

Ecological Screening Assessment Report

Long-chain (C9–C20) Perfluorocarboxylic Acids, their Salts and their Precursors

Environment Canada

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Synopsis

Under the *Canadian Environmental Protection Act, 1999* (CEPA 1999), the Ministers of the Environment and of Health conducted an ecological screening assessment of long-chain (C9–C20) perfluorocarboxylic acids (PFCAs), their salts and their precursors under sections 68 and 74 of CEPA 1999. In this assessment, the long-chain (C9–C20) perfluorocarboxylic acids will be referred to as long-chain PFCAs. Although the long-chain PFCAs themselves are not on Canada's Domestic Substances List (DSL), some precursors to long-chain PFCAs, which are present on the DSL, were categorized under section 73 of CEPA 1999. Assessment was undertaken in response to empirical evidence that demonstrated that some PFCAs are bioaccumulative, persistent, subject to long-range transport (via precursors), are widespread and show a trend toward increasing concentrations in Arctic wildlife.

This ecological assessment focuses on the PFCAs 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 PFCAs, were considered on the basis of their contribution to the total presence of long-chain PFCAs 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 PFCAs, 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 CEPA 1999 found that long-chain PFCAs were not reported to be manufactured or imported into Canada. However, in both surveys, several precursors to the long-chain PFCAs were reported to be imported into Canada.

In standard toxicity studies with aquatic organisms, long-chain PFCAs were of low to moderate toxicity, with acute toxicity values ranging from 8.8 to 285 mg/L. There are two studies on the toxicity of long-chain PFCAs in terrestrial species. In one study, no adverse effects were observed up to 1.0 mg/kg body weight for male chickens dosed three times/week for three weeks with C10 PFCA. In another study, exposure of C9 PFCA to a soil-dwelling nematode resulted in acute lethality at 306 mg/L and multi-generation effects (decreased fecundity) at 0.000464 mg/L.

There are other studies showing the potential for long-chain PFCAs to cause other types of effects. C9 and C10 PFCAs 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 PFCAs induced vitellogenesis in rainbow trout exposed for 14 days at 2.56×10^{-5} to 2 mg/g diet. C9 PFCA may cause oxidative stress in the common cormorant. C9 to C11 PFCAs activated the mammalian peroxisome proliferator-activated receptor α (PPAR α) in the livers of Baikal seals; PPAR α 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*, 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 PFCAs. 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 PFCAs would be persistent. Furthermore, long-chain PFCAs 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 PFCAs.

Empirical bioconcentration factors (BCFs) of > 5000 have been reported for C11, C12 and C14 PFCAs. Furthermore, empirical food-web data also indicate that there is a significant potential for biomagnification and/or trophic magnification in both water-breathing and air-breathing organisms for C9 to C14 PFCAs. There are no experimental or predicted bioaccumulation data available for long-chain PFCAs 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. However, the numeric criteria for bioaccumulation, outlined in the *Persistence and Bioaccumulation Regulations*, are based on bioaccumulation data for freshwater aquatic species (fish) only, and for substances that preferentially partition to lipids. As a result, the criteria may not completely reflect the bioaccumulation potential for the long-chain PFCAs that preferentially partition to the liver, blood and kidneys in terrestrial and marine mammals. Therefore, most long-chain PFCAs, their salts and their precursors do not meet the numeric criteria for bioaccumulation as outlined in the *Persistence and Bioaccumulation Regulations*.

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 wet weight, with concentrations greatest for polar bears, followed by Greenland shark, narwhals and beluga whales. Worldwide, C9 to C15 PFCAs have been reported in ringed, fur and harbour seals, dolphins (i.e., white-sided, bottlenose, white-beaked, humpback), finless porpoises, glaucous gulls, sperm whale, beavers, tigers, wild rats and several species of birds. 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 PFCAs in ringed seal livers from Greenland increased 3.3 and 6.8% per year for C10 and C11 PFCAs, respectively. From 1992 to 2005, the mean concentrations of C9 and C10 PFCAs 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 PFCAs. From 1993 to 2004, concentrations in ringed seal liver samples increased, with a

doubling time of 4 to 10 years for C9 to C12 PFCAs. In northern fulmar liver samples, C9 to C15 PFCA 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 PFCA concentrations from 1975 to 2004. Concentrations of C9 to C13 PFCAs 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 PFCAs from 1980 to 2010.

The assessment is based on a weight-of-evidence approach regarding persistence, bioaccumulation, the widespread occurrence, temporal trends in some species (i.e., Canadian Arctic birds, terrestrial and marine mammals), long-range transport and concentrations of long-chain PFCAs in the environment and biota (including remote areas of Canada).

Based on the available information, it is concluded that long-chain PFCAs, their salts and their precursors are entering or may enter 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. In addition, it is concluded that long-chain PFCAs and their salts are extremely persistent and meet the criteria for persistence as set out in the *Persistence and Bioaccumulation Regulations*. Long-chain PFCAs do not meet the criteria for bioaccumulation as set out in the *Persistence and Bioaccumulation Regulations*. Nevertheless, the weight of evidence is sufficient to conclude that long-chain PFCAs and their salts accumulate and biomagnify in terrestrial and marine mammals.

It is concluded that long-chain PFCAs, their salts and their precursors meet one or more of the criteria in section 64 of CEPA 1999.

Introduction

Under the *Canadian Environmental Protection Act, 1999* (CEPA 1999) (Canada 1999), the Minister of the Environment has conducted an ecological screening assessment of the long-chain perfluorocarboxylic acids (PFCAs), their salts and precursors under sections 68 and 74 of CEPA 1999. 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* (Environment Canada 2006). In 2004, Health Canada and Environment Canada assessed four fluorotelomer-based substances under the New Substances provisions of CEPA 1999. These substances were suspected of being "toxic," as they contained direct precursors to PFCAs and were deemed capable of degrading to PFCAs. Amendments to the *Prohibition of Certain Toxic Substances Regulations, 2005* were published in the *Canada Gazette, Part I*, on June 17, 2006 (Canada 2006). These amendments were made in order to establish regulations that would maintain the prohibitions on these new sources of PFCAs. In addition, the precursors, CAS RNs 65530-63-4, 65530-71-4, 65530-72-5, 65530-74-7, 68391-08-2, 68412-68-0, 115592-83-1, 65530-61-2, 70969-47-0, 65530-66-7, 65605-58-5, 65605-70-1, 65636-35-3, 68239-43-0 and 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 (DSL).

This ecological assessment focuses on the PFCAs with carbon chain lengths from 9 to 20 inclusive, their salts and their precursors. This range of carbon chain lengths corresponds to the range considered in the assessment under the New Substances program. Precursors were considered on the basis of their contribution to the total presence of long-chain PFCAs in the environment.

Data relevant to the screening assessment of long-chain PFCAs were identified in review and assessment documents, stakeholder research reports and literature searches, up to February 2011. 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 CEPA 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 CEPA 1999 (Canada 1999). The approach taken in this ecological screening assessment was to examine relevant scientific and technical information and develop conclusions based on multiple lines of evidence including a substance's persistence, bioaccumulation, toxicity, temporal trends in biota, 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 screening assessment was prepared by staff in the Existing Substances program at Environment Canada. This ecological assessment has undergone external written peer review/consultation. Additionally, the draft of this screening assessment was subject to a 60-day public comment period. Although external and public comments were taken into consideration, the final content and outcome of the screening risk assessment remain the responsibility of Environment Canada.

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

Substance Identity

This report assesses the long-chain (C9-C20) PFCAs, their salts and their precursors. 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. Long-chain PFCAs and their salts are a homologous series of substances with the molecular formula of $C_nF_{2n+1}CO_2H$ (where $8 \leq n \leq 20$). In this document, long-chain (C9–C20) perfluorocarboxylic acids will be referred to as “long-chain PFCAs.”

Long-chain PFCAs are not on the DSL and were not subject to the categorization provisions of CEPA 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 PFCAs that could transform or degrade to a C9–C20 PFCA, given similar use applications and similarities in their physical and 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 directly consider the potential additive effects of long-chain PFCAs and their precursors and their salts, it is recognized that the precursors and salts may contribute to the total presence of long-chain 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 PFCAs, salts or their precursors (see Appendix II: Long-chain PFCA Precursor Identification). The long-chain PFCA grouping was defined using expert judgment, chemical structures and biodegradation estimation modelling, using CATABOL (Mekenyan et al. 2002). Using these approaches, structures were analyzed for their potential to degrade to long-chain 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 than indicated by CATABOL 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.

