SCIENTIFIC CRITERIA DOCUMENT FOR THE DEVELOPMENT OF THE CANADIAN WATER QUALITY GUIDELINES FOR THE PROTECTION OF AQUATIC LIFE

Perfluorooctanoic Acid (PFOA)

NOTE TO READER

The Canadian Council of Ministers of the Environment (CCME) is the primary minister-led intergovernmental forum for collective action on environmental issues of national and international concern.

This document was prepared by the National Guidelines and Standards Office of Environment and Climate Change Canada (ECCC). It provides background information, rationale, and technical documentation for the development of the Canadian Water Quality Guidelines for Perfluorooctanoic Acid (PFOA).

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AFFF	aqueous film-forming foam
AIC	Akaike information criterion
APFO	ammonium perfluorooctanoate
CALA	Canadian Association for Laboratory Accreditation
CAS RN	Chemical Abstracts Service registry number
CEPA	*Canadian Environmental Protection Act*
CCME	Canadian Council of Ministers of the Environment
CMC	critical micelle concentration
CWQG	Canadian Water Quality Guideline
ECCC	Environment and Climate Change Canada
EC_x	effect concentration (affecting x% of the test organisms)
HC_5	hazard concentration for the fifth percentile
IC_x	inhibitory concentration
ISO	International Organization for Standardization
K_{OW}	octanol-water partition coefficient
LC-MS/MS	liquid chromatography tandem mass spectrometry
LC_x	lethal concentration (for x% of the test organisms)
LOEC	lowest observed effect concentration
MATC	maximum acceptable toxicant concentration
MLE	maximum likelihood estimation
NOEC	no observed effect concentration
OMOECC	Ontario Ministry of Environment and Climate Change (currently Ontario Ministry of Environment, Conservation and Parks)
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substances
PFCA	perfluorocarboxylic acid
PFO	perfluorooctanoate
PFOA	perfluorooctanoic acid
SAR	screening assessment report
SSA	sea spray aerosol
SSD	species sensitivity distribution
U.S. EPA	United States Environmental Protection Agency

EXECUTIVE SUMMARY

Perfluorooctanoic acid (PFOA; Chemical Abstracts Service Registry Number [CAS RN] 335-67-1) is an anthropogenic substance with a chain length of eight carbons, seven of which are perfluorinated. It belongs to a class of chemicals known as perfluorocarboxylic acids (PFCAs), which is under the broader class of per- and polyfluoroalkyl substances (PFAS). PFOA and its salts have been used in industrial processes and in commercial and consumer products, including as polymerization aids in the production of fluoropolymers and fluoroelastomers. PFOA is currently prohibited from being manufactured in Canada and is not known to have been manufactured in Canada in the past; however, it can enter through the importation of manufactured items. Releases to the environment can occur directly via industrial and consumer use of products containing PFAS, including the application of fire-fighting foams, from wastewater effluents and landfill leachates, or via the long-range transport of PFOA or its precursors.

In 2012, the Government of Canada's Screening Assessment Report (SAR) concluded that PFOA, its salts and its precursors meet the criteria to be declared toxic to the environment as defined under section 64 of the *Canadian Environmental Protection Act* (CEPA) (Environment Canada and Health Canada [EC and HC] 2012a). Additionally, PFOA and its salts were identified as being persistent as well as having the potential to accumulate and biomagnify in terrestrial and marine mammals. The manufacture, use, sale, offer for sale and import of PFOA, its salts and its precursors, including products containing these substances, were prohibited with some exemptions (Environment and Climate Change Canada and Health Canada [ECCC and HC] 2016).

PFOA has high water solubility and low volatility in the ionized form, and as a result is expected to partition primarily to the aquatic environment (EC and HC 2012a). Once in the water column, PFOA is considered to be stable owing to the strong carbon-fluorine bond that is resistant to breakdown via hydrolysis, photolysis or biodegradation. PFOA may undergo long-range transport, particularly via ocean currents, and has been detected in the Canadian Arctic. Concentrations of PFOA in the ambient environment are generally low; however, greater amounts of anthropogenic activity may contribute to elevated concentrations, and levels are higher in areas with known point-sources of pollution.

Canadian Water Quality Guidelines (CWQG) for the Protection of Aquatic Life are important tools supporting the evaluation of ambient water quality. Long-term guidelines are derived to protect all forms of aquatic life over an indefinite exposure period, including the most sensitive life stage of the most sensitive species (Canadian Council of Ministers of the Environment [CCME] 2007). The CWQG represents the level of PFOA below which no direct impacts on the ecosystem are expected. Environmental concentrations of PFOA can be compared with the CWQG to help assess whether ambient concentrations may pose a risk to aquatic life. Short-term benchmark values are estimators of severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe but transient situations (CCME 2007).

The development of the freshwater short-term benchmark and of the long-term Canadian Water Quality Guideline for PFOA followed the CCME *Protocol for Derivation of Water Quality Guidelines for the Protection of Aquatic Life* (CCME 2007). Their derivation considered toxicity data for the acid (CAS RN 335-67-1), its conjugate base, branched PFOA and PFOA's principal salt forms. The guidelines do not apply to precursors of PFOA, nor do they apply to commercial mixtures containing PFOA as these mixtures may not be well characterized and could include products with varying amounts of PFOA. Additionally, the protocol does not address exposure through food or bioaccumulation to higher trophic levels. A statistical (or Type A) approach was used for guideline derivation in which a species sensitivity distribution (SSD) of acceptable toxicity data were fit to several regression models. The guideline is defined as the intercept of the fifth percentile of the y-axis with the fitted weighted average SSD curve. The freshwater short-term benchmark and long-term CWQG are presented in Table 1. Insufficient data were available to meet CCME minimum data requirements for guidelines for the protection of marine life.

Table 1. Short-term benchmark and Canadian Water Quality Guideline for the protection of aquatic life for PFOA (μg/L)

	Short-term benchmark (μg/L)	**Long-term Canadian Water Quality Guideline (μg/L)**
Freshwater	93,800	73.4
Marine	NRG[a]	NRG[a]

Notes:
NRG = no recommended guideline
[a] Insufficient data were available to meet CCME minimum data requirements for derivation of a short-term benchmark or long-term guideline for protection of marine life (CCME 2007).

1.0 INTRODUCTION

Perfluorooctanoic acid (PFOA) is an anthropogenic substance belonging to the broader class of per- and polyfluoroalkyl substances (PFAS). PFAS are a large group of over 4,700 substances used as surfactants, lubricants and repellents in applications such as firefighting foams, cosmetics, food packaging and textiles. Furthermore, PFOA belongs to the class of perfluoroalkyl acids (PFAAs) and the subgroup of perfluorocarboxylic acids (PFCAs). Although PFOA is not known to have been manufactured in Canada and is currently prohibited from being manufactured, it can enter through the importation of manufactured items. Releases to the environment can occur directly via industrial or consumer use of products containing PFAS, including from the application of firefighting foams, from wastewater effluents and landfill leachates, or via the long-range transport of PFOA or its precursors that then transform to PFOA.

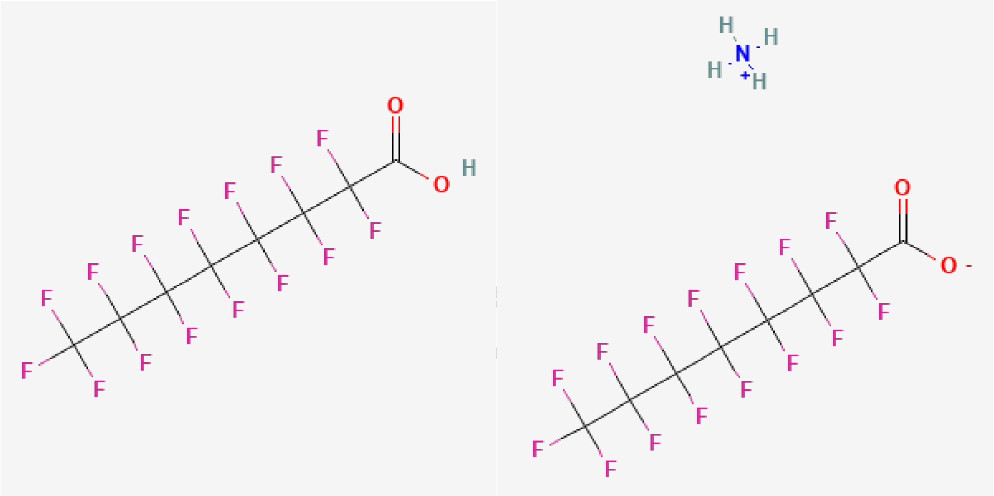
In 2012, the Government of Canada published a Screening Assessment Report (SAR) that concluded, based on available information, that PFOA and its salts and precursors are entering or may enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity (EC and HC 2012a). Additionally, it was concluded that PFOA and its salts met the criteria for persistence as set out in the Persistence and Bioaccumulation Regulations (Government of Canada 2000) under the *Canadian Environmental Protection Act* (CEPA) (EC and HC 2012a). PFOA did not meet the criteria for bioaccumulation as set out in the Regulations; however, the weight of evidence was sufficient to conclude that PFOA and its salts did accumulate and biomagnify in the liver, kidney and blood of terrestrial and marine mammals (EC and HC 2012a). As a result of the conclusions in the SAR, PFOA was added to the List of Toxic Substances in Schedule 1 of CEPA (EC and HC 2013).

