have been shifts in the dietary preferences for adult herring gulls in northern Norway – these gulls have a limited annual feeding range and are primarily fish-feeders although they may also feed on crustaceans, seabird chicks, eggs, and other terrestrial

food sources (human refuse). Löfstrand et al. (2008) determined spatial trends in guillemot (*Uria aalge*) eggs collected from Iceland, Sweden, the Faroe Islands, and Norway (Sklinna and Hjelmsøya). C9 PFCA was detected only in Sweden at 48 ng/g-ww. C10 PFCA was detected only in Iceland and Norway at 38 – 42 ng/g-ww. C11 PFCA appears to be the most dominant compound with concentrations ranged from 9 – 140 ng/g-ww followed by C12 PFCA with concentrations ranging from ND to 81 ng/g-ww. The  $\Sigma$ PFCAs were highest in Sweden (150 ng/g-ww) followed by Iceland (96 ng/g-ww), and the Faroe Islands (76 ng/g-ww). Lofstrand et al. (2008) suggested that the spatial patterns differ likely due to the differing feeding habits of the guillemot across the Atlantic and that the Swedish eggs were sampled in locations nearest industrial areas and heavily populated areas.

Levels of PFCAs in ringed seal livers from eastern and western Greenland measured from 1980 and 2000 increased 3.3 and 6.8% per year for C10 and C11, respectively (Bossi et al. 2005). Butt et al. (2007b) examined temporal trends in liver samples from two ringed seal (*Phoca hispida*) populations in the Canadian Arctic: Arviat (1992, 1998 and 2005) and Resolute Bay (1972, 1993, 2000 and 2005). C9–C15 PFCAs showed concentration increases from 1992 to 1998 but later sampling points (1998, 2003, and 2005) were not statistically different. Concentrations increased by 117% for C14 PFCA to 310 % for C9 PFCA. No significant differences between sex were identified for any PFCA with any of the two populations. Overall, concentrations of the PFCAs increased from 1993-2005; however, the increases in the most recent years were not statistically significant. Doubling times ranged from 10.0 (C9 PFCA) to 19.4 (C12 PFCA). Butt et al. (2008) detected long-chain PFCAs in liver samples from eleven ringed seal populations in the Canadian Arctic from 2002 to 2005. Concentrations of C9–C11 PFCAs ranged from 1 to 10 ng/g-ww, whereas those of C12–C15 PFCAs were less than 1 ng/g-ww. In addition, 8:2 and 10:2 FTUCAs were detected in all populations; however, concentrations were less than the detection limit. Quantifiable levels were measured in two ringed seal populations, from 4 to 6 ng/g ww. Some statistically significant spatial trends were observed between individual populations; however, it was concluded that variations were largely attributable to elevated levels in two populations and lower levels in another population (Butt et al. 2008).

Temporal trends were investigated in the Baikal seal (*Pusa sibirica*) from Lake Baikal, eastern Siberia, Russia (Ishibashi et al. 2008b). C9 to C12 PFCAs were measured in the liver and serum of the Baikal seal. The Baikal seal is an endemic species and is a high trophic level predator in the food web of Lake Baikal. In male and female Baikal seal liver, the concentration of C9-C12 PFCAs ranged from <0.56 to 72 ng/g-ww. In male and female Baikal seal serum, C9-C12 PFCAs concentrations ranged from <0.33 -4 ng/g-ww (Ishibashi et al. 2008b). The mean concentrations of C9 and C10 PFCA in livers of seals collected in 2005 were 1.2 and 1.7-fold greater than in seals collected in 1992. C10 PFCA concentrations were significantly higher in 2005 than in 1992. For C9 PFCA, although there was a trend of increasing concentration from 1992 to 2005, no significant differences were observed.



In the studies by De Silva and Mabury (2004) and Smithwick et al. (2005a), levels of longer-chain PFCAs in polar bear liver were found to be generally higher in the east (Greenland), with evidence of C9 and C10 higher in the west. Examination of the tropospheric airflow patterns indicates that the central eastern regions would tend to receive air from eastern North America and those in the east (Greenland) would receive airflow from North America and Europe (De Silva and Mabury 2004). The higher C9 and C10 in western Arctic polar bears may be due to higher emissions of these congeners from Asia (Smithwick et al. 2005a). A similar west-to-east trend was observed with PFCA levels in ringed seal liver samples, although the highest levels were reported in the southern Hudson Bay region (Butt et al. 2008). Dietz et al (2008) examined a subsample of 128 subadult (3–5 years old) polar bears from 1984 to 2006 from Ittliqqortoormiit (Scoresby Sound) in central Greenland. Linear regression analysis of logarithmic-transformed median concentrations showed annual increases for C9 PFCA (6.1%), C10 PFCA (4.3%), C11 PFCA (5.9%), C12 PFCA (52%), and C13 PFCA (8.5%). Mean doubling times for concentrations in polar bear livers from North American Arctic regions ranged from 5.8 years in the east to 9.1 years in the west for C9, C10 and C11 from 1972 to 2002 (Smithwick et al. 2006).

Tomy et al. (2009a) measured the temporal trends of  $\Sigma$ PFCAs (C8-C12) in male beluga whales from Pangnirtung, Nunavut which showed an annual increase of 1.8 +/- 0.5 ng/g-ww between liver-based concentrations for the years 1980 to 2010. The  $\Sigma$ PFCAs (C8-C12) concentrations in the male beluga whales from Pangnirtung ranged from 2.4 to 171.05 ng/g-ww. However, male beluga whales from Hendrickson Island showed a decline of 7.41 +/- 0.71 ng/g-ww between liver-based concentrations for the years 1980 to 2009 (Tomy et al. 2009a). Concentrations for the  $\Sigma$ PFCAs (C8-C12) in the Hendrickson Island male beluga whales ranged from 4.87 to 313.10 ng/g-ww.