The Organisation 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 are considered stable and are thus not included as PFCA precursors 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 PFCAs are 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 long-chain perfluorocarboxylic acids

Chemical Abstracts Index name	Acronym	Molecular formula	Structural formula	Chemical Abstracts Service Registry Number and DSL/NDSL	Synonyms
Nonanoic acid, heptafluoro- (C9 PFCA)	PFNA	C ₉ H F ₁₇ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_7-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	375-95-1 (NDSL)	C 1800; Heptafluorononanoic acid; Perfluorononanoic acid; Perfluoropelargonic acid
Decanoic acid, nonafluoro- (C10 PFCA)	PFDA	C ₁₀ H F ₁₉ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_8-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	335-76-2 (NDSL)	Nonafluoro-n-decanoic acid; Nonafluorodecanoic acid; Perfluoro-n-decanoic acid; Perfluorocapric acid; Perfluorodecanoic acid
Undecanoic acid, heneicosafluoro- (C11 PFCA)	PFUnDA	C ₁₁ H F ₂₁ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_9-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	2058-94-8 (not listed on NDSL or DSL)	Heneicosafluoroundecanoic acid; Perfluoroundecanoic acid; Perfluoroundecylic acid
Dodecanoic acid, tricosafluoro- (C12 PFCA)	PFDoDA	C ₁₂ H F ₂₃ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{10}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	307-55-1 (NDSL ¹)	Perfluorododecanoic acid; Perfluorolauric acid
Tridecanoic acid, pentacosafuoro- (C13 PFCA)	PFTrDA	C ₁₃ H F ₂₅ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{11}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	72629-94-8 (not listed on NDSL or DSL)	Perfluorotridecanoic acid
Tetradecanoic acid, heptacosafuoro- (C14 PFCA)	PFTDA	C ₁₄ H F ₂₇ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{12}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	376-06-7 (NDSL)	Perfluoromyristic acid; Perfluorotetradecanoic acid
Pentadecanoic acid, nonacosafuoro- (C15 PFCA)	PFPeDA	C ₁₅ H F ₂₉ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{13}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	141074-63-7 (not listed on NDSL or DSL)	Perfluoropentadecanoic acid

Chemical Abstracts Index name	Acronym	Molecular formula	Structural formula	Chemical Abstracts Service Registry Number and DSL/NDSL	Synonyms
Hexadecanoic acid, hentriacontafluoro- (C16 PFCA)	PFHxDA	C ₁₆ HF ₃₁ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{14}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	67905-19-5 (NDSL)	Perfluoropalmitic acid, perfluorohexadecanoic acid Hexadecanoic acid
Perfluoroheptadecanoic acid (C17 PFCA)	PFHpDA	C ₁₇ HF ₃₃ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{15}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	57475-95-3 (not listed on the NDSL or DSL)	—
Octadecanoic acid, pentatriacontafluoro- (C18 PFCA)	PFODA	C ₁₈ HF ₃₅ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{16}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	16517-11-6 (NDSL)	Perfluorostearic acid Perfluorooctadecanoic acid Octadecanoic acid
Perfluorononadecanoic acid (C19 PFCA)	PFNDA	C ₁₉ HF ₃₇ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{17}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	133921-38-7 (not listed on NDSL or DSL)	—
Perfluoroeicosanoic acid (C20 PFCA)		C ₂₀ HF ₃₉ O ₂	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{C}-(\text{CF}_2)_{18}-\text{CO}_2\text{H} \\ \\ \text{F} \end{array}$	68310-12-3 (NDSL)	Eicosanoic acid, nonatriacontafluoro- (9CI); Nonatriacontaeicosanoic acid

DSL = Domestic Substances List

NDSL = Non-Domestic Substances List. Substances not appearing on the DSL are considered to be new to Canada and are subject to notification. Substances listed on the NDSL are subject to notification but with reduced information requirements.

Physical and Chemical Properties

Information relating to the physical and chemical properties of long-chain PFCAs is limited. Table 2 shows the available physical and chemical data for the 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); however, no physical and chemical data are available for helical long-chain PFCAs.

Table 2. Available physical and chemical properties of long-chain PFCAs

Property	Value	Type	Reference
C9 PFCA			
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 ₄)		Benficemalouet 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 ¹
	1.3 g/L (critical micelle concentration)	Experimental	Kunieda and Shinoda 1976 ¹
pK _a (dimensionless)	< 0.8	Calculated	Goss 2008
log K _{oc} (dimensionless)	2.3–2.48	Experimental	Higgins and Luthy 2006
C10 PFCA			
Molecular mass (g/mol)	514.08	–	-
Melting point (°C)	87.4–88.2 (CCl ₄)	Experimental	Bernett and Zisman 1959
	87.4–88.2 (toluene)		Bernett and Zisman 1959
	83.5–85.5 (CCl ₄ , 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	3.1–99.97 kPa (129.6-218.9°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 ¹
	0.46 (critical micelle concentration at 30°C)		Klevens and Raison 1954 ¹
pKa (dimensionless)	2.58	Calculated	Moroi et al.2001
log K _{oc} (dimesionless)	2.65–2.87	Experimental	Higgins and Luthy 2006
C11 PFCA			
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	0.6–99.97 kPa (112-to 237.7°C)	Calculated	Kaiser et al. 2005
	-0.98	Experimental	Arp et al. 2006
log K _{oc} (dimesionless)	3.19–3.41	Experimental	Higgins and Luthy 2006
C12 PFCA			
Molecular mass (g/mol)	614.1	–	-
Melting point (°C)	112.6–114.7 (CCl ₄ , 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	0.9–99.96 kPa (127.6-to 247.7°C)	Calculated	Kaiser et al. 2005
C13 PFCA			
Molecular mass (g/mol)	664.0989	–	-

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

¹ 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 the addition of, for example, a mineral acid, the proportion of protonated acid will increase and the overall solubility will decrease.

Abbreviations: K_{oc} , sediment organic carbon coefficient; pK_a , acid dissociation constant.

Sources

There are no known natural sources of long-chain 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 CEPA 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 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 PFCAs were not reported to be manufactured or imported in Canada (Environment Canada 2005). In both surveys, between 1000 and 100 000 kg of precursors to the long-chain PFCAs were reported to be imported into Canada.

Uses

C9 PFCA is used for surfactant applications and in the production of fluoropolymers, primarily polyvinylidene fluoride (Prevedouros et al. 2006). Based on available information, long-chain PFCAs are rarely used intentionally in products. However, commonly used precursors that are present in commercial products, such as fluorotelomers, e.g., substances derived from fluorotelomer alcohols (FTOHs), or other fluorotelomer-based substances, can degrade to long-chain 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 through industrial use/manufacturing of long-chain PFCAs to the Canadian environment.

Indirect Releases

There is empirical evidence available regarding the degradation of fluorotelomer-based polymers into long-chain PFCAs. Fluorotelomer alcohols (FTOHs) with x number of carbons produces intermediates such as fluorotelomer unsaturated carboxylates ($x:2$ FTUCA) and fluorotelomer carboxylic acids ($x:2$ FTCA) that can further degrade to long-chain PFCAs. FTOHs can be biodegraded or metabolized to long-chain PFCAs as shown in various studies (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; 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). A small amount of C9 PFCAs was produced through a photo-induced hydrogen peroxide system (10 mM and 100 μ M solutions), demonstrating rapid degradation 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).

Recognition of FTOHs as potential sources of long-chain 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.

Yoo et al. (2010) measured FTOHs in soil from fields (near Decatur, Alabama) to which sewage sludge had been applied. Sludges generated at a wastewater treatment plant (WWTP) in Decatur, Alabama, have been applied to agricultural fields for more than a decade—this WWTP received waste streams from industries that worked with fluorotelomer compounds (Washington et al. 2010). Yoo et al. (2010) found that sludge-amended fields had surface soil FTOH concentrations ranging from 5 to 73 ng/g

dry weight. The highest FTOH concentration was 10:2 FTOH, which had concentrations ranging from < 5.6 to 166 ng/g. The half-lives for FTOHs ranged from 0.85 to 1.8 years, suggesting that sludge application is a possible pathway for the degradation of FTOHs to PFOA and other perfluorocarboxylic acids. Washington et al. (2010) also found that these sludge-amended fields have high concentrations of PFCAs, including C10 PFCA (< 990 ng/g) and C11 PFCA (< 530 ng/g). 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH have been measured in the air at two landfill sites in Ontario; concentrations were < 5000 pg/m³ (upwind) and ranged between 0 and < 25 000 pg/m³ for on-site (Ahrens et al. 2010a).

The relative abundance of linear vs. branched forms of PFCAs can provide some indication of their potential source. Linear PFCAs may reflect degradation largely from linear FTOHs and may indicate that the source of PFCAs originates from telomerization rather than electrochemical fluorination (a process that would produce about 20% branched isomers). It is further proposed 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 (De Silva and Mabury 2004; Ellis et al 2004b). 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. FTOHs have been shown to degrade to a relatively equal concentration of even-chain length and odd-chain length PFCAs (Ellis et al. 2004b), indicating the possibility for FTOHs as a source of PFCAs. The odd-chain length PFCAs are proposed 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 seem to indicate a single uniform source (Smithwick et al. 2005b; van de Vijver et al. 2005). FTOHs appear to be available to biota in the environment and are being metabolized, in vivo, to intermediates (other PFCA precursors) that 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. Linear isomers then 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) in which 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 residual¹ 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.