The development of the CWQG and short-term benchmark involved the compilation and interpretation of aquatic toxicity data. The CWQG provides an important tool to support the evaluation of ambient water quality. Long-term guidelines for the protection of aquatic life are derived to protect all forms of aquatic life over an indefinite exposure period, including the most sensitive life stage of the most sensitive species (CCME 2007). By comparing environmental concentrations of PFOA with the CWQG, it is possible to determine the level of PFOA below which no direct impacts on the ecosystem are expected.

The *Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life* accounts for the unique properties of contaminants, which influence their bioavailability and toxicity, and incorporates a species sensitivity distribution (SSD) method, which uses all available toxicity data (provided these data pass quality control criteria) in a more flexible approach (CCME 2007). All of the customary components of scientific supporting documents have been included (physical and chemical properties, production and uses, environmental fate and behaviour, environmental concentrations and toxicity data).

2.0 SUBSTANCE IDENTITY

PFOA has a chain length of eight carbons, seven of which are perfluorinated, the eighth being part of the carboxylate functional group. It has a long perfluorocarbon tail that is both hydrophobic and oleophobic and a charged head that is hydrophilic, which makes it useful as a surfactant (Agency for Toxic Substances and Disease Registry [ATSDR] 2021). The chemical structure of PFOA, as well as the structure of the most common commercially used salt, ammonium salt (ammonium perfluorooctanoate [APFO]), is shown in Figure 1. The derivation of the CWQG and short-term benchmark for PFOA considered data for the acid (CAS RN 335-67-1), its conjugate base (perfluorooctanoate [PFO]), branched PFOA and PFOA’s principal salt forms (Table 2). The PFOA guidelines do not apply to precursors of PFOA; however, guideline users should be aware that precursors can degrade into PFOA and may result in the accumulation of PFOA in the environment. In this document, the term “PFOA” may refer to the acid, its conjugate base or its principal salt forms. In cases where it is important to distinguish between both species and where specific knowledge is available, it is clearly indicated that which is meant: the acid PFOA (neutral form), the conjugate base PFO (anionic form) or the salt form. Note that PFOA has various synonyms and trade names, which have been summarized elsewhere (EC and HC 2012; ATSDR 2021).



a) PFOA b) APFO

Figure 1. Chemical structure of linear isomer of a) perfluorooctanoic acid (PFOA) and b) its ammonium salt (APFO)

Source: NCBI 2022 a; b.

Table 2. List of perfluorooctanoic acid (PFOA) forms and PFOA's principal salts

Name	CAS RN	Molecular formula
PFOA free acid (octanoic acid, pentadecafluoro-)	335-67-1	$C_8HF_{15}O_2$
Perfluorooctanoate (PFO, conjugate base of the free acid)	45285-51-6	$C_8F_{15}O_2^-$
Branched perfluorooctanoic acid	90480-55-0	$C_8HF_{15}O_2$
Principal salts		
PFOA ammonium salt (APFO, octanoic acid, pentadecafluoro-, ammonium salt)	3825-26-1	$C_8F_{15}O_2^-NH_4^+$
Ammonium salt, linear/branched PFOA (octanoic acid, pentadecafluoro-, branched, ammonium salt)	90480-56-1	$C_8F_{15}O_2^-NH_4^+$
PFOA sodium salt	335-95-5	$C_8F_{15}O_2^-Na^+$
PFOA potassium salt	2395-00-8	$C_8F_{15}O_2^-K^+$
PFOA silver salt	335-93-3	$C_8F_{15}O_2^-Ag^+$

Source: EC and HC (2012), Table 2.

3.0 PHYSICAL AND CHEMICAL PROPERTIES

Various physical and chemical properties for PFOA have been compiled in Appendix A. PFOA is an anionic surfactant having both a lipophilic and hydrophilic end (EC and HC 2012a; Li *et al.* 2021). It tends to associate with surfaces and interfaces, and it accumulates at the air-water interface (Costanza *et al.* 2019). The octanol-water partition coefficient (K_{OW}) for surface-active perfluorinated substances has not been considered a reliable indicator of partitioning behavior (National Industrial Chemicals Notification and Assessment Scheme [NICNAS] 2015), which is discussed in more detail in Section 8.0.

Water solubility is an important property influencing PFOA and its salts in the environment. At 20°C, the free acid and the ammonium salt are in a solid state. The free acid readily dissociates to its conjugate base, PFO, at most environmentally relevant pH values. Both PFO and its salts are highly soluble in water. Under acidic conditions where PFOA predominates, water solubility is in the range of 0.0007 g/L, whereas at neutral and alkaline pH values, it is primarily present as PFO, with solubility values ranging from 3.3 to 9.5 g/L (Appendix A). Although PFOA salts self-associate at the water surface of the air/water interface, it has been noted that they disperse with agitation and form micelles at higher concentrations (United States Environmental Protection Agency [U.S. EPA] 2003a). Solubility for surfactants is often based on the critical micelle concentration (CMC). The CMC for PFOA been estimated in the range of 3.6 to 3.7 g/L (Prevedouros *et al.* 2006; Kissa 1994). Water solubility values for PFOA salts have been reported as 12 g/L for PFOA potassium salt at a temperature of 25.6°C and 14 g/L for PFOA ammonium salt at 2.5°C (Shinoda *et al.* 1972).

Water solubility is dependent on the acid dissociation constant (pKa) of the acid form (EC and HC 2012a). There has been discussion over the value of the pKa as reported values vary (see Appendix A). The value commonly reported and used is approximately 2.5 (Kissa 1994; EC and HC 2012a). Burns *et al.* (2008) determined a value of 3.8 ± 0.1, which suggests that the neutral species can exist in the environment, however it is unlikely that it would exist to any significant extent except under extremely acidic conditions. Goss (2008) suggested that the pKa value of PFOA is likely low, such that >99% of PFOA will occur as PFO under most environmental conditions. This further suggests that its environmental partitioning will be dominated by its anionic form (i.e., PFO).

4.0 SOURCES, EMISSIONS, PRODUCTION AND USES

PFOA is an anthropogenic substance with no known natural sources (Kissa 1994). It is not known to have been manufactured in Canada, although it was imported. In the past, approximately 600,000 kg of PFAS were imported into Canada between 1997 and 2000, of which PFOA, primarily imported as its ammonium salt APFO, comprised less than 1,000 kg. These volumes do not include quantities imported in manufactured items (Environment Canada 2001). In addition, the SAR reported importation of APFO into Canada in the 2004 calendar year in quantities ranging from 100 to 100,000 kg (Environment Canada 2005, EC and HC 2012a).

PFOA was primarily used as a reactive intermediate, whereas APFO was used in the manufacture of fluoropolymers as a polymerization aid (EC and HC 2012b; U.S. EPA 2003b; Organisation for Economic Co-operation and Development [OECD] 2006; Prevedouros *et al.* 2006). These fluoropolymers were used in the manufacture of water-resistant or non-stick coatings for textiles and carpet, cables and hoses, non-stick coatings on cookware, and personal care products (U.S. EPA 2003b) as well as in the formulation of paints and photographic film additives as a constituent of aqueous fluoropolymer dispersions (OECD 2006). While not intended to remain in the fluoropolymers, APFO might be present in trace amounts as a contaminant or as a degradation product of its precursors. In addition, APFO has also been used as a component of aqueous firefighting foams (Prevedouros *et al.* 2006).