## Ecological Effects Assessment

### *Aquatic Organisms*

Boudreau et al. (2002) examined the toxicity of C10 on the aquatic macrophyte *Lemna gibba*, and determined that the IC<sub>50</sub> (inhibitory concentration) value (based on growth) was 99 mg/L. The IC<sub>50</sub> values (based on growth) of C10 on the freshwater algae *Selenastrum capricornutum* and *Chlorella vulgaris* were 218 mg/L and 198 mg/L respectively, indicating little difference in sensitivity between the two species (Boudreau et al. 2002). The acute and chronic toxicity of C10 on two species of water fleas, *Daphnia magna* and *Daphnia pulex*, were investigated. The acute LC<sub>50</sub> (based on mortality) and chronic EC<sub>50</sub> values (based on immobilization) were 259 and 130 mg/L, respectively for *Daphnia magna* and 285 and 150 mg/L, respectively for *Daphnia pulex* (Boudreau et al. 2002). These values indicate that there may be few sensitivity differences between the two species. Hoke et al. (2009) determined acute toxicity values for C10 PFCA: a 96hr rainbow trout (*Oncorhynchus mykiss*) LC<sub>50</sub> value of 32 mg/L, a 48hr EC<sub>50</sub> for *Daphnia magna* of >100 mg/L, and a 72hr EC<sub>50</sub> for the green algae, *Pseudokirchneriella subcapitata*, of 10.6 mg/L.

Chronic toxicity studies of C9 on the two species of water fleas indicated increased sensitivity of *Daphnia pulicaria* versus *Daphnia magna* (Boudreau et al. 2002). The 21-day LC<sub>50</sub> values (based on mortality) were 8.8 mg/L and 39 mg/L, respectively. Chronic toxicity studies also indicated that, for *Daphnia magna*, the number of young produced was a more sensitive endpoint than mean time to first brood. The 21-day no-observed-effect concentration and lowest-observed-effect concentration values (both based on number of young produced) were 13 and 25 mg/L, respectively for *Daphnia magna* and 6 and 13 mg/L, respectively for *Daphnia pulicaria*.

#### *Terrestrial Organisms*

The 48-hour EC<sub>50</sub> (based on acute lethality) for C9 for the soil-dwelling nematode *Caenorhabditis elegans* was 0.66 mM (306.29 mg/L) from surface contact exposure in a 1.7% agar nematode growth medium (Tominaga et al. 2004). Multi-generation effects following nematode exposure to C9 were found at concentrations as low as approximately 1 nM (0.000464 mg/L), which induced a 70% decline in fecundity by the fourth generation (Tominaga et al. 2004). Generation-response relationships and concentration-response relationships were not observed, although the results suggest that C9 could have longer-term multi-generational effects at relatively low exposure concentrations.

Yeung et al. (2009a) exposed one-day old male chickens (*Gallus gallus*) to C10 PFCA at 0.1 and 1.0 mg/kg body weight three times a week for three weeks. No adverse effects on body weight, organ indexes, blood clinical parameters or organ histopathology were observed at the 0.1 or the 1.0 mg/kg body weight of C10 PFCA. However, the half-life for PFDA at 0.1 and 1.0 mg/kg body weight was 11 and 16 days, respectively indicating the bioaccumulative properties of C10 PFCA in chickens.

#### *Other Effects*

Stevenson et al. (2006a) examined the toxicity of C9 and C10 with respect to the multi-xenobiotic resistance mechanism in the marine mussel *Mytilus californianus*. This mechanism acts as a cellular first line of defense against broad classes of xenobiotics exporting moderately hydrophobic chemicals from the cell via adenosine triphosphate (ATP)-dependent, transmembrane transport proteins. The most studied transporter is the p-glycoprotein which, in humans, is active in the kidney, adrenal gland, liver, blood-testes barrier and blood-brain barrier. This defense mechanism is fragile and can be compromised by some xenobiotics. This increased sensitivity, referred to as chemosensitization, arises from the ability of the p-glycoprotein to recognize and bind to multiple xenobiotic substrates, resulting in the saturation of the binding capacity. Even non-toxic substances can be chemosensitizers and cause adverse effects on organisms by allowing normally excluded toxic substances to accumulate in the cell. Stevenson et al. (2006a) found that C9 and C10 had average IC<sub>50</sub>s (based on p-glycoprotein inhibition) of 4.8 µM (2.23 mg/L) and 7.1 µM (3.65 mg/L), respectively, which significantly inhibited the p-glycoprotein in *Mytilus californianus*. This result indicates that C9 and C10 are chemo sensitizers for this organism. C9 inhibits the p-glycoprotein by an indirect mechanism, and this inhibition is reversible. C9 also induces expression of the p-

glycoprotein transporter after a 2-hour exposure—a stress response that may result in a metabolic cost to the organism.

Liu et al. (2008) investigated the effects of C12 and C14 PFCA on the membrane systems of the freshwater alga species, *Scenedesmus obliquus*. C12 and C14 PFCA inhibited algal growth rate in a concentration-dependent manner (i.e. inhibition increased with increasing exposure concentration). The IC<sub>10</sub>, IC<sub>50</sub>, and IC<sub>90</sub> for cell density calculated were 90 uM (46.27 mg/L), 183 uM (94.08 mg/L), and 367 uM (188.67 mg/L) for C10 PFCA and 41 uM (29.28 mg/L), 134 uM (95.69 mg/L), and 292 uM (208.52 mg/L) for C14 PFCA. For C10 PFCA, an enhancement of the mitochondrial membrane potential was observed between 30 and 100 uM (15.42 – 51.40 mg/L). For C14 PFCA, an enhancement of the mitochondrial membrane potential was observed between 50 and 100 uM (35.70 – 71.41 mg/L). The increase in mitochondrial membrane potential indicates damage to the mitochondrial function – mitochondria are multi-tasking organelle involved in oxidative energy metabolism as well as apoptosis by integrating death signals. In addition, C12 and C14 PFCA caused an increase in cell membrane permeability at 20 – 100 uM (12.28 - 61.41 mg/L) for C12 PFCA and 50 – 100 uM (35.70 – 71.41 mg/L) for C14 PFCA. Effects on the permeability status of the cell membrane could play a role in mediating the adverse effects of other contaminants. Liu et al. (2008) used flow cytometric measurements to investigate the effects of C12 and C14 PFCA on the membrane systems of the freshwater alga *Scenedesmus obliquus*. The IC<sub>50</sub> values (cell density) for C12 and C14 were 183 µM (112.38 mg/L) and 134 µM (95.69 mg/L), respectively. Liu et al (2008) noted that the impairment of energy production by the interruption of the mitochondrial function may account for the inhibition of cell division caused by C12 and C14 observed as a reduction in growth rate (i.e., cell density).