¹ 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.

The levels of long-chain PFCAs measured in Canadian urban aquatic compartments suggest indirect input sources, e.g., 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-chain-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-chain-length PFCAs over odd-chain-length PFCAs in WWTP effluent waters in plants in New York State.

WWTPs with simple primary treatment did not have releases of long-chain PFCAs. However, WWTPs that included secondary treatment increased the presence of long-chain 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 of FTOHs to long-chain 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 to 6 ng/L) and biosolids (concentrations ranging from 0.4 to 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 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 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. Gewurtz et al. (2009) found C9–C14 PFCAs as well as 8:2 FTUCA and 10:2 FTUCA in window films from indoor/outdoor/downtown/suburban/rural/carpet store locations in Toronto, Ontario. Floor waxes and stone/tile/wood sealants that contain fluorotelomer products are potential sources of C9 to C12 PFCAs in homes and commercial buildings containing these materials (Gewurtz et al. 2009; Guo et al. 2009). Other potential sources include treated home textile, upholstery and apparel and household carpet/fabric care liquids and foams (Guo et al. 2009). Nilsson et al. (2010) found C9–C11 PFCAs in the blood of ski wax technicians (concentrations ranged from 0.1 to 535 ng/L). Nilsson et al. (2010) suggested that fluorinated organic compounds are added to glide waxes to prevent adhesion of snow, ice and dirt. Fluorinated ski waxes are applied using heat of approximately 130–220°C, where airborne particles and fumes containing a blend of gaseous organochlorine compounds are emitted. However, the authors did not analyze the

glide waxes themselves to determine the presence of perfluorinated compounds. 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 in small amounts 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

Long-chain 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 (Table 2). Based on the K_{oc} values reported by Higgins and Luthy (2006) (Table 2), it is expected that some partitioning to sediment and soil is likely for C9–C11 PFCAs.

The presence of the acid functional group imparts a distinctive nature and character to the long-chain PFCAs. The acid functional group is hydrophilic and is completely dissociated in the aqueous phase at ambient pHs (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), 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). The calculated vapour pressures for C9–C12 PFCAs (Kaiser et al. 2005) suggest that these substances are volatile; however, significant volatilization under relevant environmental conditions is unlikely given that these substances are ionized at environmental pHs.

Persistence and Bioaccumulation Potential

Persistence

Although little empirical information on the degradation of long-chain PFCAs is available, 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).

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 (equivalent to a half-life of about 90 days) due to OH radical reactions, with a lifetime of the order of 10 days (equivalent to a half-life of about 7 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 days) is considerably greater than that estimated for removal of PFCAs from the atmosphere by wet/dry deposition (~ 10 days). In other words, even if PFCAs are formed in the atmosphere from FTOHs, they will not remain there long enough to be significantly degraded.

The presence of long-chain PFCAs in the Canadian Arctic (Martin et al. 2004a) indicates the long-range transport either of long-chain PFCAs (e.g., via air or ocean currents) (Wania 2007; Prevedouros et al. 2006) or of volatile precursors to long-chain PFCAs such as FTOHs (e.g., via atmospheric transport) or both (Wallington et al. 2006, Stock et al. 2007). Wania (2007) used simulations with the zonally averaged global fate and transport model Globo-POP, in combination with historical emission estimates for FTOHs, to evaluate the relative efficiency and importance of long-range transport pathways, whereas Wallington et al. (2006) used a three-dimensional global atmospheric chemistry model (IMPACT) to indicate that FTOHs degrade in the atmosphere to form C9 PFCA.

A suggested hypothesis for the presence of long-chain 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 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/m³, followed by 10:2 FTOH at 1.9–17 pg/m³ and then 6:2 FTOH at below detection limit to 6.0 pg/m³. Ellis et al. (2004a) suggested that the nature of PFCAs, e.g., their strong tendency to ionize, would likely cause them to be more prevalent in the aqueous phase, and they are not expected to partition significantly to the atmosphere. However, 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 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.

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 to 860 kg/year; C10 PFCA showed a flux ranging from 16 to 84 kg/year and C11 PFCA showed a flux ranging from 26 to 62 kg/year (Young et al. 2007).

Webster and Ellis (2010) further proposed sea spray as a mechanism for the generation of PFOA in the gas phase from PFO (its conjugate base) in a water body which has the potential to contribute large amounts of PFOA and PFCAs in general to the atmosphere and so significantly contribute to the concentrations measured in remote areas. The authors considered this mechanism comparable to global stack emissions to the atmosphere.

There is also a possibility that the presence of some perfluorinated compounds in the Canadian Arctic may, in part, be due to the presence of local sources—particularly former military bases (Iqaluit, Sarcpa Lake, Resolution Island) and/or Distant Early Warning Line (DEW) stations (northern shores of Alaska to Cape Dyer on the Baffin Island coast) that may have used perfluorinated-based products (Stow et al. 2005; Poland

et al. 2001). These sites are considered remediated but it is unknown whether perfluorinated compounds such as the long-chain PFCAs were found or measured, as the available literature (Stow et al. (2005) and Poland et al. (2001)) only identified the concentrations of polychlorinated biphenyls (PCBs) and metals during the remediation process. Regardless, measured concentrations of PFOA in biota or the environment appear to be far from possible local sources.

Therefore, based on the empirical as well as physical and chemical properties, long-chain PFCAs meet the persistence criteria in water, soil, sediment and air (half-lives in soil and water ≥ 182 days and half-life in sediment ≥ 365 days; half-life in air ≥ 2 days or evidence of atmospheric transport to remote regions such as the Arctic) as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000).

Bioaccumulation

PFCAs have the combined properties of oleophobicity, hydrophobicity and hydrophilicity over different portions of these molecules. The carboxylate functional group attached to the perfluorinated chain, for example, imparts polarity to the molecule. Due to these properties, the assumption that the hydrophobic and lipophilic interactions between compound and substrate are the main mechanisms governing partitioning is considered not applicable for long-chain PFCAs. Houde et al (2006b) indicate that there are no reported K_{ow} measurements for any long-chain PFCA, and the use of this physical property for estimation of bioaccumulation potential is considered unlikely to be useful because these substances can sit at the interphase between organic and aqueous phases rather than partition between the two phases. However, Webster and Ellis (2011) state that PFCAs, in general, are not surface-active and that the K_{ow} is a predictor of both lipid and protein partitioning in biota. Therefore, the authors state that the equilibrium distribution models for the hydrophobic neutral partitioning of PFCAs, including PFOA, are applicable.

Regulatory criteria (BCFs and BAFs) have been developed under CEPA 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 identify lipophilic substances with the potential to bioaccumulate primarily in freshwater aquatic systems. 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 $\log K_{ows}$ is only part of the overall weight of evidence in determining the overall potential of a substance to accumulate in organisms. Furthermore, a substance may be deemed to be sufficiently bioaccumulative to cause concern, even if regulatory criteria are not met.

Given the number of available experimental studies, the emphasis in this assessment has been placed on the results of experimental bioaccumulation and biomagnification studies.

Measures of bioaccumulation that 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 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. Similar to BMF, a TMF value exceeding 1 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, for neutral organic chemicals, 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.

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 2006).

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 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 normally 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 PFCAs or of indirect toxicity to organisms that consume prey containing long-chain 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 PFCAs, the site of toxic action is often considered to be the liver. Concerning the potential for toxicity to predator 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 PFCA 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 PFCA in the contaminated field sediment remained essentially constant. The biota-sediment accumulation factors (BSAF), wet weight (ww), were as follows: C9 PFCA (0.64–1.60), C10 PFCA (0.59–1.02), C11 PFCA (0.42–0.62) and C12 PFCA (0.42–0.55). The authors suggest that the long-chain PFCA may not have reached steady-state conditions.

Martin et al. (2003a, 2003b) used juvenile rainbow trout (*Oncorhynchus mykiss*), dietary exposure and a flow-through aqueous exposure using C9–C14 PFCA. 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, 2003b) 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–C14 PFCA 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 PFCA measured in the study (C9–C14 PFCA); lake trout / smelt BMFs ranged from 0.6 (C9 PFCA) to 2.2 (C14 PFCA); and lake trout/sculpin BMFs ranged from 0.1 (C9) to 0.4 (C13). The authors report that alewife make up 90% of lake trout prey, suggesting that lake trout/alewife results provide the best BMF estimates. Given that the other prey species accounted for 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 PFCAs, 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 PFCAs over the whole food web. Concentrations of C10, C11 and C13 PFCAs increased significantly within the pelagic food web, resulting in TMFs greater than 1 for C10, C11 and C13 PFCAs. Trophic magnification was greatest for C11 PFCA (4.7) and decreased for longer and shorter PFCAs alike. TMFs equal to 1 for C9, C12 and C14 PFCAs 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 mollissima*)—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 should likely be considered as 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 composed 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.