The manufacture, import, use, sale and offer for sale of PFOA are prohibited under the *Prohibition of Certain Toxic Substances Regulations, 2012* (the Regulations), with some exemptions. Notable exemptions include aqueous film forming foam (AFFF) used in firefighting, and the import, use, sale and offer for sale of manufactured items which contain PFOA. The Regulations define a manufactured item as a product "formed into a specific physical shape or design during its manufacture and that has, for its final use, a function or functions dependent in whole or in part on its shape or design" (EC and HC 2012a). Proposed regulations were published on May 14, 2022, by the Government of Canada that would repeal and replace the current Regulations and would further restrict exempted uses of PFOA, as well as PFOS, long-chain PFCAs and products containing these substances, by removing or providing time limits for many remaining exemptions (Government of Canada 2022).

Current major sources of PFOA exposure in Canada include the importation and use of manufactured items, as mentioned above. PFOA may enter the environment via wastewater effluent and leachate from landfills where the items are disposed of. It can also be formed from the breakdown of precursor compounds (ATSDR 2021). AFFF containing PFOA is also commonly used at airports and military bases to fight fires caused by flammable liquids and fuels, where it may contaminate the soil and water. Due to the high water solubility of PFOA, it can migrate via groundwater, surface water and leachate to water sources away from contaminated sites. The composition of AFFF and the amount of PFOA it contains can vary by product, and the type of PFAS contained in foams has changed over time (Interstate Technology Regulatory Council [ITRC] 2022). Existing stocks of AFFF containing PFOA may have continued to be used as products shifted to other PFAS, and these can represent a source of contamination to the environment. Additionally, legacy foams that did not contain PFOA could contain fluorinated precursors that could then break down into PFOA in the environment (ITRC 2022).

5.0 ENVIRONMENTAL CONCENTRATIONS

As discussed in Section 4.0, although PFOA is not known to have been manufactured in Canada, it can enter Canada through the importation of manufactured items and can enter the environment and water bodies through wastewater effluents, landfill leachates and the application of firefighting foams. Additionally, it has been shown to be persistent in the environment and can undergo transport to some degree (see Section 7.0) (EC and HC 2012a; ATSDR 2021). As such, surface waters in unpolluted areas may contain very low levels of PFOA, while greater amounts of anthropogenic activity (i.e., urban sites) may contribute to elevated concentrations. Surface waters in the vicinity of and impacted by contaminated sites are expected to have the highest concentrations of PFOA.

5.1 Concentrations in Surface Water

Data from sampling sites are summarized for various water bodies in Canada (tables B1 and B2), as well as for the Great Lakes specifically (Table B3), in Appendix B. Levels of PFOA can differ between fresh water and sea water, with higher concentrations observed in fresh water compared to marine based on available data. Freshwater concentrations ranged from <0.6 to 2.6 ng/L at remote or rural sites (sampled between 2010 and 2015), up to 14 ng/L at an urban site sampled in 2006, up to 6.4 ng/L at other urban sites sampled in 2015, and up to 62.4 ng/L for sites impacted by AFFF (sampled in 2015) (tables B1 and B2, Appendix B). A monitoring study that included 38 rivers across Canada sampled between 2001 and 2008 found that PFOA and PFOS were the predominant perfluorinated alkyl acids detected and that values of PFOA ranged from 0.044 to 9.9 ng/L, with highest concentrations from densely populated areas, generally at downstream sites (Scott *et al.* 2009). A recent study by Lalonde and Garron (2022) investigating PFAS in freshwater sites across Canada between 2013 and 2020 (including reference, urban and mixed development sites as well as sites associated with municipal wastewater treatment plants (MWWTP)) found that maximum and median concentrations of PFOA were 24.4 and 1.52 ng/L, respectively. PFOA was among the most frequently detected PFAS and demonstrated a decreasing temporal trend over the sampling years (Lalonde and Garron 2022). In addition, a study conducted by the Saskatchewan Water Security Agency between 2017 and 2019 reported PFOA levels in surface water in urban areas ranging from 5.6 to 31.8 ng/L (Thirunavukkarasu *et al.* 2019). Overall trends in available data suggest that PFOA concentrations are lower in rural sites compared to urban sites, and lower in the Arctic compared to urban and maritime locations (see data in Appendix B).

In the Great Lakes specifically, PFOA levels generally decreased between 2006 and 2018 (Gewurtz *et al.* 2019). Existing data indicate that PFOA concentrations are lower overall in the upstream Great Lakes (Lakes Huron and Superior) than in the downstream lakes (Lakes Erie and Ontario) (Gewurtz *et al.* 2019; Remucal 2019). In Lake Ontario, comparisons between concentrations in surface water and concentrations in precipitation show additional sources to wet deposition (e.g., wastewater effluent). However, in Lakes Huron and Superior, wet deposition seems to be the primary source despite the possible presence of local anthropogenic input (Gewurtz *et al*. 2019). PFOA is likely to persist in the Great Lakes in particular due to their relatively long hydraulic residence times, despite any decreases in input (Gewurtz *et al.* 2019; Remucal 2019).

5.1.1 Contaminated Sites

PFOA levels are significantly higher in areas with known point-sources of pollution. Surface water sites downstream from or close to areas that have used AFFF can have greatly elevated levels of PFOA relative to background sites in both northern and southern Canada (Stock *et al*. 2007; de Solla *et al.* 2012). Indeed, the highest concentrations noted in Appendix B are all from sites impacted by AFFF. Bhavsar *et al.* (2016) and Moody *et al.* (2002) have reported the highest known PFOA concentrations to date in Canadian freshwater at sites in close proximity to historical contamination from firefighting training activities and the accidental release of fire-fighting foam. Bhavsar *et al*. (2016) reported a concentration of 4,700 ng/L (4.7 µg/L) of PFOA for a pond on Hamilton International Airport collected in 2011 near a firefighting training facility. Moody *et al.* (2002) reported surface water concentrations reaching 11,300 ng/L (11.3 µg/L) of PFOA at Etobicoke Creek (sampled in 2000) near the site of an accidental release of firefighting foam containing perfluorinated surfactants at L. B. Pearson International Airport in Toronto, Ontario.

It is noted that the composition of AFFF has changed over time. Up until the early 2000s, mainly AFFF formulations containing PFOS were used, after which the prevalence of fluorotelomer-based formulations increased (CONservation of Clean Air and Water in Europe [CONCAWE] 2016; ITRC 2022). Legacy fluorotelomer AFFF (produced in the United States from the 1970s until 2016), while not containing PFOA, contains fluorotelomers that could degrade to PFOA. Modern fluorotelomer-based AFFF do not contain PFOA precursors that can degrade to PFOA (ITRC 2022). Therefore, the concentration of PFOA found at an AFFF-contaminated site is dependent on the type of AFFF used.

PFOA exposure can occur via groundwater that discharges into nearby surface water bodies. Along with other PFAS, it has been detected in the leachate of historic closed landfills, which can contaminate groundwater and be discharged into the surface (Propp *et al.* 2021; Roy *et al.* 2021). Elevated PFAS levels have been shown to be present within the footprint of groundwater plumes at varying surface water zones and may also move downstream from the site of exposure (Roy *et al.* 2021). Although PFOA concentrations are not among the most dominant, PFOA still constitutes a major portion of the PFAS compounds detected, and exposure via landfill leachate should be considered.

6.0 EXISTING PFOA WATER QUALITY GUIDELINES IN OTHER JURISDICTIONS

PFAS is an active area of research, and various jurisdictions may be in the process of developing or updating guidelines for PFOA as new data become available. As such, the information included in this section was current at the time of publication, but individual jurisdictions should be consulted for the most up-to-date values. Additionally, individual jurisdictions have varying protection goals and derivation procedures, so values may not be directly comparable with CCME guideline values.

The State of Michigan has surface water quality values for PFOA for aquatic life, including a final chronic value of 880 µg/L, an acute aquatic maximum value of 7,700 µg/L and a final acute value of 15,000 µg/L (Michigan Department of Environment, Great Lakes and Energy [EGLE] 2022). Surface water quality criteria were developed for the State of Minnesota including a chronic criterion of 1,705 µg/L based on toxicity to aquatic organisms and using an acute-to-chronic ratio and a maximum criterion of 15,346 µg/L (STS Consultants 2007). Draft or interim surface water values were available from other jurisdictions at the time this document was developed, including from the states of Florida, Texas and California as well as from the U.S. EPA, Australia and New Zealand.

The U.S. EPA published draft freshwater Aquatic Life Ambient Water Quality Criteria for PFOA for public review in April 2022, including a criterion maximum concentration of 49,000 µg/L (acute exposures) and a criterion continuous concentration of 94 µg/L (chronic exposures). In addition, in the absence of sufficient data to derive a criterion for estuarine and marine waters, a draft benchmark for estuarine marine environments was provided for consideration for acute exposures using available data in addition to new approach methodologies (U.S. EPA 2022).