Benninghoff et al. (2007) found that C9–C12 PFCA significantly induced vitellogenin, a biomarker of estrogen exposure, in rainbow trout. C9–C12 PFCA demonstrated weak affinity to the rainbow trout hepatic estrogen receptor. In juvenile rainbow trout, C10 increased vitellogenin in a dose-dependent manner in vivo and significantly increased plasma vitellogenin at moderately low (0.0256–2000 µg/g diet) concentrations. The authors note that the trout hepatic estrogen receptor has greater affinity to more xenoestrogens than other mammalian estrogen receptors, including humans.

Nakayama et al. (2008) studied the common cormorant (*Phalacrocorax carbo*), a fish-eating bird that is the top predator in the ecosystem of Lake Biwa in Japan. C9 concentrations were measured in the liver of wild common cormorants (male and female) and related to gene expression. C9 concentrations for females ranged from < 0.005 to 0.0088 µg/g-ww, and for males, concentrations ranged from < 0.005 to 0.043 µg/g-ww. Significant sex differences were not detected. Gene expression analysis showed significant positive relationships between C9 and glutathione peroxidase 1 (enzyme in the antioxidant system) and heterogenous nuclear ribonucleoprotein U (RNA processing). The induction of the antioxidant enzymes may be an adaptive response to oxidative stress caused by C9.

Ishibashi et al. (2008a) showed that C9-C11 PFCAs induced peroxisome proliferator-activated receptor  $\alpha$  (PPAR $\alpha$ ) in Baikal seal (*Pusa sibirica*) livers at lowest observed effect concentrations of 125  $\mu$ M (58.00 mg/L)(C9 PFCA), 125  $\mu$ M (64.26 mg/L) (C10 PFCA), and 62.5  $\mu$ M (35.25 mg/L)(C11 PFCA). PPAR $\alpha$  plays a critical physiological role as a lipid sensor and a regulator in lipid metabolism. Expression levels of PPAR $\alpha$  mRNA showed a positive correlation with C9 PFCA and the expression of the hepatic CYP4A-like protein was correlated with the hepatic concentrations of C9 and C10 PFCAs suggesting modulation of the PPAR $\alpha$ -CYP4A signalling pathway in wild Baikal seals.

The potential impact from exposure to perfluorinated compounds was investigated on liver lesions in east Greenland polar bears (Sonne et al. 2007). Parameters included mononuclear cell infiltrations, lipid granulomas, steatosis, Ito cells and bile duct hyperplasia/portal fibrosis. The population size consisted of 28 females and 29 males sampled by local hunters from 1999 to 2002. Liver samples were analyzed for several perfluorinated compound including C9, C10, C11, C12 and C13 PFCAs. Sixty-five percent of the polar bears had  $\Sigma$ PFA concentrations above 1000 ng/g-ww. In female bears, the  $\Sigma$ PFA ranged from 256 to 2770 ng/g-ww, and in male bears the  $\Sigma$ PFA ranged from 114 to 3052 ng/g-ww. Given that all PFA compounds in the analysis were summed, a direct cause-effect correlation with a particular perfluorinated compound, such as the long-chain PFCAs, is not possible to deduce. In addition, east Greenland polar bears are also contaminated with other substances such as organochlorines (PCBs, DDTs) and mercury which may be confounding synergistic co-factors in the development of the lesions. The authors concluded that the statistical analysis did not provide evidence as to whether chronic exposure to perfluorinated compounds is associated with liver lesions in polar bears; however, these lesions were similar to those produced by perfluorinated compounds under laboratory conditions (Sonne et al. 2007).

### Characterization of Ecological Risk

The approach taken in this ecological screening assessment was to examine various supporting information and develop conclusions based on multiple lines of evidence such as persistence, exposure, trends, ecological risk, inherent toxicity, bioaccumulation and widespread occurrence in the environment.

In traditional toxicity studies, long-chain (C9-C20) PFCAs were found to be low to moderately toxic, with acute toxicity values ranging from 8.8 to 285 mg/L. There are two studies on the toxicity of long-chain (C9-C20) PFCAs in terrestrial species. In one study, no adverse effects were observed up to 1.0 mg/kg body weight for male chickens dosed with C10 PFCA. In another study, a soil-dwelling nematode showed acute lethality at 306 mg/L and multi-generation effects (decreased fecundity) at 0.000464 mg/L when exposed to C9 PFCA.

There is the potential for PFAs, including long chain (C9-C20) PFCAs to cause hepatotoxicity, i.e., liver lesions in polar bears at 114 – 3052 ng/g-ww total PFAs, and the activation of the PPAR $\alpha$  in Baikal seal livers at 35.25 – 64.26 mg/L C9-C11 PFCAs. There is also the potential for long chain (C9-C20) PFCAs to cause affect endocrine function such as vitellogenesis in rainbow trout at 0.0256- 2000 ug/g diet C10 PFCA. C9-C10 PFCAs are also chemical sensitizers for the marine mussel, *Mytilus californianus*, by allowing normally excluded toxic substances to accumulate in the marine mussel. C12 and C14 PFCAs increased the mitochondrial membrane potential in the freshwater alga, *Scenedesmus obliquus*, indicating damage to the mitochondrial function.