Jeon et al. (2010a) studied the effects of salinity on the bioaccumulation of perfluorinated compounds, including C10 and C11 PFCAs, in the Pacific oyster (*Crassostrea gigas*). With increasing salinity (10–34 practical salinity units or psu), the BCFs for C10 PFCA fluctuated between 23.9 and 94.4, whereas the BAFs increased from 75.5 to 212.8. With increasing salinity (10–34 psu), the BCFs for C11 PFCA fluctuated between 633.9 and 1652.7, whereas the BAFs increased from 954.6 to 2555.2. The authors suggest that the increased accumulation is mainly due to the increase in dietary uptake due to a possible altered physiology of oysters with changing salinity, which can increase the risks to benthic organisms and filter-feeding bivalves.

Jeon et al. (2010b) determined the BCFs of perfluorinated compounds on blackrock fish (*Sebastes schlegeli*) at varying salinities (10, 17.5, 25 and 34 psu). The bioconcentration at 34 psu was greater for the perfluorinated compounds than at other salinities. The serum BCFs for C10 PFCA ranged between 4321 and 5239 and the liver BCFs ranged from 667 to 811. The serum BCFs for C11 PFCA ranged between 13 553 and 16 370 and the liver BCFs ranged from 1070 to 1345. The authors suggest that the salting-out effect on the chemical activity of perfluorinated compounds can be significant at high salinity levels. Enhanced fugacity in salt water can force molecules to move to other phases such as the gill surface (a primary site for active transport), which might account for the increased BCFs with increasing salinity.

Kwadijk et al. (2010) determined the BAFs between water, sediment and eel (*Anguilla anguilla*) from 21 locations in the Netherlands. The BAF for C9 PFCA was calculated to be 2.52.

Tomy et al. (2009c) determined trophic-level-adjusted BMFs for C9–C11 PFCAs for a marine food web in the western Canadian Arctic (Hendrickson Island and Holman Island) composed 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 an Arctic copepod (*Calanus hyperboreus*). The trophic-level-adjusted BMFs ranged from 0.1 (C10 PFCA, Arctic cod / *Themisto libellula*) to 353 (C11 PFCA, 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–C12 PFCAs were measured in seawater, marine sediment, zooplankton (Sarasota Bay only; species not identified) and a variety of fish or marine mammal species: Atlantic croaker (*Micropogonias undulatus*), pinfish (*Lagodon rhomboides*), red drum (*Sciaenops ocellatus*), spotfish (*Leiostomus xanthurus*), spotted sea trout (*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 PFCA) to 3.7 (C10 PFCA), 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 PFCAs. 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 PFCAs, 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 PFCAs suggest that these PFCAs 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 PFCAs 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 PFCAs exceeded 1 for the dolphin food web, indicating that trophic magnification is occurring.

Martine 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 PFCAs were accumulating 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 PFCAs as they lack roots and receive their nutrients from the atmosphere. Lichen is a 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. 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 composed of three different species of zooplankton (*Calanis 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 PFCA (56–78 ng/g ww), C12 PFCA (4.7–8.2 ng/kg ww), C13 PFCA (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 BMFs for ringed seal liver–polar bear liver for C9–C15 PFCAs by grouping 11 populations of ringed seals to corresponding, 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 PFCA. However, there is the potential that long-chain PFCAs greater than C14 PFCA could accumulate or biomagnify in marine and/or terrestrial mammalian 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 greater ability to accumulate in organisms. C14 and C15 PFCAs 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).

Table 3. Summary of bioaccumulation data for long-chain PFCAs
(Italics and bold indicate BCF or BAF 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
C9 PFCA					
<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 ¹	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
Sea trout / 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 / sea trout (whole)	Field	Charleston, SC	BMF	2.1	Houde et al. 2006a
Pelagic food web ³	Field	Lake Ontario	TMF	1 ²	Martin et al. 2004b

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Bottlenose dolphin food web (dolphin plasma) ⁴	Field	Charleston, SC	TMF	4.7	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) ⁴	Field	Charleston, SC	TMF	2.4	Houde et al. 2006a
Cod (blood)	Field	Gulf of Gdansk, Poland	BAF ⁵	3000	Gulkowska et al. 2005
Common scoter / cod (blood)	Field	Gulf of Gdansk, Poland	BMF	0.83	Gulkowska et al. 2005
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)	0.7	Tomy et al. 2009c

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
			adjusted)		
Cod (liver) / <i>Themisto libellula</i> (whole body)	Field	Western Canadian Arctic	BMF (trophic level adjusted)	0.3	Tomy et al. 2009c
Water / sediment / eel	Field	The Netherlands	BAF	2.52	Kwadijk et al 2010
C10 PFCA					
<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 L/kg	Martin et al. 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 ¹	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
Sea trout / 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.

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
					2006a
Dolphin / sea trout (whole)	Field	Charleston, SC	BMF	2.4	Houde et al. 2006a
Pelagic food web ³	Field	Lake Ontario	TMF	3.7	Martin et al. 2004b
Bottlenose dolphin food web (dolphin plasma) ⁴	Field	Charleston, SC	TMF	3.4	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) ⁴	Field	Charleston, SC	TMF	22	Houde et al. 2006a
Ringed seal / polar bear (liver)	Field	Canadian Arctic	BMF	2.3	Butt et al. 2008
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
Seawater / Pacific oyster	Lab	Oyster farm, Korea	BCF	23.9–94.4	Jeon et al 2010a
<i>Chlorella ellipsoidea</i> /Pacific oyster	Lab	Oyster farm, Korea	BAF	75.5–212.8	Jeon et al 2010a
Seawater/Blackrock fish (liver)	Lab	Korea	BCF	708–811	Jeon et al 2010b
<i>Seawater / Blackrock fish (serum)</i>	<i>Lab</i>	<i>Korea</i>	<i>BCF</i>	<i>4321–5239</i>	<i>Jeon et al 2010b</i>
C11 PFCA					
<i>L. variegatus</i>	Lab/field	California, downstream WWTP	BSAF ww	0.42–0.62	Higgins et al. 2007

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Juvenile rainbow trout (carcass)	Lab	NA	BCF	2700 L/kg	Martin et al. 2003b
<i>Juvenile rainbow trout (blood)</i>	<i>Lab</i>	<i>NA</i>	<i>BCF</i>	<i>11 000 L/kg</i>	<i>Martin et al. 2003b</i>
Juvenile rainbow trout (liver)	Lab	NA	BCF	4900 L/kg	Martin et al. 2003b
Juvenile rainbow trout (carcass)	Lab	NA	BMF ¹	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
Sea trout / pinfish (whole)	Field	Charleston, SC	BMF	0.9	Houde et al. 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 / sea trout (whole)	Field	Charleston, SC	BMF	2.5	Houde et al. 2006a
Pelagic food web ³	Field	Lake Ontario	TMF	4.7	Martin et al., 2004b
Bottlenose dolphin food web (dolphin plasma) ⁴	Field	Charleston, SC	TMF	3	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) ⁴	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,	BMF	3.2	van den Heuvel- Greve et al. 2009

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
		Netherlands			
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 Canadian Arctic	BMF (trophic level adjusted)	229	Tomy et al. 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
Seawater / Pacific oyster	Lab	Oyster farm, Korea	BCF	633.9–1652.7	Jeon et al 2010a
<i>Chlorella ellipsoidea</i> / Pacific oyster	Lab	Oyster farm, Korea	BAF	954.6–2555.2	Jeon et al 2010a
Seawater / Blackrock fish (liver)	Lab	Korea	BCF	1070–1345	Jeon et al 2010b
<i>Seawater / Blackrock fish (serum)</i>	<i>Lab</i>	<i>Korea</i>	<i>BCF</i>	<i>13 553–16 370</i>	<i>Jeon et al 2010b</i>
C12 PFCA					

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
<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>	Lab	NA	BCF	18 000 L/kg	Martin et al. 2003b
<i>Juvenile rainbow trout (blood)</i>	Lab	NA	BCF	40 000 L/kg	Martin et al 2003b
<i>Juvenile rainbow trout (liver)</i>	Lab	NA	BCF	18 000 L/kg	Martin et al. 2003b
Juvenile rainbow trout (carcass)	Lab	NA	BMF ¹	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
Sea trout / 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
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 / sea trout (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
Sea trout / zooplankton (whole)	Field	Sarasota Bay, FL	BMF	35	Houde et al. 2006a
Sea trout / striped mullet (whole)	Field	Sarasota Bay, FL	BMF	0.4	Houde et al. 2006a

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
Sea trout / pigfish (whole)	Field	Sarasota Bay, FL	BMF	14	Houde et al. 2006a
Sea trout / sheephead (whole)	Field	Sarasota Bay, FL	BMF	0.2	Houde et al. 2006a
Sea trout / 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 ³	Field	Lake Ontario	TMF	1 ²	Martin et al. 2004b
Bottlenose dolphin food web (dolphin plasma) ⁴	Field	Charleston, SC	TMF	0.7	Houde et al. 2006a
Bottlenose dolphin food web (dolphin whole body) ⁴	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
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

Species, predator/prey, food web (tissue in brackets)	Study type	Location	Endpoint	Result	Reference
C13 PFCA					
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 ³	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
C14 PFCA					
<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 ¹	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
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 ³	Field	Lake Ontario	TMF	1 ²	Martin et al. 2004b

¹Martin 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.