PFOA surface water values based on Australia and New Zealand draft technical default guideline values were available as ecological screening levels (Cooperative Research Centre for Contamination Assessment and Remediation of the Environment [CRC CARE] 2018), investigation levels (Department of the Environment and Energy 2016) or as ecological water quality guideline values developed by water regulators (Heads of EPAs Australia and New Zealand [HEPA] 2020). The freshwater value at a 95% species protection level was 220 µg/L to apply in exposure scenarios of slightly to moderately disturbed systems. Freshwater values were also available at additional species protection levels (CRC CARE 2018; HEPA 2020).

7.0 ENVIRONMENTAL FATE AND BEHAVIOUR

PFOA has a high water solubility in the ionic form (Section 3.0) which is the most prevalent form at environmental pH, and together with the low volatility of the ionized form, it is expected that PFOA will partition primarily to the aquatic environment (EC and HC 2012a). Once PFOA is in the aqueous phase, partitioning to sediments is possible; however, they are not likely to be a major sink (Masungaga and Odaka 2005 as cited in EC and HC 2012a; Ahrens *et al*. 2011). Sorption of PFOA to sediment has been shown to increase with increasing organic carbon content, and where sediments have negligible organic carbon content, the density of the sediment is an important factor influencing partitioning (Ahrens *et al.* 2011). Salinity has also been shown to influence the sediment-water distribution coefficient (Kd) of PFOA, with an increasing Kd value as salinity increases (Xiao *et al*. 2021). Other factors influencing PFOA adsorption to different mineral compounds in surface water and groundwater include electrostatic interactions between PFOA and the mineral, which in turn may be influenced by pH, ionic strength as well as concentrations of Ca^{2+} (Ahrens *et al.* 2009; Ferrey *et al*. 2012; SNC 2012; Wang *et al.* 2012). PFOA is considered to be stable in the water column as the strong carbon-fluorine bond renders it resistant to breakdown via hydrolysis, photolysis or biodegradation. Based on soil adsorption coefficient data and monitoring data, PFOA is expected to be mobile in soil and can leach into groundwater (ATSDR 2021), where it could then migrate to other water sources.

The solubility of PFOA is dependent on the acid dissociation constant (pKa) of the acid form. Because PFOA is expected to have a low pKa, more than 99% of the compound is expected to occur in its anionic form under the majority of environmental conditions (Goss 2008; Nielsen 2012).

The long-range transport of PFOA has been explained by two processes: first, transport by ocean currents, and second, atmospheric oxidative transformations of airborne precursors to PFOA and its subsequent wet and dry deposition (Muir *et al.* 2019). Estimates of oceanic transport to the Arctic have ranged from 2 to 23 tonnes per year (Prevedouros *et al.* 2006; Armitage *et al.* 2006), which exceeds estimates via atmospheric transport or degradation of precursors (Arcadis 2015). As PFOA is expected to exist mainly in its anionic form, which has low vapour pressure, it is expected that relatively little PFOA will partition into the vapour phase under most environmental conditions (Trapp *et al.* 2010). As such, long-range atmospheric transport of PFOA is not considered a significant pathway.

PFOA can be formed from the breakdown of precursor compounds, such as fluorotelomer alcohols (FTOH). PFOA detected in regions without direct sources may be explained by the long-range transport of volatile precursors that are then oxidized in the atmosphere (Loewen *et al.* 2005; Schenker *et al*. 2008; Young *et al.* 2007). Studies on the atmospheric degradation of FTOH have shown it yields PFCA compounds, including PFOA (Ellis *et al.* 2004, Wallington *et al.* 2006, Young *et al.* 2007). FTOH degradation is likely an important contributor to PFOA concentrations in remote areas such as the Canadian Arctic. In the Arctic, the amount yielded varies by season, being greater in the summer months than in winter.

PFOA may also be emitted and travel in the gas phase in the form of aerosols or particles (e.g., sea spray aerosols [SSA]) (Gewurtz *et al.* 2019). Results from modelling and experimental studies suggest PFOA released from oceans in the gas phase via spray may partially explain concentrations of PFOA observed in remote regions (Webster and Ellis 2010; Reth *et al.* 2011). Sha *et al.* (2022) conducted air sampling at two Norwegian coastal sites and found SSA to be a major contributor of PFOA to the atmosphere in coastal areas. Their findings suggested SSA transport may potentially impact inland environments as well. Similarly, experiments by Johansson *et al*. (2019) suggest that SSA could be an important source of PFAAs found in the atmosphere and, over some areas, a source of those found in terrestrial environments as well.

Precipitation has been identified as an important removal mechanism of PFAAs from the atmosphere via sequestration of particles and sorption to water droplets (Gewurtz *et al.* 2019). During rain events, PFOA can be transported from the atmosphere to terrestrial and surface water environments on water droplets. Simultaneous assessment of the concentrations of PFAAs in precipitation and in surface water can provide information about fate, transport and the relative importance of atmospheric deposition versus local anthropogenic sources impacting surface water concentrations (Gewurtz *et al.* 2019).

8.0 BIOACCUMULATION

CCME (2006) defines bioconcentration as the process by which contaminants are directly taken up by terrestrial or aquatic organisms from the medium. This typically refers to the situation whereby resulting concentrations in the organism are higher than concentrations in the medium. Bioaccumulation is defined as the process by which chemical compounds are taken up by terrestrial or aquatic organisms directly from the medium as well as through consuming contaminated food at a faster rate than the compounds are lost through excretion or metabolism (CCME 2006). Finally, biomagnification is defined as the process of bioaccumulation by which tissue concentrations of accumulated chemical compounds are passed up through two or more trophic levels so that tissue residue concentrations increase systematically as trophic level increases (CCME 2006).

The potential for a substance to bioaccumulate is often evaluated using the octanol-water partition coefficient (K_{OW}) since the hydrophobic and lipophilic interactions between a compound and a substrate are the main mechanisms governing partitioning. However, perfluorocarboxylic acids (PFCAs), such as PFOA, have oleophobic, hydrophobic and hydrophilic properties over different portions of the molecule and have a tendency to aggregate at the interface of a liquid-liquid system rather than establish partitioning equilibrium (EC and HC 2012a; Arcadis 2015). Therefore, K_{OW} has largely not been considered a reliable indicator of bioaccumulation potential for perfluorinated substances, although some research states that PFCAs, including PFOA, are not surface-active and that K_{OW} does predict both lipid and protein partitioning within organisms (Webster and Ellis 2011).

The Government of Canada concluded in 2012 that PFOA and its salts did not meet the criteria for bioaccumulation as set out in the *Persistence and Bioaccumulation Regulations*; however, the weight of evidence was sufficient to conclude that PFOA and its salts accumulate and biomagnify in terrestrial and marine mammals (EC and HC 2012a). The SAR noted low to moderate potential for PFOA to accumulate in aquatic species based on whole-body data; however, it may be considered to accumulate and biomagnify in terrestrial and marine mammals based on organ-specific data. Within an organism, PFOA predominantly binds to protein in the blood and hence is found in blood and perfused tissues of biota, such as liver and kidney, rather than in lipid tissue (EC and HC 2012a). It was noted in the SAR that the criteria for bioaccumulation outlined in the Regulations are based on bioaccumulation data for freshwater fish species only and for substances that primarily partition to lipids. Therefore, the criteria may not fully reflect the bioaccumulation potential in marine and terrestrial mammals for PFOA, which preferentially partitions to liver, blood and kidney proteins (EC and HC 2012a).

Bioaccumulation factors and bioconcentration factors from aquatic exposure have been observed below 5,000 for fish and aquatic invertebrates, indicating that PFOA does not bioaccumulate in gill-breathing organisms (Arcadis 2015). Due to the high water solubility of PFOA, fish and other gill-breathing aquatic organisms may be able to excrete PFOA through gill permeation (EC and HC 2012a). In contrast, air-breathing organisms, such as birds and marine mammals, lack this route of elimination. Additionally, PFOA may not be likely to escape to the air across the alveolar membrane of the lung because of the low vapour pressure and negative charge of PFOA (Arcadis 2015). Therefore, PFOA accumulation is expected to be greater in air-breathing organisms than in fish. Estimates of the half-life of PFOA in fish compared to humans support this hypothesis, with half-lives in fish ranging from three to nine days (Falk *et al*. 2015; Martin *et al*. 2003a) and half-lives in humans ranging from 3.8 to 4.37 years (Olsen *et al*. 2007; Kudo and Kawashima 2003). Field biomagnification factors for terrestrial and marine mammals ranged from 0.03 to 31, and polar bears demonstrated the most PFOA contamination amongst Arctic terrestrial animals (EC and HC 2012a).