Long-chain (C9-C20) PFCAs have been measured in the Canadian aquatic environment in concentrations ranging from <0.5 ng/L to 19 ng/L. C9-C12 PFCAs were measured in sediment from the Canadian Arctic ranging in concentration from 0.5 – 3.3 ng/g. C9 to C15 PFCAs were measured in the liver of seals, foxes, fish, polar bears, Greenland shark, narwhals, beluga whales and birds either in the Canadian Arctic or the Great Lakes region. Concentrations ranged from below detection levels to 180 ng/g liver-ww with concentrations greatest for polar bears followed by Greenland shark, narwhals and beluga whales. Worldwide, levels of C9 to C15 have been reported in ringed, fur and harbour seals, dolphins (i.e. white-sided, bottlenose, white-beaked, Franciscana, humpback), finless porpoises, glaucous gulls, sperm whale, beavers, Amur tigers, wild rats and several species of birds (little egret, little ringed plover, parrotbills, black-crowned herons). Concentrations ranged from below detection levels to 480 ng/g-ww, with concentrations highest in the white-beaked dolphin.

For C11 (2700<BCF<11000), C12 (18000<BCF<40000), and C14 (23000<BCF<30000) PFCAs, there is a high potential for bioconcentration in fish and potential for biomagnification in fish and marine mammals. For the other long-chain PFCAs, there is evidence of biomagnification and trophic magnification in the environment. There are no experimental or predicted bioaccumulation data available for long-chain PFCAs greater than C14. Nevertheless, there is the potential that long chain PFCAs could bioaccumulate or biomagnify in marine and/or terrestrial species based on chemical conformations. In addition, C14 and C15 PFCAs have been found in fish, invertebrates and polar bears.

Increasing trends of long-chain (C9-C20) PFCAs have been shown in polar bears, ringed seals and birds. From 1980 to 2000, C10 and C11 PFCAs in ringed seal livers from Greenland increased 3.3 and 6.8% per year, respectively. From 1992 to 2005, the mean concentrations of C9 and C10 PFCA in the livers of Baikal seals were 1.2 to 1.7-fold higher. From 1972 to 2002, mean doubling times for concentrations in polar bear livers from the Arctic ranged from 5.8 to 9.1 years for C9 to C11. From 1993 to 2004, concentrations in ringed seal liver samples increased, with a doubling time of 4 to 10 years for C9 to C12. In northern fulmar liver samples, C9 to C15 levels increased from 1987 to 1993 and remained steady from 1993 to 2003. Thick-billed murre liver samples showed an increase in C9 to C15 concentrations from 1975 to 2004. Concentrations of C9 to C13 increased significantly in whole eggs of herring gulls in Norway from 1983 to 1993. Temporal increases of C9-C12 were observed in male beluga whales from Nunavut at 1.8 ng/g-ww liver from 1980-2010.

## **Uncertainties in Evaluation of Ecological Risk**

Certain data gaps and uncertainties exist such as limited physical and chemical properties, experimental persistence data, and toxicity data. There is, nonetheless, a substantial body of information on long-chain (C9-C20) PFCAs and their precursors. For example, while the mechanisms of transport of long chain (C9-C20) PFCAs and their precursors to the Arctic are not clear, they appear to be mobile in some form, as both the long-chain PFCAs (C9-C15) and their precursors have been measured in biota throughout the Canadian Arctic, far from known sources.

Environmental pathways of long-chain (C9-C20) PFCAs to biota are not well understood, as there are relatively few monitoring data on concentrations of various precursors in air, water, effluents and sediments in Canada. While mechanisms of toxic action of long-chain (C9-C20) PFCAs are not well understood, a range of toxicological effects, including vitellogenin induction and hepatotoxicity have been reported in a variety of species. In addition, analytical results from individual laboratories may not be directly comparable, according to studies by van Leeuwen et al. (2006), indicating variability in analytical results between individual laboratories.

There is also limited information on the toxicology of long-chain PFCA precursors, their relative contribution from different sources (e.g., significance of precursors from the degradation of fluorotelomer-based substances), and their potential for combined or synergistic effects with other perfluorinated compounds.

## **Conclusion**

The approach taken in this ecological screening assessment was to examine various supporting information and develop conclusions based on multiple lines of evidence approach. Evidence that a substance is highly persistent and bioaccumulative together with evidence of potential for releases associated with commercial activity (including precursors) provides a significant indication of its potential to enter the environment under conditions that may have harmful long-term ecological effects. Substances that are persistent remain in the environment for a long time after being released, increasing the potential magnitude and duration of exposure. Substances (or their precursors) that have long half-lives in mobile media such as air and water, and partition into these media in significant proportions, have the potential to cause widespread contamination. Releases of small amounts of bioaccumulative substances (or related precursors) may lead to high internal concentrations in exposed organisms. Highly bioaccumulative and persistent substances are of special concern, since they may biomagnify in food webs, resulting in very high internal exposures, especially for top predators.

The presence of long-chain (C9-C20) PFCAs, their salts and their precursors results from anthropogenic activity. The long-chain (C9-C20) PFCAs and their salts are persistent. They have been found in remote regions, likely due to the long-range atmospheric or

oceanic transport of volatile precursors and/or the acids themselves. Long-chain (C9-C20) PFCAs and their precursors have been detected in biota in Canada, including the Canadian Arctic. There is evidence that environmental concentrations are increasing with time for Canadian Arctic species such as polar bears, ringed seals, northern fulmars and thick-billed murre. There is empirical evidence that long-chain (C9-C20) PFCAs are bioaccumulative and can biomagnify in fish, some piscivorous birds, and mammals.