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

³Organisms included mysid shrimp, alewife, rainbow smelt and lake trout.

⁴Organisms included striped mullet, pinfish, red drum, Atlantic croaker, spotfish, spotted sea trout and bottlenose dolphin.

⁵The 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.

For C11 ($2700 < \text{BCF} < 11\,000$), C12 ($18\,000 < \text{BCF} < 40\,000$) and C14 ($23\,000 < \text{BCF} < 30\,000$) PFCAs, there is empirical evidence that these substances are highly bioaccumulative in fish and have the potential for biomagnification in fish and marine mammals. Although C14 and C15 PFCAs have been found in fish, invertebrates

and polar bears, there are no experimental or predicted bioaccumulation data available for long-chain PFCAs greater than C14 PFCA. However, there remains the potential that long-chain PFCAs could accumulate or biomagnify in marine and/or terrestrial species based on chemical conformations (Wang and Ober 1999).

Based on the available empirical values, long-chain PFCAs and their salts do not meet the bioaccumulation criterion (BAF or BCF ≥ 5000) as set out in the *Persistence and Bioaccumulation Regulations* (Canada 2000). However, there is sufficient weight of evidence that long-chain PFCAs and their salts can accumulate and biomagnify in terrestrial and marine mammals.

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 in air (< 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 pg/m^3 (8:2 FTOH). The 8:2 and 10:2 FTUCAs were measured at mean concentrations of 0.06–0.07 pg/m^3 . C9 and C10 PFCAs were measured at mean concentrations of 0.4 pg/m^3 , while C11, C13 and C14 PFCAs were measured at mean concentrations ranging from 0.02 to 0.06 pg/m^3 . Shoeib et al. (2006) took 20 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 pg/m^3 , followed by 10:2 FTOH at 1.9–17 pg/m^3 and 6:2 FTOH at below detection to 6.0 pg/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 pg/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^3 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^3). 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/m³. 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 and 47 pg/m³.

As previously discussed, FTOHs may degrade to long-chain PFCAs; therefore, levels of FTOHs in the atmosphere may contribute to levels of long-chain 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 PFCAs (Ellis et al. 2004b), whereas aerobic biodegradation of FTOH tends to yield predominantly even-chain-length PFCAs (Dinglasan et al. 2004).

Water

Certain long-chain 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 FTFCAs 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 FTFCAs and FTUCAs in rainwater samples in Winnipeg, Manitoba.

Simcik and Dorweiler (2005) measured levels of certain long-chain 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 the 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 to 4.1 ng/L. C10 PFCA mean concentrations ranged from 1.1 to 19 ng/L and C11 PFCA concentrations ranged from 0.3 to 4.9 ng/L. C12 PFCA mean concentrations ranged from 0.2 to 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.

Scott et al. (2009) sampled 38 rivers (upstream and downstream of populated areas) across Canada for perfluorinated compounds during 2001 to 2008. C9 PFCA was present in most samples (< 0.008 to 2.26 ng/L), but the other long-chain PFCAs analyzed (C10 to C14 PFCAs) were not often detected. C10 PFCA ranged from 0.005 to 1.12 ng/L; C11 PFCA ranged from 0.004 to 0.61 ng/L; C12 PFCA ranged from 0.001 to 0.06 ng/L; and C14 PFCA ranged from < 0.004 to 2.69 ng/L. C13 PFCA was not detected. Most sites downstream of urban areas had higher concentrations than upstream sites. Background sites, such as glacial meltwater from British Columbia, had lower to non-detectable concentrations of long-chain PFCAs.

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 PFCAs were detected in the particulate phase and in the two deep water samples at 200 m and 3800 m. Dissolved-phase 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 the eastern part of the Beaufort Sea near Banks Island. Ahrens et al. (2010b) collected surface water samples from November 2 to December 30, 2008, along the latitudinal gradient from the North Sea (northern Europe) and Antarctica. C9 to C12 PFCA were measured in the dissolved-phase samples but not in the particulate phase. C10 PFCA was measured in concentrations ranging from < 0.005.5 to 0.037 ng/L. C9, C11, and C12 PFCAs were below the quantification limit. Del Vento et al. (2009) also measured snow concentrations in the Amundsen Gulf for C9–C11 PFCAs ranging from 0.035 to 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 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, 2005b, 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 PFCAs 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 PFCA). After 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 (*Notropis 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 PFCA) and decreased as the chain length increased. Stern (2009) measured C9–C11 PFCAs 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 to 7.97 ng/g ww for C9, 1.2 to 36.85 ng/g ww for C10 PFCA, and 7 to 2.25 ng/g ww for C11 PFCA. Butt et al. (2007a) noted a predominance of C11 to C15 PFCAs in Arctic seabirds, although the PFCA detected in most wildlife, e.g., ringed seals, is often C8 to C11 PFCAs. Powley et al. (2008) detected C9–C12 PFCAs in a variety of organisms from Banks Island (eastern edge of the Beaufort Sea in the Northwest Territories). Concentrations in zooplankton (*Calanis 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 PFCAs 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 to 47.6 ng/g ww; narwhal liver-based concentrations ranged from 11.71 to 50.78 ng/g ww; harp seal liver-based concentrations ranged from 2.93 to 12.78 ng/g ww; ringed seal liver-based concentrations ranged from 2.18 to 23.4 ng/g ww; and Greenland shark liver-based concentrations ranged from 17.76 to 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 PFCAs, and C14 PFCAs 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 PFCA. 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 PFCAs 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.

Delinsky et al. (2010) measured C10–C12 PFCAs in bluegill (*Lepomis macrochirus*), black crappie (*Pomoxis nigromaculatus*) and pumpkinseed (*Lepomis gibbosus*) from the Upper Mississippi River in Minnesota and from lakes in 81 major watersheds throughout Minnesota in 2007. Predominant land uses in these watersheds ranged from forested (86%), to developed (47%), to cultivated crops/hay/pasture lands (87%). C10–C12 PFCAs concentrations in fillets ranged from 2.13 to 15.0 ng/g in five sampling locations and were non-detectable in the remaining 16 sampling locations.

Worldwide, a number of studies have reported levels of certain long-chain PFCAs 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). K.I. van de Vijver et al. (2007) collected liver samples from harbour porpoises (*Phocena phocena relicta*) 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. K.I. van de Vijver et al. (2003) also have shown the presence of C9–C11 PFCAs 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 PFCAs 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 PFCAs 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 PFCAs 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*), tilapia (*Oreochromis* sp.) and Japanese seaperch (*Lateolabrax japonicus*) in Taiwan. C10 PFCA concentrations in the oysters ranged from 140 to 320 ng/g ww. Liver and fish muscle concentrations of C10 PFCA in tilapia were 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) attempted to measure 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 were 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–C12 PFCA, with mean concentrations ranging from 0.792 to 7.3 ng/mL. C9 and C10 PFCA 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 PFCA was found at 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 (Luciaciu 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–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, C12 and C13 PFCAs having the highest concentrations. Most PFCA concentrations in 1988 and/or 1993 (< 3 ng/g) were generally higher than in 1979 (< 1 ng/g) 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 1988 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 Σ PFCAs in thick-billed murre 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 murre 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 PFCA. 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) and 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 Σ 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 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 Σ 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 and 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). Lofstrand 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 ranging from 9 to 140 ng/g ww, followed by C12 PFCA, with concentrations ranging from ND to 81 ng/g ww. The Σ 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.

Increasing temporal trends in C9–C15 PFCA concentrations were found in peregrine falcon (*Falco peregrinus*) eggs from 1974 to 2007 (Holmström et al. 2010). Peregrine falcon eggs were collected in the southwest of Sweden. However, due to the low breeding success in the first 20 years, only a few eggs were collected and no eggs were collected between 1987 and 1991. Therefore, all eggs up to 1999 were analyzed individually. Eggs were pooled from the year 2000 and onward. C13 PFCA was detected as early as 1974 and was the most dominant PFCA, followed by C11 PFCA. Temporal trends increased exponentially through the years, although the rate of increase ranged from 5.6 (C13

PFCA) to 9% (C14 PFCA) per year. C11–C15 PFCA are showing a tendency to level off in the latest years.