9.0 TOXICITY OF PFOA TO AQUATIC ORGANISMS

9.1 Mode of Action

Although the mechanism of toxic action of PFAS and PFOA in aquatic organisms is an ongoing field of research, the available information has previously been well summarized (Ankley *et al.* 2020; Lee *et al.* 2020). In general, the adverse impacts of PFAAs on aquatic organisms include disruptions to metabolism, reproduction, immune system and hormones, as well as neuronal and developmental toxicity (Lee *et al.* 2020). The effects are initiated by the activation of various nuclear receptors or by other factors, such as oxidative stress or membrane interaction, which in turn result in transcription-level changes followed by metabolite-level changes and subsequently tissue-level changes (Lee *et al.* 2020). Adverse effects from PFAAs can be influenced by the sex and developmental stage of the aquatic organism (Lee *et al.* 2020).

Studies with invertebrates have demonstrated that PFAS cause signs of oxidative stress as well as effects on the antioxidant defense systems, including alterations in lipid peroxidation, reactive oxygen species and antioxidant enzyme activities and expression (Ankley *et al.* 2020). PFAS exposure has also been associated with genotoxic and behavioural effects in invertebrate species (Ankley *et al.* 2020). Exposure to PFOA in invertebrate species has been associated with neurotoxic effects (Ankley *et al.* 2020).

In fish, studies have again shown PFAS to cause oxidative stress as well as apoptosis. Although the mechanism through which PFAS elicits the oxidative stress is currently not well understood, some potential triggers include increased β-oxidation of fatty acids as well as mitochondrial toxicity (Ankley *et al.* 2020). PFAS exposure in fish has also been associated with endocrine disruption, which can impact reproduction and sexual development (Ankley *et al.* 2020). PFOA has been shown to be estrogenic, binding to estrogen receptors in rainbow trout (Benninghoff *et al.* 2011). PFOA has also been shown to activate nuclear receptors involved in lipid metabolism in fish (Ankley *et al.* 2020).

9.2 Toxicity to Freshwater Organisms

This section presents an overview of acceptable (primary or secondary data quality) toxicity values reported for the short-term and long-term toxicity of PFOA to freshwater aquatic organisms. Note that this section relates only to those data selected for inclusion in the Species Sensitivity Distribution (SSD) for guideline derivation (see Section 10 for further details on SSDs and guideline derivation). See Appendix C for a full list of all PFOA aquatic toxicity data considered and evaluated for inclusion in guideline derivation (including details on chemical identity, test organism, experimental conditions, results, and rationale for data categorization as primary, secondary or unacceptable in terms of acceptability for guideline derivation). Note that toxicity data for commercial mixtures containing PFOA were not included in the derivation of the guideline, as these mixtures may not be well characterized and could include products with varying amounts of PFOA. Also note that all studies included in the SSD were for tests conducted with the ionic form of PFOA unless otherwise specified. Endpoints based on concentrations of PFOA salts (including ammonium salt and sodium salt) were standardized to the ionic form of PFOA prior to inclusion in the SSD to allow the comparison of toxicity on the same chemical basis.

Standardization of endpoints for PFOA salts was done by multiplying the concentration (based on the salt) by the ratio of the molar mass of PFOA to its salt (Appendix A) as follows:

$$\frac{\mu\text{g PFOA salt}}{\text{L}} \times \frac{\text{mol}}{\text{g PFOA salt}} \times \frac{\text{g PFOA}}{\text{mol}}$$

The ratio of the molar mass of PFOA to its ammonium salt is 0.96; that of PFOA to its sodium salt is 0.95.

9.2.1 Short-term Toxicity

The endpoints included in the short-term SSD for the derivation of a short-term benchmark for PFOA are provided in Section 10.3 (Table 7). A summary of the range in sensitivity of short-term SSD data points for fish, aquatic invertebrates and amphibians is included in sections 9.2.1.1, 9.2.1.2 and 9.2.1.3, respectively.

9.2.1.1 Fish

Short-term LC_{50} values for six species of fish were included in the SSD for derivation of the short-term benchmark. The most sensitive fish species was the zebrafish (*Danio rerio*), with a 96-hour LC_{50} value of 118,820 µg/L PFOA (Zhao *et al.* 2015). Although not a resident Canadian species, *D. rerio* is considered an appropriate surrogate species and is commonly used in laboratory toxicity tests (see Appendix D for rationale for surrogate species included in the SSD). The least sensitive fish species was rainbow trout (*Oncorhynchus mykiss*) with a 96-hour LC_{50} of 707,000 µg/L APFO (Colombo *et al.* 2008) standardized to 679,071 µg/L PFOA. In general, fish species appeared in the middle and towards the top of the SSD, demonstrating that they were not the most sensitive taxon.

9.2.1.2 Aquatic Invertebrates

Short-term EC/LC_{50} values were included in the SSD for 14 species of aquatic invertebrates. In general, aquatic invertebrates demonstrated the greatest sensitivity to PFOA with the majority of invertebrate endpoints appearing in the bottom half of the SSD. The most sensitive aquatic invertebrate, as well as the most sensitive species overall in the SSD, was the cladoceran *Daphnia carinata*, with a 48-hour EC_{50} for immobility of 78,200 µg/L PFOA (Logeshwaran *et al.* 2021). Although not a Canadian resident species, *D. carinata* is considered a reliable surrogate species (Appendix D). The cladoceran *Chydorus sphaericus* was the second most sensitive invertebrate and second most sensitive species overall in the SSD with a 48-hour EC_{50} for immobility of 91,100 µg/L PFOA (Le and Peijnenburg 2013). The least sensitive aquatic invertebrate was the mud snail (*Cipangopaludina cathayensis*) with a 96-hour LC_{50} of 740,070 µg/L PFOA (Yang *et al.* 2014). Although not a Canadian resident species, *C. cathayensis* was considered an appropriate surrogate species (Appendix D).

9.2.1.3 Amphibians

Short-term LC_{50} values were included in the SSD for 11 species of amphibians. Data points for amphibians appeared throughout the SSD at the bottom, middle and top of the distribution; however, six of the 11 amphibian endpoints in the SSD were the six least sensitive endpoints in the curve. The most sensitive amphibian was the Asiatic toad (*Bufo gargarizans*) with a 96-hour LC_{50} of 114,740 µg/L PFOA (Yang *et al.* 2014). Although not a resident species of Canada, *B. gargarizans* was considered an appropriate surrogate species (Appendix D). The endpoint for *B. gargarizans* was the third most sensitive endpoint overall in the SSD. The least sensitive amphibian species were the green frog (*Lithobates clamitans,* formerly *Rana clamitans*) and the Jefferson salamander (*Ambystoma jeffersonianum*), both with 96-hour LC_{50} values of 1,070,000 µg/L PFOA (Tornabene *et al.* 2021). It should be noted that for *Hyla versicolor*, the endpoint for larval stage 26 was included in the SSD over the more sensitive larval stage 40 (Tornabene *et al.* 2021), as the stage-40 endpoint was ranked as unacceptable due to high control mortality. Therefore, the stage-26 endpoint was considered more reliable and was included in the SSD, though it is possible that other life stages for this species may be more sensitive.

9.2.2 Long-term Toxicity

The endpoints included in the long-term SSD for derivation of a Canadian Water Quality Guideline for PFOA are presented in Section 10.4 (Table 8). A summary of the range in sensitivity of long-term SSD data points for fish, aquatic invertebrates, amphibians, and algae and aquatic plants is provided in sections 9.2.2.1, 9.2.2.2, 9.2.2.3 and 9.2.2.4, respectively. Information regarding acceptable effects endpoints for guideline derivation is provided in CCME's protocol (CCME 2007).

9.2.2.1 Fish

Acceptable long-term PFOA toxicity values for fish included endpoints obtained in tests with a duration of 21 days or longer for adult fish, and seven days or longer for early life stages (CCME 2007). Data were available for five species of fish for inclusion in the long-term SSD.