Based on the information presented in this draft screening assessment, it is proposed that long-chain (C9-C20) perfluorocarboxylic acids, their salts and their precursors are entering or may be entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. While there is scientific evidence that long chain (C9-C20) PFCAs and their salts accumulate and biomagnify in terrestrial and marine mammals, only C11, C12 and C14 long chain PFCAs and their salts meet the numeric criteria for bioaccumulation as defined in the *Persistence and Bioaccumulation Regulations*. Additionally, it is proposed that long chain PFCAs and their salts meet the criteria for persistence as set out in the *Persistence and Bioaccumulation Regulations*. It is, therefore, proposed that long-chain (C9-C20) perfluorocarboxylic acids, their salts, and their precursors meet one or more of the criteria in section 64 of CEPA 1999.

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**Appendix 1 - LIST OF LONG-CHAIN (C9-C20) PFCAS, THEIR SALTS AND THEIR PRECURSORS**

<b>CAS Registry Number</b>	<b>Chemical Name</b>	<b>Type of PFA</b>
65530-63-4	Ethanol, 2,2'-iminobis-, compd. with $\alpha$ -fluoro- $\omega$ -[2-(phosphonooxy)ethyl]poly(difluoromethylene) (2:1)	> 8 PFCA precursor, Fluoro phosphates
375-95-1	Nonanoic acid, heptadecafluoro-	Long-chain PFCA Not on DSL
335-76-2	Decanoic acid, nonadecafluoro-	Long-chain PFCA Not on DSL
2058-94-8	Undecanoic acid, heneicosafluoro-	Long-chain PFCA Not on DSL
307-55-1	Dodecanoic acid, tricosafuoro-	Long-chain PFCA Not on DSL
72629-94-8	Tridecanoic acid, pentacosafuoro-	Long-chain PFCA Not on DSL
376-06-7	Tetradecanoic acid, heptacosafuoro-	Long-chain PFCA Not on DSL
141074-63-7	Pentadecanoic acid, nonacosafuoro-	Long-chain PFCA Not on DSL

CAS Registry Number	Chemical Name	Type of PFA
67905-19-5	Hexadecanoic acid, hentriacontafluoro-	Long-chain PFCA
57475-95-3	Perfluoroheptadecanoic acid	Long-chain PFCA Not on the DSL
16517-11-6	Octadecanoic acid, pentatriacontafluoro-	Long-chain PFCA Not on DSL
133921-38-7	Perfluorononadecanoic acid	Long-chain PFCA Not on DSL
68310-12-3	Eicosanoic acid, nonatriacontafluoro-	Long-chain PFCA Not on DSL
65530-64-5	Ethanol, 2,2'-iminobis-, compd. with $\alpha,\alpha'$ -[phosphinicobis(oxy-2,1-ethanediyl)]bis[ $\omega$ -fluoropoly(difluoromethylene)] (1:1)	> 8 PFCA precursor Fluoro phosphates
65530-69-0	Poly(difluoromethylene), $\alpha$ -[2-[(2-carboxyethyl)thio]ethyl]- $\omega$ -fluoro-, lithium salt	> 8 PFCA precursor Fluoro thioether
65530-70-3	Poly(difluoromethylene), $\alpha,\alpha'$ -[phosphinicobis(oxy-2,1-ethanediyl)]bis[ $\omega$ -fluoro-, ammonium salt	> 8 PFCA precursor Fluoro phosphates
65530-71-4	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-(phosphonooxy)ethyl]-, monoammonium salt	> 8 PFCA precursor Fluoro phosphates

CAS Registry Number	Chemical Name	Type of PFA
65530-72-5	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-(phosphonooxy)ethyl]-, diammonium salt	> 8 PFCA precursor Fluoro phosphates
65530-74-7	Ethanol, 2,2'-iminobis-, compd. with $\alpha$ -fluoro- $\omega$ -[2-(phosphonooxy)ethyl]poly(difluoromethylene) (1:1)	> 8 PFCA precursor Fluoro phosphates
65530-83-8	Poly(difluoromethylene), $\alpha$ -[2-[(2-carboxyethyl)thio]ethyl]- $\omega$ -fluoro-	> 8 PFCA precursor Fluoro thioether
65545-80-4	Poly(oxy-1,2-ethanediyl), $\alpha$ -hydro- $\omega$ -hydroxy-, ether with $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly(difluoromethylene) (1:1)	> 8 PFCA precursor Fluoro alcohol derivatives
68187-25-7	Butanoic acid, 4-[[3-(dimethylamino)propyl]amino]-4-oxo-, 2(or 3)-[( $\gamma$ - $\omega$ -perfluoro-C <sub>6-20</sub> -alkyl)thio] derivs.	> 8 PFCA precursor Fluoro thioether
68187-47-3	1-Propanesulfonic acid, 2-methyl-, 2-[[1-oxo-3-[( $\gamma$ - $\omega$ -perfluoro-C <sub>4-16</sub> -alkyl)thio]propyl]amino] derivs., sodium salts	> 8 PFCA precursor Fluoro thioether
68391-08-2	Alcohols, C <sub>8-14</sub> , $\gamma$ - $\omega$ -perfluoro	> 8 PFCA precursor Fluorotelomer alcohol
68412-68-0	Phosphonic acid, perfluoro-C <sub>6-12</sub> -alkyl derivs.	> 8 PFCA precursor Fluoro phosphates
68412-69-1	Phosphinic acid, bis(perfluoro-C <sub>6-12</sub> -alkyl) derivs.	> 8 PFCA precursor Fluoro phosphates

CAS Registry Number	Chemical Name	Type of PFA
68891-05-4	Ethene, tetrafluoro-, homopolymer, $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)-, citrate, reaction products with 1,6-diisocyanatohexane	> 8 PFCA precursor
86508-42-1	Perfluoro compounds, C <sub>5-18</sub>	> 8 PFCA precursor
865-86-1	1-Dodecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12-heneicosafuoro-	> 8 PFCA precursor Fluorotelomer alcohol
2144-54-9	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12-heneicosafuorododecyl ester	> 8 PFCA precursor Fluoro acrylates
4980-53-4	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,16-nonacosafuorohexadecyl ester	> 8 PFCA precursor Fluoro acrylates
6014-75-1	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,14-pentacosafuorotetradecyl ester	> 8 PFCA precursor Fluoro acrylates
17741-60-5	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12-heneicosafuorododecyl ester	> 8 PFCA precursor Fluoro acrylates
39239-77-5	1-Tetradecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,14-pentacosafuoro-	> 8 PFCA precursor Fluorotelomer alcohol