Levels of PFCA 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 PFCA 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 between 1992 and 2005. No significant differences between sex were identified for any PFCA with either of the two populations. Overall, concentrations of the PFCA increased from 1993 to 2005; however, the increases in the most recent years were not statistically significant. Doubling times ranged from 10.0 (C9 PFCA) to 19.4 years (C12 PFCA). Butt et al. (2008) detected long-chain PFCA in liver samples from eleven ringed seal populations in the Canadian Arctic from 2002 to 2005. Concentrations of C9–C11 PFCA ranged from 1 to 10 ng/g ww, whereas those of C12–C15 PFCA were less than 1 ng/g ww. In addition, 8:2 and 10:2 FTUCA were analyzed in all populations; however, concentrations were less than the detection limit (not specified). 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–C12 PFCA 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 PFCA ranged from < 0.56 to 72 ng/g ww. In male and female Baikal seal serum, C9–C12 PFCA concentrations ranged from < 0.33 to 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 times 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 statistically significant differences were observed.

In the North American Arctic studies by De Silva and Mabury (2004) and Smithwick et al. (2005a), levels of long-chain PFCA in polar bear liver were found to be generally higher in the east (Greenland), with evidence of C9 and C10 PFCA 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 PFCA 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 Ittiqortoormiit (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 PFCAs from 1972 to 2002 (Smithwick et al. 2006).

Tomy et al. (2009a) measured the temporal trends of Σ PFCAs (C8–C12) in male beluga whales from Pangnirtung, Nunavut, which showed an annual increase of 1.8 +/- 0.5 ng/g ww for liver-based concentrations for the years 1980 to 2010. The Σ PFCAs (C8–C12) concentrations in the male beluga whales from Pangnirtung ranged from 2.4 to 171 ng/g ww. However, male beluga whales from Hendrickson Island showed a decline of 7.41 +/- 0.71 ng/g ww for liver-based concentrations for the years 1980 to 2009 (Tomy et al. 2009a). Concentrations for the Σ PFCAs (C8–C12) in the Hendrickson Island male beluga whales ranged from 4.87 to 313 ng/g ww.

O'Connell et al. (2010) analyzed 163 juvenile loggerhead turtle (*Caretta caretta*) plasma and serum samples for spatial and temporal trends of perfluorinated compounds. The turtles were captured within 8.4 km of the nearest shore from Charleston (South Carolina), Cape Canaveral (Florida), Core Sound (North Carolina), Chesapeake Bay (Maryland) and Florida Bay (Florida). C9–C14 PFCAs were detected in most plasma/serum samples (ranging from 0.034 to 16.04 ng/g). Spatially, there was an increasing northward trend, with Florida Bay turtles accumulating more C9 PFCA, suggesting local sources for turtles residing in Florida Bay. Temporal trends were examined over a nine-year period in loggerheads captured near Charleston. C9 PFCA concentrations decreased by 11% annually; however, the other long-chain PFCAs did not significantly change over time.

Ecological Effects Assessment

Aquatic Organisms

Boudreau et al. (2002) examined the toxicity of C10 PFCA on the aquatic macrophyte *Lemna gibba* and determined that the 7-day IC₅₀ (median inhibitory concentration) value (based on growth) was 99 mg/L. The 7-day IC₅₀ 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 PFCA on two species of water fleas, *Daphnia magna* and *Daphnia pulex*, were investigated. The acute 48-h median lethal concentration (LC₅₀) and 48-h median effects concentration (EC₅₀ – based on immobilization) values 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 96-h rainbow trout

(*Oncorhynchus mykiss*) LC₅₀ value of 32 mg/L, a 48-h EC₅₀ for *Daphnia magna* of > 100 mg/L, and a 72-h EC₅₀ for the green algae, *Pseudokirchneriella subcapitata*, of 10.6 mg/L.

Chronic toxicity studies of C9 PFCA on the two species of water fleas indicated greater sensitivity of *Daphnia pulicaria* versus *Daphnia magna* (Boudreau et al. 2002). The 21-day LC₅₀ 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-h EC₅₀ (based on acute lethality) for C9 PFCA 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 PFCA 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 PFCA 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 (kg-bw) 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-bw doses of C10 PFCA. However, the half-life for C10 PFCA at 0.1 and 1.0 mg/kg-bw doses was 11 and 16 days, respectively, indicating the bioaccumulative properties of C10 PFCA in chickens.

Other Effects

Stevenson et al. (2006) examined the toxicity of C9 and C10 PFCAs 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 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.

(2006) found that C9 and C10 PFCA had average IC_{50} s (based on p-glycoprotein inhibition) of 4.8 μ M (2.23 mg/L) and 7.1 μ M (3.65 mg/L), respectively, which significantly inhibited the p-glycoprotein in *Mytilus californianus*. This result indicates that C9 and C10 PFCA are chemosensitizers for this organism. C9 PFCA inhibits the p-glycoprotein by an indirect mechanism, and this inhibition is reversible. C9 PFCA 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_{10} , IC_{50} , and IC_{90} for cell density calculated were 90 μ M (46.27 mg/L), 183 μ M (94.08 mg/L) and 367 μ M (188.67 mg/L) for C10 PFCA, and 41 μ M (29.28 mg/L), 134 μ M (95.69 mg/L) and 292 μ M (208.52 mg/L) for C14 PFCA. For C10 PFCA, an enhancement of the mitochondrial membrane potential was observed between 30 and 100 μ M (15.42–51.40 mg/L). For C14 PFCA, an enhancement of the mitochondrial membrane potential was observed between 50 and 100 μ M (35.70–71.41 mg/L). The increase in mitochondrial membrane potential indicates damage to the mitochondrial function—mitochondria are multi-tasking organelles 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 μ M (12.28–61.41 mg/L) for C12 PFCA and 50–100 μ M (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.

Benninghoff et al. (2007) found that C9–C12 PFCA significantly induced vitellogenin, a biomarker of estrogen exposure, in rainbow trout in 14-day tests. C9–C12 PFCA demonstrated weak affinity to the rainbow trout hepatic estrogen receptor. In juvenile rainbow trout exposed *in vivo* to C10 PFCA at doses of < 1 to 2000 μ g/g diet, plasma vitellogenin was found to increase in a dose-dependent manner (with significant increases at concentrations as low as 0.0256 μ g/g diet). 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 PFCA concentrations were measured in the liver of wild common cormorants (male and female) and related to gene expression. C9 PFCA concentrations for females ranged from < 0.005 to 0.0088 μ g/g ww, and for males, concentrations ranged from < 0.005 to 0.043 μ g/g ww. Significant sex differences were not detected. Gene expression analysis showed significant positive relationships between C9 PFCA and glutathione peroxidase 1 (enzyme in the antioxidant system) and heterogenous nuclear ribonucleoprotein U (RNA processing). The authors suggest that the induction of the antioxidant enzymes may be an adaptive response to oxidative stress caused by C9 PFCA.

Ishibashi et al. (2008a) showed that C9–C11 PFCAs induced peroxisome proliferator-activated receptor α (PPAR α) in Baikal seal (*Pusa sibirica*) livers at lowest-observed-effect-concentrations of 125 μ M (58.00 mg/L) (C9 PFCA), 125 μ M (64.26 mg/L) (C10 PFCA), and 62.5 μ M (35.25 mg/L) (C11 PFCA). PPAR α plays a critical physiological role as a lipid sensor and a regulator in lipid metabolism. Expression levels of PPAR α 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 α -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). Liver parameters examined 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 compounds including C9, C10, C11, C12 and C13 PFCAs. Sixty-five percent of the polar bears had Σ PFA concentrations above 1000 ng/g ww. In female bears, the Σ PFA ranged from 256 to 2770 ng/g ww, and in male bears the Σ 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).

In another study by Flanary et al. (2010), no correlations were found between C9–C13 PFCAs and blood chemistry parameters (e.g., cholesterol, creatinine, albumin, total serum ion) for the northern fur seal (*Callorhinus ursinus*).

Characterization of Ecological Risk

The approach taken in this ecological screening assessment was to examine relevant scientific and technical information and develop conclusions based on multiple lines of evidence including consideration of persistence, exposure, temporal trends in biota, toxicity, bioaccumulation and widespread occurrence in the environment.