The most sensitive fish endpoint came from a transgenerational test with medaka (*Oryzias latipes*), where a lowest observed effect concentration (LOEC) for F1 survival of 100 µg/L PFOA was observed for F0 and F1 exposures to 100 µg/L PFOA for 14 days and 28 days post-hatch, respectively (Ji *et al.* 2008). This LOEC was associated with >40% F1 mortality. The CCME protocol recommends that endpoints included in a long-term SSD for effects on lethality should have an effect level of ≤25% (CCME 2007). Statistical analysis of the toxicity-effect data from this study was conducted; however, a reliable no- or low-effect-level regression-based endpoint could not be calculated, nor could the more preferred endpoint type of maximum acceptable toxicant concentration (MATC) be calculated, as the LOEC was the first concentration level tested after the control. If the endpoint is not included, the protection clause of the protocol would be triggered, resulting in the LOEC of 100 ug/L becoming the guideline value. However, this option was not selected, as approximately 40% mortality in the F1 generation is expected at this concentration. Therefore, it was decided to include this LOEC value in the SSD, as doing so results in a lower guideline value and is considered to be scientifically defensible given that the true, non-calculable low effect level (e.g., ≤LC25) would occur at a lower concentration than the LOEC value. The application of a safety factor to the LOEC was also considered, but was not done at this time for a number of reasons. Firstly, while *O. latipes* is considered to be an appropriate surrogate species (Appendix D) and is commonly used in laboratory toxicity tests, there is uncertainty regarding whether a similar sensitivity to PFOA would be observed with Canadian resident species. Secondly, there is a lack of intergenerational fish studies to support the findings, resulting in additional uncertainty.

The least sensitive fish in the long-term SSD was the fathead minnow (*Pimephales promelas*), with a 21-day no observed effect concentration (NOEC) for growth of >76,000 µg/L PFOA (Bartlett *et al.* 2021). CCME protocol allows the inclusion of endpoints from tests where an insufficient concentration range has been tested on the higher end, as it will not result in an under-protective guideline (CCME 2007). Scientific judgement was applied for the inclusion of this endpoint in the long-term SSD based on the low number of greater-than endpoints in the data set as well as the limited number of fish species for which data were available.

9.2.2.2 Aquatic Invertebrates

Acceptable long-term endpoints for invertebrates include non-lethal endpoints of at least 96 hours for shorter-lived invertebrates, non-lethal endpoints of at least seven days for longer-lived invertebrates, and lethal endpoints of 21 days or longer for longer-lived invertebrates (CCME 2007). Lethal endpoints from shorter-lived invertebrates from tests with less than 21-day exposure durations may be considered on a case-by-case basis (CCME 2007). Long-term endpoints were included in the SSD for six species of aquatic invertebrates. The most sensitive aquatic invertebrate as well as the most sensitive endpoint overall in the long-term SSD was the cladoceran *Daphnia carinata*, with a 21-day MATC for reproduction of 31.6 µg/L PFOA (Logeshwaran *et al.* 2021). The least sensitive invertebrate was the midge *Chironomus dilutus*, with a 19-day EC_{10} for survival of 89,800 µg/L PFOA (McCarthy *et al.* 2021).

9.2.2.3 Amphibians

Acceptable data for one amphibian species was available for inclusion in the long-term SSD. The Asiatic toad (*Bufo gargarizans*) had a 30-day EC_{10} for longevity of 5,890 µg/L PFOA (Yang *et al.* 2014).

9.2.2.4 Algae and Aquatic Plants

Due to the rapid growth and turnover of algal and aquatic plant standard test species, most toxicity tests are considered to be long--term relative to the lifespan of the alga or plant. All toxicity tests for *Lemna sp*. following standard test protocols are generally considered long-term exposures. All algal toxicity tests with durations longer than 24 hours are considered long-term exposures (CCME 2007). Acceptable data for inclusion in the long-term SSD were available for five algal species and three aquatic plant species. The endpoints ranged from a 10-day EC_{10} for growth of 2,900 µg/L APFO for green algae *Raphidocelis subcapita* (formerly *Selenastrum capricornutum* and *Pseudokirchneriella subcapitata*) (Elnabarawy 1981), standardized to 2,785 µg/L PFOA, to a 96-hour EC_{50} for growth of 269,630 µg/L PFOA for the green algae *Scenedesmus quadricauda* (Yang *et al.* 2014).

9.3. Toxicity to Marine Organisms

Acceptable data for guideline derivation were limited for marine organisms. Short-term toxicity data were available for three species of marine invertebrates. The most sensitive species was the Mediterranean mussel (*Mytilus galloprovincialis*), with an LC_{50} of 9,980 µg/L PFOA (Hayman *et al.* 2021). The purple sea urchin (*Strongylocentrotus purpuratus*) had an EC_{50} for development of 19,000 µg/L PFOA and the opossum shrimp (*Americamysis bahia*) had a 96-hour LC_{50} value of 24,000 µg/L PFOA (Hayman *et al.* 2021). No acceptable short-term toxicity data were available for marine fish. Additionally, there was a complete lack of acceptable long-term toxicity data for guideline derivation for marine organisms. For a full list of all PFOA marine toxicity data considered and evaluated, see Appendix C. The available short-term marine toxicity data suggest that marine invertebrate species are more sensitive to PFOA than freshwater organisms. Therefore, it is not appropriate to apply the freshwater PFOA guideline in marine environments.

10.0 DERIVATION OF THE SHORT-TERM BENCHMARK CONCENTRATION AND THE CANADIAN WATER QUALITY GUIDELINE

10.1 Evaluation of Toxicity Data

All PFOA aquatic toxicity data were evaluated for scientific acceptability before being considered for or used in the derivation of the short-term benchmark and CWQG. Data from toxicity studies were ranked as primary, secondary or unacceptable in terms of acceptability for guideline derivation following criteria described in the protocol (CCME 2007). Toxicity data evaluated for consideration in the PFOA short-term benchmark and long-term water quality guideline are current to February 2022.

10.2 Methods Used for the Derivation of Guidelines

The *Protocol for the Derivation of Canadian Water Quality Guidelines* (CCME 2007) includes guideline values for both long-term and short-term exposure that risk assessors and risk managers in Canada can use to help protect aquatic species. The long-term exposure guideline is derived such that it is consistent with the guiding principle of the CWQG—namely, to protect all species and all life stages over an indefinite exposure to the substance in water. Aquatic life may experience long-term exposure to a substance as a result of continuous release from point or non-point sources, gradual release from soils or sediments, and gradual entry through groundwater or runoff and long-range transport. The short-term exposure value is derived for use as an additional management tool. It is an estimator of severe effects to the aquatic ecosystem and is intended to give guidance on the impacts of severe but transient situations (CCME 2007).

While separate data sets are used to calculate short-term and long-term guidelines, both are derived using one of three approaches. The three approaches are detailed by CCME (2007) and only briefly outlined here. In order of preference, the approaches are, first, the statistical approach (Type A or SSD approach); second, the lowest endpoint approach using only primary data (Type B1); and third, the lowest endpoint approach using primary or secondary data (Type B2).

A guideline derived using the statistical approach is called a Type A guideline. An SSD captures the variation in toxicological sensitivity to a contaminant among a set of species. An SSD is a cumulative distribution function, with effect concentrations plotted on the x-axis and cumulative probability, expressed as a percentage, plotted on the y-axis (Posthuma *et al.* 2002). Short-term, lethal endpoints (e.g., 24-hour LC_{50}) comprise the data set for short-term benchmarks, while long-term exposure, no- or low-effect endpoints (e.g., 21-day EC_{10} for growth) comprise the data set for long-term guidelines. From each data set, the benchmark or guideline value is equal to the concentration on the x-axis that corresponds to 5% cumulative probability on the y-axis. In contrast, the lowest endpoint approach (Types B1 and B2) uses, as the name implies, the lowest acceptable endpoint with a safety factor to estimate the guideline.

The minimum data requirements for application of each of the three methods are captured in Table 3 and Table 4 for freshwater environments and in Table 5 and Table 6 for marine environments, for both short-term and long-term exposures, respectively. If available data are insufficient for deriving a guideline using the statistical approach, the guideline is developed using the lowest endpoint approach. Depending on the quantity and quality of data, a Type B1 or Type B2 approach is used. The Type B1 approach uses only acceptable primary toxicity data to derive the guideline, while the Type B2 approach can use acceptable primary or secondary data (or both). In every case, a guideline must be developed using the highest ranked method that the data allow.