CAS Registry Number	Chemical Name	Type of PFA
59778-97-1	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,17,17,18,18,18-tritriacontafluorooctadecyl ester	> 8 PFCA precursor Fluoro acrylates
60699-51-6	1-Hexadecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,16-nonacosafuoro-	> 8 PFCA precursor Fluorotelomer alcohol
65104-65-6	1-Eicosanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,17,17,18,18,19,19,20,20-heptatriacontafuoro-	> 8 PFCA precursor Fluorotelomer alcohol
65104-66-7	2-Propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,17,17,18,18,19,19,20,20-heptatriacontafluoroeicosyl ester	> 8 PFCA precursor Fluoro acrylates
65104-67-8	1-Octadecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,15,15,16,16,17,17,18,18,18-tritriacontafuoro-	> 8 PFCA precursor Fluorotelomer alcohol
115592-83-1	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 12-heneicosafuorododecyl ester, polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-propenoate, hexadecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, octadecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12, 13,13,14,14,14-pentacosafuorotetradecyl 2-	> 8 PFCA precursor Fluoro acrylate polymers

CAS Registry Number	Chemical Name	Type of PFA
	propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-propenoate	
85631-54-5	2-Propenoic acid, $\gamma$ - $\omega$ -perfluoro-C <sub>8-14</sub> -alkyl esters	> 8 PFCA precursor Fluoro acrylates
144031-01-6	2-Propenoic acid, dodecyl ester, polymers with Bu (1-oxo-2-propenyl)carbamate and $\gamma$ - $\omega$ -perfluoro-C <sub>8-14</sub> -alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers
65530-59-8	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)-, 2-hydroxy-1,2,3-propanetricarboxylate (3:1)	> 8 PFCA precursor Fluoro carboxylate
65530-66-7	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-	> 8 PFCA precursor Fluoro acrylates
65605-56-3	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)-, dihydrogen 2-hydroxy-1,2,3-propanetricarboxylate	> 8 PFCA precursor Fluoro carboxylate
65605-57-4	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)-, hydrogen 2-hydroxy-1,2,3-propanetricarboxylate	> 8 PFCA precursor Fluoro carboxylate
65605-58-5	2-Propenoic acid, 2-methyl-, dodecyl ester, polymer with $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene)	> 8 PFCA precursor Fluoro acrylate polymers



CAS Registry Number	Chemical Name	Type of PFA
65605-70-1	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-[(1-oxo-2-propenyl)oxy]ethyl]-	> 8 PFCA precursor Fluoro acrylates
65636-35-3	Ethanaminium, <i>N,N</i> -diethyl- <i>N</i> -methyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]-, methyl sulfate, polymer with 2-ethylhexyl 2-methyl-2-propenoate, $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), 2-hydroxyethyl 2-methyl-2-propenoate and <i>N</i> -(hydroxymethyl)-2-propenamide	> 8 PFCA precursor Fluoro acrylate polymers
68239-43-0	2-Propenoic acid, 2-methyl-, 2-ethylhexyl ester, polymer with $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), 2-hydroxyethyl 2-methyl-2-propenoate and <i>N</i> -(hydroxymethyl)-2-propenamide	> 8 PFCA precursor
71002-41-0	Poly(difluoromethylene), $\alpha$ -[2-(acetyloxy)-2-[(carboxymethyl)dimethylammonio]ethyl]- $\omega$ -fluoro-, hydroxide, inner salt	> 8 PFCA precursor Fluoro alcohol derivatives
110053-43-5	Imidodicarbonic diamide, <i>N,N'</i> ,2-tris(6-isocyanatohexyl)-, reaction products with 3-chloro-1,2-propanediol and $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly(difluoromethylene)	> 8 PFCA precursor Fluoro urethane
123171-68-6	Poly(difluoromethylene), $\alpha$ -[2-(acetyloxy)-3-[(carboxymethyl)dimethylammonio]propyl]- $\omega$ -fluoro-, hydroxide, inner salt	> 8 PFCA precursor Fluoro alcohol derivatives

CAS Registry Number	Chemical Name	Type of PFA
125328-29-2	2-Propenoic acid, 2-methyl-, C <sub>10-16</sub> -alkyl esters, polymers with 2-hydroxyethyl methacrylate, Me methacrylate and perfluoro-C <sub>8-14</sub> -alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers
129783-45-5	2-Propenoic acid, 2-methyl-, C <sub>10-16</sub> -alkyl esters, polymers with 2-hydroxyethyl methacrylate, Me methacrylate and $\gamma$ - $\omega$ -perfluoro-C <sub>8-14</sub> -alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers
148878-17-5	2-Propenoic acid, 2-methyl-, C <sub>2-18</sub> -alkyl esters, polymers with $\alpha$ -fluoro- $\omega$ -[2-[(1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene) and vinylidene chloride	> 8 PFCA precursor Fluoro ester Not on DSL
70983-60-7	1-Propanaminium, 2-hydroxy- <i>N,N,N</i> -trimethyl-, 3-[( $\gamma$ - $\omega$ -perfluoro-C <sub>6-20</sub> -alkyl)thio] derivs., chlorides	> 8 PFCA precursor Not on DSL
148240-84-0	1,3-Propanediol, 2,2-bis[( $\gamma$ - $\omega$ -perfluoro-C <sub>4-10</sub> -alkyl)thio]methyl] derivs., phosphates	> 8 PFCA precursor Not on DSL
203743-03-7	2-Propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, $\gamma$ - $\omega$ --perfluoro-C <sub>10-16</sub> -alkyl acrylate and stearyl methacrylate	>8 PFCA precursor Not on DSL
277752-44-0	3-cyclohexene-1-carboxylic acid, 6-[(di-2-propenylamino)carbonyl](1R, 6R), reaction products with pentafluoridoethane-tetrafluoroethylene telomer, ammonium salts	>8 PFCA precursor Not on DSL