In traditional toxicity studies (e.g., lethality, growth), several long-chain 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 PFCAs in terrestrial species. In one study, no adverse effects were observed up to 1.0 mg/kg-bw for male chickens dosed with C10 PFCA three times per week for three weeks. 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 PFCAs to cause hepatotoxicity in polar bears at 114–3052 ng/g ww total PFAs—based on associations observed in field studies—and the activation of the PPAR α in Baikal seal livers at 35.25–64.26 mg/L C9–C11 PFCAs—based on data from *in vitro* laboratory studies. There is also the potential for long-chain PFCAs to affect endocrine function, e.g., vitellogenesis in rainbow trout at 0.0256–2000 μ g/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.

Certain long-chain 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–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–C15 PFCAs 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 night herons). Concentrations ranged from below detection levels to 480 ng/g ww, with concentrations highest in the white-beaked dolphin.

All long-chain PFCAs are considered to be persistent. For C11 (2700 < BCF < 11 000), C12 (18 000 < BCF < 40 000), and C14 (23 000 < BCF < 30 000) PFCAs, there is empirical evidence that these substances are highly bioaccumulative in fish and have the potential for biomagnification in fish and marine mammals. 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 accumulate 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 PFCA concentrations 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 times 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 PFCAs. From 1993 to 2004, concentrations in ringed seal liver samples increased, with a doubling time of 4 to 10 years for C9 to C12 PFCAs. In northern fulmar liver samples, C9 to C15 PFCA 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 PFCAs concentrations from 1975 to 2004. Concentrations of C9 to C13 PFCAs increased significantly in whole eggs of

herring gulls in Norway from 1983 to 1993. Annual temporal increases of C9–C12 PFCAs were observed in male beluga whales from Nunavut at 1.8 ng/g ww liver from 1980 to 2010.

The presence of long-chain PFCAs, their salts and their precursors results from anthropogenic activity. The long-chain PFCAs and their salts are persistent. There is empirical evidence that long-chain PFCAs can accumulate to a significant extent and biomagnify in marine and terrestrial mammals. 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 PFCAs and their precursors have been detected in biota over wide areas 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. Based on the above, it is concluded that long-chain PFCAs their salts and their precursors have the potential to cause ecological harm.

Uncertainties in Evaluation of Ecological Risk

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

Environmental pathways of long-chain 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. The mechanisms of toxic action of long-chain PFCAs are not well understood; however, 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 assessment is based on a weight-of-evidence approach regarding persistence, bioaccumulation, the widespread occurrence, temporal trends in some species (i.e., Canadian Arctic birds, terrestrial and marine mammals), long-range transport and

concentrations of long-chain (C9–C20) PFCAs in the environment and biota (including remote areas of Canada).

Based on the information presented in this screening assessment, it is concluded that long-chain (C9–C20) PFCAs, their salts and their precursors are entering or may enter 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. In addition, it is concluded that long-chain (C9–C20) PFCAs and their salts are extremely persistent and meet the criteria for persistence as set out in the *Persistence and Bioaccumulation Regulations*. Long-chain (C9–C20) PFCAs do not meet the criteria for bioaccumulation as set out in the *Persistence and Bioaccumulation Regulations*. Nevertheless, the weight of evidence is sufficient to conclude that long-chain (C9–C20) PFCAs and their salts accumulate and biomagnify in terrestrial and marine mammals.

It is, therefore, concluded that long-chain (C9–C20) PFCAs, their salts, and their precursors meet one or more of the criteria in section 64 of CEPA 1999.

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.

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Appendix 1 - LIST OF LONG-CHAIN (C9–C20) PFCAs, THEIR SALTS AND THEIR PRECURSORS (this list is not considered exhaustive)

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

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 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 α,α' -[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω -fluoropoly(difluoromethylene)] (1:1)	> 8 PFCA precursor Fluoro phosphates
65530-69-0	Poly(difluoromethylene), α -[2-[(2-carboxyethyl)thio]ethyl]- ω -fluoro-, lithium salt	> 8 PFCA precursor Fluoro thioether
65530-70-3	Poly(difluoromethylene), α,α' -[phosphinicobis(oxy-2,1-ethanediyl)]bis[ω -fluoro-, ammonium salt	> 8 PFCA precursor Fluoro phosphates
65530-71-4	Poly(difluoromethylene), α -fluoro- ω -[2-(phosphonooxy)ethyl]-, monoammonium salt	> 8 PFCA precursor Fluoro phosphates
65530-72-5	Poly(difluoromethylene), α -fluoro- ω -[2-(phosphonooxy)ethyl]-, diammonium salt	> 8 PFCA precursor Fluoro phosphates

CAS Registry Number	Chemical Name	Type of PFA
65530-74-7	Ethanol, 2,2'-iminobis-, compd. with α -fluoro- ω -[2-(phosphonooxy)ethyl]poly(difluoromethylene) (1:1)	> 8 PFCA precursor Fluoro phosphates
65530-83-8	Poly(difluoromethylene), α -[2-[(2-carboxyethyl)thio]ethyl]- ω -fluoro-	> 8 PFCA precursor Fluoro thioether
65545-80-4	Poly(oxy-1,2-ethanediyl), α -hydro- ω -hydroxy-, ether with α -fluoro- ω -(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(<i>or</i> 3)-[(γ - ω -perfluoro-C ₆₋₂₀ -alkyl)thio] derivs.	> 8 PFCA precursor Fluoro thioether
68187-47-3	1-Propanesulfonic acid, 2-methyl-, 2-[[1-oxo-3-[(γ - ω -perfluoro-C ₄₋₁₆ -alkyl)thio]propyl]amino] derivs., sodium salts	> 8 PFCA precursor Fluoro thioether
68391-08-2	Alcohols, C ₈₋₁₄ , γ - ω -perfluoro	> 8 PFCA precursor Fluorotelomer alcohol
68412-68-0	Phosphonic acid, perfluoro-C ₆₋₁₂ -alkyl derivs.	> 8 PFCA precursor Fluoro phosphates
68412-69-1	Phosphinic acid, bis(perfluoro-C ₆₋₁₂ -alkyl) derivs.	> 8 PFCA precursor Fluoro phosphates
68891-05-4	Ethene, tetrafluoro-, homopolymer, α -fluoro- ω -(2-hydroxyethyl)-, citrate, reaction products with 1,6-diisocyanatohexane	> 8 PFCA precursor

CAS Registry Number	Chemical Name	Type of PFA
86508-42-1	Perfluoro compounds, C ₅₋₁₈	> 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 -heneicosaf fluoro-	> 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 -heneicosaf luorododecyl 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- nonacosaf luorohexadecyl 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-pentacosaf luorotetradecyl 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 -heneicosaf luorododecyl 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-pentacosaf luoro-	> 8 PFCA precursor Fluorotelomer alcohol
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- trtriacontaf luorooctadecyl ester	> 8 PFCA precursor Fluoro acrylates

CAS Registry Number	Chemical Name	Type of PFA
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, 20-heptatriacontafluoro-	> 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, 20-heptatriacontafluoroecicosyl 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- tritriacontafluoro-	> 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, <i>N</i> -(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- propenoate and 3,3,4,4,5,5,6,6,7,7,8,8,8- tridecafluorooctyl 2-propenoate	> 8 PFCA precursor Fluoro acrylate polymers
85631-54-5	2-Propenoic acid, γ - ω -perfluoro-C ₈₋₁₄ -alkyl esters	> 8 PFCA precursor Fluoro acrylates

CAS Registry Number	Chemical Name	Type of PFA
144031-01-6	2-Propenoic acid, dodecyl ester, polymers with Bu (1-oxo-2-propenyl)carbamate and γ - ω -perfluoro-C ₈₋₁₄ -alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers
65530-59-8	Poly(difluoromethylene), α -fluoro- ω -(2-hydroxyethyl)-, 2-hydroxy-1,2,3-propanetricarboxylate (3:1)	> 8 PFCA precursor Fluoro carboxylate
65530-66-7	Poly(difluoromethylene), α -fluoro- ω -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]-	> 8 PFCA precursor Fluoro acrylates
65605-56-3	Poly(difluoromethylene), α -fluoro- ω -(2-hydroxyethyl)-, dihydrogen 2-hydroxy-1,2,3-propanetricarboxylate	> 8 PFCA precursor Fluoro carboxylate
65605-57-4	Poly(difluoromethylene), α -fluoro- ω -(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 α -fluoro- ω -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene)	> 8 PFCA precursor Fluoro acrylate polymers
65605-70-1	Poly(difluoromethylene), α -fluoro- ω -[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, α -fluoro- ω -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), 2-hydroxyethyl 2-methyl-2-propenoate and <i>N</i> -(hydroxymethyl)-2-propenamamide	> 8 PFCA precursor Fluoro acrylate polymers