Sections 10.3 and 10.4 describe the derivation of the short-term benchmark and long-term CWQG, respectively, for the protection of freshwater life in surface water for PFOA. Data requirements for the most preferred approach, Type A (SSD), were met for both short-term and long-term exposures for PFOA in freshwater. Data requirements for the derivation of a short-term benchmark concentration or a CWQG for protection of marine life were not met for any approach.

Table 3. Minimum data set requirements for the generation of a short-term benchmark concentration for freshwater environments

Group	Guideline		
	Type A	Type B1	Type B2
Fish	Three species, including at least one salmonid and one non-salmonid.		Two species, including at least one salmonid and one non-salmonid.
Aquatic invertebrates	Three aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be a mayfly, caddisfly or stonefly.		Two aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be a mayfly, caddisfly or stonefly.
Plants	Toxicity data for aquatic plants or algae are highly desirable, but not necessary. However, if a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and two studies on non-target freshwater plant or algal species are required.		
Amphibians	Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.		
Preferred endpoints	Acceptable LC_{50} or equivalent (e.g., EC_{50} for immobility in small invertebrates).		
Data quality requirement	Primary and secondary LC_{50} (or equivalent) data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary LC_{50} (or equivalent) data. The value used to set the guideline must be primary.	The minimum data requirement must be met with primary LC_{50} (or equivalent) data. Secondary data are acceptable. The value used to set the guideline may be secondary.

Source: CCME (2007).

Table 4. Minimum data set requirements for the generation of a long-term guideline value for freshwater environments

Group	Guideline		
	Type A	Type B1	Type B2
Fish	Three species, including at least one salmonid and one non-salmonid.		Two species, including at least one salmonid and one non-salmonid.
Aquatic invertebrates	Three aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be a mayfly, caddisfly or stonefly.		Two aquatic or semi-aquatic invertebrates, at least one of which must be a planktonic crustacean. For semi-aquatic invertebrates, the life stages tested must be aquatic. It is desirable, but not necessary, that one of the aquatic invertebrate species be a mayfly, caddisfly or stonefly.
Plants	At least one study on a freshwater vascular plant or freshwater algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and three studies on non-target freshwater plant or algal species are required.		Toxicity data for plants are highly desirable, but not necessary. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and two studies on non-target freshwater plant or algal species are required.
Amphibians	Toxicity data for amphibians are highly desirable, but not necessary. Data must represent fully aquatic stages.		
Preferred endpoints	The acceptable endpoints representing the no-effects threshold and EC_{10}/IC_{10} for a species are plotted. The other, less preferred, endpoints may be added sequentially to the data set to fulfill the minimum data requirement condition	The most preferred acceptable endpoint representing a low-effects threshold for a species is used as the critical study; the next less preferred endpoint will be used sequentially only if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: most appropriate EC_x/IC_x representing a low-effects threshold > EC_{15-25}/IC_{15-25} > LOEC >	

Group	**Guideline**		
	Type A	**Type B1**	**Type B2**
	and improve the result of the modelling for the guideline derivation if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: most appropriate EC_x/IC_x representing a no-effects threshold > EC_{10}/IC_{10} > EC_{11-25}/IC_{11-25} > MATC > NOEC > LOEC > EC_{26-49}/IC_{26-49} > nonlethal EC_{50}/IC_{50}. Multiple comparable records for the same endpoint are to be combined by the geometric mean of these records to represent the averaged species effects endpoint.	MATC > EC_{26-49}/IC_{26-49} > nonlethal EC_{50}/IC_{50} > LC_{50}.	
Data quality requirement	Primary and secondary no-effects and low-effects level data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary data. The value used to set the guideline must be primary. Only low-effect data can be used to fulfill the minimum data requirement.	Secondary data are acceptable. The value used to set the guideline may be secondary. Only low-effect data can be used to fulfill the minimum data requirement.

Source: CCME (2007).

Table 5. Minimum data set requirements for the generation of a short-term benchmark concentration for marine environments

Group	**Guideline**		
	Type A	**Type B1**	**Type B2**
Fish	At least three studies on three or more marine fish species, at least one of which is a temperate species.		At least two studies on two or more marine fish species, at least one of which is a temperate species.
Aquatic invertebrates	At least two studies on two or more marine species from different classes, at least one of which is a temperate species.		At least two studies on two or more marine species.
Plants	At least one study on a temperate marine vascular plant or marine algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and two studies on non-target marine plant or algal species are required.		Toxicity data for marine plants are highly desirable, but not necessary. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and two studies on non-target marine plant or algal species are required.
Preferred endpoints	Acceptable LC_{50} or equivalent (e.g., EC_{50} for immobility in small invertebrates).		
Data quality requirement	Primary and secondary LC_{50} (or equivalent) data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary LC_{50} (or equivalent) data. The value used to set the guideline must be primary.	The minimum data requirement must be met with primary LC_{50} (or equivalent) data. Secondary data are acceptable. The value used to set the guideline may be secondary.

Source: CCME (2007).

Table 6. Minimum data set requirements for the generation of a long-term guideline value for marine environments

Group	Guideline		
	Type A	**Type B1**	**Type B2**
Fish	At least three studies on three or more marine fish species, at least one of which is a temperate species.		At least two studies on two or more marine fish species, at least one of which is a temperate species.
Aquatic invertebrates	At least two studies on two or more marine species from different classes, at least one of which is a temperate species.		At least two studies on two or more marine species.
Plants	At least one study on a freshwater vascular plant or freshwater algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and three studies on non-target freshwater plant or algal species are required.	At least **one** study on a freshwater vascular plant or freshwater algal species. If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and two studies on non-target freshwater plant or algal species are required.	If a toxicity study indicates that a plant or algal species is among the most sensitive species in the data set, then this substance is considered to be phyto-toxic, and two studies on non-target freshwater plant or algal species are required.
Preferred endpoints	The acceptable endpoints representing the no-effects threshold and EC_{10}/IC_{10} for a species are plotted. The other, less preferred, endpoints may be added sequentially to the data set to fulfill the minimum data requirement condition and improve the result of the modelling for the guideline derivation if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: most appropriate	The most preferred acceptable endpoint representing a low-effects threshold for a species is used as the critical study; the next less preferred endpoint will be used sequentially only if the more preferred endpoint for a given species is not available. The preference ranking is done in the following order: most appropriate EC_x/IC_x representing a low-effects threshold > $EC_{15\text{-}25}$/$IC_{15\text{-}25}$ > LOEC > MATC > $EC_{26\text{-}49}$/$IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50} > LC_{50}.	

Group	Guideline		
	Type A	Type B1	Type B2
	EC_x/IC_x representing a no-effects threshold > EC_{10}/IC_{10} > $EC_{11\text{-}25}/IC_{11\text{-}25}$ > MATC > NOEC > LOEC > $EC_{26\text{-}49}/IC_{26\text{-}49}$ > nonlethal EC_{50}/IC_{50}. Multiple comparable records for the same endpoint are to be combined by the geometric mean of these records to represent the averaged species effects endpoint.		
Data quality requirement	Primary and secondary no-effects- and low-effects-level data are acceptable to meet the minimum data set requirement. Both primary and secondary data will be plotted. A chosen model should sufficiently and adequately describe data and pass the appropriate goodness-of-fit test.	The minimum data requirement must be met with primary data. The value used to set the guideline must be primary. Only low-effect data can be used to fulfill the minimum data requirement.	Secondary data are acceptable. The value used to set the guideline may be secondary. Only low-effect data can be used to fulfill the minimum data requirement.

Source: CCME (2007).

10.3 Derivation of the Short-term Freshwater Benchmark

Appendix C contains the full toxicity data set for PFOA, including reference information, chemical identity, test organism details, experimental conditions and design, results, and data quality classification. Endpoints for 31 species were included in the short-term SSD for freshwater (Table 7). Where multiple comparable endpoints were available for the same species, effect, life stage, exposure duration and chemical identity, a geometric mean was calculated. Endpoints included in the derivation of the short-term benchmark concentration included LC_{50} values or equivalent (e.g., EC_{50} values for immobility). Low- or no-effect endpoints are not included in derivation of guidelines for short-term exposure (CCME 2007).

In some cases, there was more than one toxicity value available for a given species, but the exposure duration, life stages or chemical identity of the test substance differed, meaning that the geometric mean of the values could not be taken. In these cases, the most sensitive data point (or geometric mean value) was selected for inclusion in the short-term SSD. Full details regarding short-term data point selection are provided by CCME (2007).