CAS Registry Number	Chemical Name	Type of PFA
333784-46-6	Graft polymer of alkyl methacrylate-maleic anhydride-2- [[((mercaptoethyl)oxy)carbonyl]amino)ethyl methacrylate copolymer and octadecyl methacrylate-2- (perfluoro(alkyl(C=6,8,10,12,14)))ethyl acrylate copolymer	>8 PFCA precursor, Not on DSL
333784-44-4	Poly[3-chloro-2-hydroxypropyl methacrylate, 2,3-dihydroxypropyl methacrylate, hydroxypoly(2-23)(oxypropylene)methacrylate, methoxypoly(2-23)(oxyethylene)methacrylate, 2-(perhalo(alkyl(C=6,8,10,12,14)))ethyl acrylate]	>8 PFCA precursor Not on DSL
70983-59-4	Poly(oxy-1,2-ethanediyl), $\alpha$ -methyl- $\omega$ -hydroxy-, 2-hydroxy-3-[( $\gamma$ - $\omega$ -perfluoro-C <sub>6-20</sub> -alkyl)thio]propyl ethers	> 8 PFCA precursor Not on DSL
A11863-1	Poly(alkyl acrylate-co-2-[perfluoro(alkyl(C=6,8,10,12,14)))ethyl acrylate-co-hydroxymethylcarbamoylene-co-(3-chloro-2-hydroxypropylmethacrylate)-co-(2,3-epoxypropyl methacrylate)-co-(2-ethylhexylmethacrylate)	> 8 PFCA precursor

CAS Registry Number	Chemical Name	Type of PFA
A13216-4	2-Propenoic acid, hexadecyl ester, polymer with $\alpha$ fluoro-[2-[(1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), octadecyl 2-propenoate, 1,1-dichloroethane, 2-hydroxyethyl 2-methyl-2-propenoate, N-(hydroxymethyl)-2-propenamide and $\alpha$ -(2-methyl-1-oxo-2-propenyl)-hydroxypoly(oxy-1,2-ethanediyl)	> 8 PFCA precursor
A13498-7	Polymer reaction product of poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-{(2-methyl-1-oxo-2-propenyl)-oxy}ethyl], 2-propenoic acid, 2-methyl, (diethylamino, ethylester, ethanoic acid, and 2,2-azobis) 2,4-dimethylvaleronitrile	> 8 PFCA precursor
A13887-0	Hexane, 1,6-diisocyanato-, polymer reaction product with $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly(difluoromethylene), $\alpha$ -methyl- $\omega$ -hydroxypoly(oxy-1,2 ethanediol), and water	> 8 PFCA precursor
A14064-6	Alkyl acrylate-perfluoroalkylethyl acrylate-substituted alkyl acrylic acid derivative-alkyl methacrylic acid derivative-vinyl halide copolymer	> 8 PFCA precursor
A15736-4	2-Propenoic acid, $\gamma$ - $\omega$ -.perfluoro-C8-C14-alkyl ester, polymer with perfluoro (C6-C12) alkyl ethyl methacrylate, stearylacrylate, N-methylolmethacrylamine, glycidylmethacrylate and vinylidene chloride	> 8 PFCA precursor

CAS Registry Number	Chemical Name	Type of PFA
No CAS identified	Trichloro(perfluoroalkylethyl)silane	> 8 PFCA precursor
N/A2	2-Oxepanone, polymer with 2,4-diisocyanato-1-methylbenzene, methyloxirane and oxirane, block, 1-decanol and 1H-imidazole-1-propanamine and $\gamma$ - $\omega$ -perfluoro C8-14 alc. blocked	> 8 PFCA precursor Fluoro acrylate polymers
34395-24-9	2-Propenoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyl ester	> 8 PFCA precursor Fluoro acrylate polymers Not on DSL
174125-96-3	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with $\delta$ - $\omega$ -perfluoro-C <sub>10-16</sub> -alkyl acrylate and vinyl acetate	> 8 PFCA precursor Not on DSL
182700-77-2	Siloxanes and silicones, di-Me, hydroxy-terminated, polymers with tetradecanedioic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-tricosafuoro-1-tridecanol-terminated	>8 PFCA precursor Not on DSL
118102-37-7	Alcohols, C8-14, $\gamma$ - $\omega$ --perfluoro, reaction products with epichlorohydrin, polyethylene glycol monomethyl ether and N,N',2-tris(6-isocyanatohexyl)imidodicarbonic diamide	>8 PFCA precursor Not on DSL
118102-38-8	Alcohols, C8-14, $\gamma$ - $\omega$ --perfluoro, reaction products with epichlorohydrin, tetrahydrofuran homopolymer and N,N',2-tris(6-isocyanatohexyl)imidodicarbonic	>8 PFCA precursor Not on DSL

CAS Registry Number	Chemical Name	Type of PFA
	diamide	
119973-85-2	2-Methyl-2-propenoic acid 3-chloro-2-hydroxypropyl ester polymer with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyl 2-propenoate, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl 2-propenoate, N-(hydroxymethyl)-2-propenamide, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-nonacosafluorohexadecyl 2-propenoate, octadecyl 2-propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-pentacosafuorotetradecyl 2-propenoate)	> 8 PFCA precursor Fluoro acrylate polymers Not on DSL
178233-67-5	2-Propenoic acid, C12-14-alkyl esters, polymers with Bu (1-oxo-2-propenyl)carbamate and $\delta$ - $\omega$ -perfluoro-C6-12-alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers Not on DSL
178535-23-4	Fatty acids, linseed oil, $\gamma$ - $\omega$ -perfluoro-C <sub>8-14</sub> -alkyl esters	> 8 PFCA precursor Other polymers Not on DSL
N/A	Fatty acids, canola oil, $\gamma$ - $\omega$ -perfluoro-C8-14-alkyl esters	> 8 PFCA precursor Other polymers