CAS Registry Number	Chemical Name	Type of PFA
68239-43-0	2-Propenoic acid, 2-methyl-, 2-ethylhexyl ester, polymer with α -fluoro- ω -[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), α -[2-(acetyloxy)-2-[(carboxymethyl)dimethylammonio]ethyl]- ω -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 α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene)	> 8 PFCA precursor Fluoro urethane
123171-68-6	Poly(difluoromethylene), α -[2-(acetyloxy)-3-[(carboxymethyl)dimethylammonio]propyl]- ω -fluoro-, hydroxide, inner salt	> 8 PFCA precursor Fluoro alcohol derivatives
125328-29-2	2-Propenoic acid, 2-methyl-, C ₁₀₋₁₆ -alkyl esters, polymers with 2-hydroxyethyl methacrylate, Me methacrylate and perfluoro-C ₈₋₁₄ -alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers
129783-45-5	2-Propenoic acid, 2-methyl-, C ₁₀₋₁₆ -alkyl esters, polymers with 2-hydroxyethyl methacrylate, Me methacrylate and γ - ω -perfluoro-C ₈₋₁₄ -alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers
148878-17-5	2-Propenoic acid, 2-methyl-, C ₂₋₁₈ -alkyl esters, polymers with α -fluoro- ω -[2-[(1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene) and vinylidene chloride	> 8 PFCA precursor Fluoro ester (<i>Not on DSL</i>)

CAS Registry Number	Chemical Name	Type of PFA
70983-60-7	1-Propanaminium, 2-hydroxy- <i>N,N,N</i> -trimethyl-, 3-[(γ - ω -perfluoro-C ₆₋₂₀ -alkyl)thio] derivs., chlorides	> 8 PFCA precursor (<i>Not on DSL</i>)
148240-84-0	1,3-Propanediol, 2,2-bis[[(γ - ω -perfluoro-C ₄₋₁₀ -alkyl)thio]methyl] derivs., phosphates	> 8 PFCA precursor (<i>Not on DSL</i>)
203743-03-7	2-Propenoic acid, 2-methyl-, hexadecyl ester, polymers with 2-hydroxyethyl methacrylate, γ - ω --perfluoro-C ₁₀₋₁₆ -alkyl acrylate and stearyl methacrylate	> 8 PFCA precursor (<i>Not on DSL</i>)
277752-44-0	3-cyclohexene-1-carboxylic acid, 6-[(di-2-propenylamino)carbonyl](1R, 6R), reaction products with pentafluoroethane-tetrafluoroethylene telomer, ammonium salts	> 8 PFCA precursor (<i>Not on DSL</i>)
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, (<i>Not on DSL</i>)
333784-44-4	Poly[3-chloro-2-hydroxypropyl methacrylate, 2,3-dihydroxypropyl methacrylate, hydroxypoly(2-23)(oxypropylene)methacrylate, methoxypoly(2-23)(oxyethylene)methacrylate,	> 8 PFCA precursor (<i>Not on DSL</i>)

CAS Registry Number	Chemical Name	Type of PFA
	2-(perhalo(alkyl(C=6,8,10,12,14)))ethyl acrylate]	
70983-59-4	Poly(oxy-1,2-ethanediyl), α -methyl- ω -hydroxy-, 2-hydroxy-3-[(γ - ω -perfluoro-C ₆₋₂₀ -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-hydroxymethylcarbamoyl ethylene-co-(3-chloro-2-hydroxypropylmethacrylate)-co-(2,3-epoxypropyl methacrylate)-co-(2-ethylhexylmethacrylate)	> 8 PFCA precursor
A13216-4	2-Propenoic acid, hexadecyl ester, polymer with α 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-propenamamide and α -(2-methyl-1-oxo-2-propenyl)-hydroxypoly(oxy-1,2-ethanediyl)	> 8 PFCA precursor

CAS Registry Number	Chemical Name	Type of PFA
A13498-7	Polymer reaction product of poly(difluoromethylene), α -fluoro- ω -[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 α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene), α -methyl- ω -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, γ - ω -perfluoro-C8-C14-alkyl ester, polymer with perfluoro (C6-C12) alkyl ethyl methacrylate, stearylacrylate, N-methylolmethacrylamine, glycidylmethacrylate and vinylidene chloride	> 8 PFCA precursor
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 γ - ω -perfluoro C8-14 alc. blocked	> 8 PFCA precursor Fluoro acrylate polymers

CAS Registry Number	Chemical Name	Type of PFA
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 (<i>Not on DSL</i>)
174125-96-3	2-Propenoic acid, 2-methyl-, 2-(dimethylamino)ethyl ester, polymers with δ - ω -perfluoro-C ₁₀₋₁₆ -alkyl acrylate and vinyl acetate	> 8 PFCA precursor (<i>Not on DSL</i>)
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 (<i>Not on DSL</i>)
118102-37-7	Alcohols, C8-14, γ - ω --perfluoro, reaction products with epichlorohydrin, polyethylene glycol monomethyl ether and N,N',2-tris(6-isocyanatohexyl)imidodicarbonic diamide	> 8 PFCA precursor (<i>Not on DSL</i>)
118102-38-8	Alcohols, C8-14, γ - ω --perfluoro, reaction products with epichlorohydrin, tetrahydrofuran homopolymer and N,N',2-tris(6-isocyanatohexyl)imidodicarbonic diamide	> 8 PFCA precursor (<i>Not on DSL</i>)

CAS Registry Number	Chemical Name	Type of PFA
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-heneicosafluorododecyl 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-propenamamide, 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-nonacosafiuorohehexadecyl 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-pentacosafiuorotetradecyl 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 δ - ω -perfluoro-C6-12-alkyl acrylate	> 8 PFCA precursor Fluoro acrylate polymers (Not on DSL)
178535-23-4	Fatty acids, linseed oil, γ - ω -perfluoro-C ₈₋₁₄ -alkyl esters	> 8 PFCA precursor Other polymers (Not on DSL)
N/A	Fatty acids, canola oil, γ - ω -perfluoro-C8-14-alkyl esters	> 8 PFCA precursor Other polymers
N/A	Fatty acids, soya oil, γ - ω -perfluoro-C8-14-alkyl esters	> 8 PFCA precursor Other polymers

CAS Registry Number	Chemical Name	Type of PFA
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, α - ω -perfluoro polyethylene glycol monoethyl ether	> 8 PFCA precursor Fluorotelomer alcohols
N/A	Polysiloxanes, Me hydrogen, reaction product with alcohols, C8-14, α - ω -perfluoro polyethylene glycol monomethyl ether and octene-1	> 8 PFCA precursor Fluorotelomer alcohols
375-95-1	Nonanoic acid, heptadecafluoro-	> 8 PFCA Perfluoro carboxylic acids (<i>Not on DSL</i>)
4149-60-4	Nonanoic acid, heptadecafluoro-, ammonium salt	> 8 PFCA Perfluoro carboxylic acids (<i>Not on DSL</i>)
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

CAS Registry Number	Chemical Name	Type of PFA
N/A2	Hexane, 1,6-diisocyanato-, polymer reaction product with α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene), α -methyl- ω -hydroxypoly(oxy-1,2-ethanediol), and water	> 8 PFCA precursor Fluoro acrylate polymer
65530-65-6	Poly(difluoromethylene), α -fluoro- ω -[2-[(1-oxooctadecyl)oxy]ethyl]-	> 8 PFCA precursor Fluoro ester (<i>Not on DSL</i>)
65605-59-6	2-Propenoic acid, 2-methyl-, dodecyl ester, polymer with α -fluoro- ω -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene) and <i>N</i> -(hydroxymethyl)-2-propenamide	> 8 PFCA precursor Fluoro ester (<i>Not on DSL</i>)
DSL 132164	2-Propenoic acid, hexadecyl ester, polymer with α -fluoro- ω -[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 α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene)	> 8 PFCA precursor Other polymers (<i>Not on DSL</i>)
DSL 132175	2-Butanone, oxime, polymer reaction product with 1,6-diisocyanatohexane, α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene), α -methyl- ω -hydroxypoly(oxy-1,2-ethanediol), and water	> 8 PFCA precursor Other polymers

CAS Registry Number	Chemical Name	Type of PFA
N/A	Ethene, 1,1-dichloro-, polymer with 2-ethylhexyl 2-propenoate, and α -fluoro- ω -[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, α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylene), oxiranemethanol and 1-octadecanol adduct	> 8 PFCA precursor
N/A	Polymeric reaction product of α -fluoro- ω -[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
N/A	Hexane, 1,6-diisocyanato-, polymer reaction product with α -fluoro- ω -(2-hydroxyethyl)poly(difluoromethylidene), α -methyl- ω -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

CAS Registry Number	Chemical Name	Type of PFA
N/A	Poly(difluoromethylene) α -fluoro- ω -[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), α -fluoro- ω -[2-(phosphonooxy)ethyl]-	Long-chain PFCA precursor
70969-47-0	Thiols, C8-20, γ - ω -perfluoro, telomers with acrylamide	Long-chain PFCA precursor

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

APPENDIX 2: Long-chain PFCA Precursor Identification