CAS Registry Number	Chemical Name	Type of PFA
N/A	Fatty acids, soya oil, $\gamma$ - $\omega$ -perfluoro-C8-14-alkyl esters	> 8 PFCA precursor Other polymers
N/A	Poly {styrene-co-{bis {3-[perfluoroalkyl(c=6,8,10,12,14,16)] -2-hydroxypropyl} maleate} -co-(ethyl methacrylate)-co-(methyl methacrylate)}	> 8 PFCA precursor Other polymers
N/A	Poly(octadecyl acrylate)-co-2-[perfluoro[alkyl(C=6,8,10,12,14)]]ethyl acrylate-co-hydroxymethylcarbamoyl ethylene-co-(3-chloro-2-hydroxypropyl methacrylate)-co-vinylchloride	> 8 PFCA precursor Fluoro acrylate polymers
N/A	Polysiloxanes, di-Me, Me hydrogen, reaction product with alcohols, C8-14, $\alpha$ - $\omega$ -perfluoro polyethylene glycol monoethyl ether	> 8 PFCA precursor Fluorotelomer alcohols
N/A	Polysiloxanes, Me hydrogen, reaction product with alcohols, C8-14, $\alpha$ - $\omega$ -perfluoro polyethylene glycol monomethyl ether and octene-1	> 8 PFCA precursor Fluorotelomer alcohols
375-95-1	Nonanoic acid, heptafluoro-	> 8 PFCA Perfluoro carboxylic acids Not on DSL
4149-60-4	Nonanoic acid, heptafluoro-, ammonium salt	> 8 PFCA Perfluoro carboxylic acids Not on DSL

CAS Registry Number	Chemical Name	Type of PFA
N/A2	2-Propenoic acid, butyl ester, polymer with 2-propenoic acid, 2-propenoic acid, 2-hydroxyethyl ester, perfluoro-C8-C14 alkyl esters and 2-(dimethylamino)ethanol	> 8 PFCA precursor Fluoro ester
N/A2	Hexane, 1,6-diisocyanato-, polymer reaction product with $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly(difluoromethylene), $\alpha$ -methyl- $\omega$ -hydroxypoly(oxy-1,2-ethanediol), and water	> 8 PFCA precursor Fluoro acrylate polymer
65530-65-6	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-[(1-oxooctadecyl)oxy]ethyl]-	> 8 PFCA precursor Fluoro ester Not on DSL
65605-59-6	2-Propenoic acid, 2-methyl-, dodecyl ester, polymer with $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene) and <i>N</i> -(hydroxymethyl)-2-propenamide	> 8 PFCA precursor Fluoro ester Not on DSL
DSL 132164	2-Propenoic acid, hexadecyl ester, polymer with $\alpha$ -fluoro- $\omega$ -[2-[(1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), 2-propenoic acid, octadecyl ester, 1,1-dichloroethane, 2-methyl-2-propenoic acid, 2-hydroxyethyl ester, 2-propenamide	> 8 PFCA precursor Fluoro acrylate polymers
126927-97-7	Hexane, 1,6-diisocyanato-, homopolymer, reaction products with $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly (difluoromethylene)	> 8 PFCA precursor Other polymers Not on DSL



CAS Registry Number	Chemical Name	Type of PFA
DSL 132175	2-Butanone, oxime, polymer reaction product with 1,6-diisocyanatohexane, $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl) poly(difluoromethylene), $\alpha$ -methyl- $\omega$ -hydroxypoly(oxy-1,2-ethanediyl), and water	> 8 PFCA precursor Other polymers
N/A	Ethene, 1,1-dichloro-, polymer with 2-ethylhexyl 2-propenoate, and $\alpha$ -fluoro- $\omega$ -[2[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene)	> 8 PFCA precursor Fluoro acrylate polymers
N/A	<i>N,N'</i> 2-Tris(6-isocyanatohexyl)imidodicarbonic diamide, $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly(difluoromethylene), oxiranemethanol and 1-octadecanol adduct	> 8 PFCA precursor
N/A	Polymeric reaction product of $\alpha$ -fluoro- $\omega$ -[2-[methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), 2-methyl-2-propenoic acid, (diethylamino) ethyl ester, ethanoic acid, and 2,2'-azobis[2,2'-azobis(2,4-dimethylvaleronitrile)]	> 8 PFCA precursor Fluoro acrylate polymers

CAS Registry Number	Chemical Name	Type of PFA
N/A	Hexane, 1,6-diisocyanato-, polymer reaction product with $\alpha$ -fluoro- $\omega$ -(2-hydroxyethyl)poly(difluoromethylidene), $\alpha$ -methyl- $\omega$ -hydroxypoly(oxy-1,2-ethanediol), and water	> 8 PFCA precursor
N/A	2-Propenoic acid, butyl acid, 2-hydroxyethyl ester, perfluoro-C8-C14 alkyl esters and 2-(dimethylamino)ethanol	> 8 PFCA precursor
N/A	Poly(difluoromethylene) $\alpha$ -fluoro- $\omega$ -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-, polymer with 2-ethylhexyl methacrylate and vinylidene chloride	> 8 PFCA precursor
678-39-7	1-Decanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluoro	Long-chain PFCA precursor
65530-61-2	Poly(difluoromethylene), $\alpha$ -fluoro- $\omega$ -[2-(phosphonooxy)ethyl]-	Long-chain PFCA precursor
70969-47-0	Thiols, C8-20, $\gamma$ - $\omega$ -perfluoro, telomers with acrylamide	Long-chain PFCA precursor

Abbreviations : DSL : Domestic Substance List; N/A. :not applicable; CAS : Chemical Abstracts Service

## APPENDIX II: Long-chain PFCA Precursor Identification