The software R (R version 4.2.2 and RStudio version 1.4.1106) and web application shinyssdtools (ssdtools version 1.0.2; shinyssdtools version 0.1.1) (Thorley and Schwarz 2018; Dalgarno 2018) were used to create SSDs from the data set. SSDTools has been used previously in the development of the CWQG for manganese (CCME 2019). The package fit several cumulative distribution functions (log-normal, log-normal_log-normal, log-logistic, log-Gumbel, gamma and Weibull) to the data using maximum likelihood estimation (MLE) as the regression method and using a model averaging approach. The package then uses Akaike information criterion corrected for small sample size (AICc) to weight each model, representing how well each fit the data relative to the others. The best predictive model is that with the lowest AICc and therefore highest weight. The distributions that successfully fit the data with delta values (i.e., AICc difference) <7 are averaged based on the respective weights. Hazard concentration (HC)x estimates with 95% confidence intervals were calculated using parametric bootstrapping (10,000 iterations). The full R script is available in Appendix E. See Fox *et al.* (2021) and Thorley and Schwarz (2018) for more information on the approach.

Several distributions provided a good fit to the data (see Appendix F for goodness-of-fit statistics). The log-normal_log-normal distribution demonstrated the best fit to the data with the lowest AICc and the highest attributed weight, with gamma and Weibull models also having high value weight (Appendix F). It is worth noting that the log-normal_log-normal distribution is a bimodal model (a mixture of two log-normal distributions). The high weighting of this distribution is consistent with the bimodality of the data set seeing as many of the sensitive endpoints (at the lower end of the curve) are invertebrates. Fox *et al*. (2021) describe that multimodality, particularly bimodality, is not uncommon in empirical SSDs. It occurs when the toxicity data included in the SSD are not from a single, common probability model as is typically assumed (Fox *et al*. 2021). Fitting a mixture of distributions to the full SSD toxicity data set is an alternative approach for handling bimodality compared to splitting out the sensitive data or weighting the lower portion of the SSD curve (Fox *et al*. 2021). Referred to as statistical mixture modeling, these models have been stated to better represent the underlying functional process that leads to bimodality compared to univariate distributions. When used within a model-averaging approach, the statistical mixture models are highly penalized in the AICc because of the increased number of parameters (Fox *et al*. 2021). Therefore, statistical mixture models would only be weighted higher than univariate distributions when the fit is discernibly improved by the use of the mixture models, as is the case here.

The short-term SSD for freshwater is shown in Figure 2. The short-term freshwater benchmark concentration is 93,800 µg/L PFOA, with 95% confidence intervals of 63,100 to 149,000 µg/L.

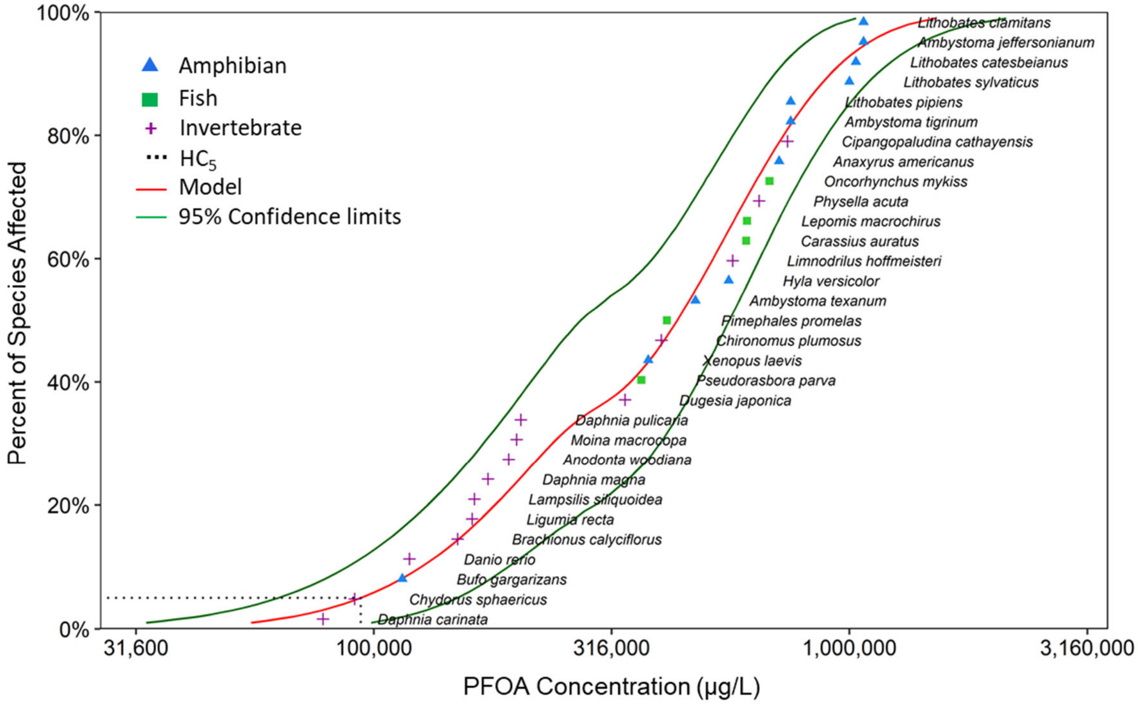


Figure 2. Short-term model-averaged species sensitivity distribution for PFOA in freshwater

Note: The HC_5 is 93,800 µg/L PFOA.

Table 7. Toxicity data points used in the short-term species sensitivity distribution to determine the benchmark concentration for PFOA in freshwater

SSD rank order	Species	Endpoint	Life cycle stage (age)	Effect concentration (µg/L PFOA)[a]	Data categorization	Reference
1	*Daphnia carinata* (water flea)	48-h EC_{50} (immobility)	Neonate	78,200	Secondary	Logeshwaran *et al.* 2021
2	*Chydorus sphaericus* (cladoceran)	48-h EC_{50} (immobility)	Neonate	91,100	Secondary	Le and Peijnenburg 2013
3	*Bufo gargarizans* (Asiatic toad)	96-h LC_{50}	Larvae	114,740	Primary	Yang *et al.* 2014
4	*Danio rerio* (zebrafish)	96-h LC_{50}	3 months	118,820	Secondary	Zhao *et al.* 2015
5	*Brachionus calyciflorus* (rotifer)	24-h LC_{50}	Neonate	150,000	Secondary	Zhang *et al.* 2013
6	*Ligumia recta* (black sandshell)	24-h EC_{50} (survival (foot movement))	Glochidia	161,000	Secondary	Hazelton *et al.* 2012
7	*Lampsilis siliquoidea* (fatmucket)	48-h EC_{50} (survival (foot movement))	Glochidia	162,600	Secondary	Hazelton *et al.* 2012
8	*Daphnia magna* (cladoceran)	48-h LC_{50}	Neonate	173,762 (geometric mean)	Primary and secondary	Yang *et al.* 2014; Lu *et al.* 2016; Boudreau 2002; Yang *et al.* 2019
9	*Anodonta woodiana* (Chinese pond mussel)	48-h LC_{50}	1 year	192,083	Secondary	Xia *et al.* 2018
10	*Moina macrocopa* (cladoceran)	48-h EC_{50} (Immobility)	Not reported	199,510	Secondary	Ji *et al.* 2008
11	*Daphnia pulicaria* (cladoceran)	48-h EC_{50} (immobility)	Neonate	203,722	Secondary	Boudreau 2002

SSD rank order	Species	Endpoint	Life cycle stage (age)	Effect concentration (µg/L PFOA)[a]	Data categorization	Reference
12	*Dugesia japonica* (dugesiid)	96-h LC_{50}	Not reported	337,200 (351,069 based on PFOA ammonium salt)[b] (geometric mean)	Secondary	Li 2009 (re-calculated in U.S. EPA 2022)
13	*Pseudorasbora parva* (topmouth gudgeon)	96-h LC_{50}	Not reported	365,020	Primary	Yang *et al.* 2014
14	*Xenopus laevis* (South African clawed frog)	96-h LC_{50}	Embryo	377,466	Secondary	Kim *et al.* 2013
15	*Chironomus plumosus* (midge)	96-h LC_{50}	Not reported	402,240	Primary	Yang *et al.* 2014
16	*Pimephales promelas* (fathead minnow)	96-h LC_{50}	Embryo, <24-h post-hatch	413,200	Secondary	Corrales *et al.* 2017
17	*Ambystoma texanum* (small-mouthed salamander)	96-h LC_{50}	Larvae (stage 40)	474,000	Secondary	Tornabene *et al.* 2021
18	*Hyla versicolor* (gray treefrog)	96-h LC_{50}	Larvae (stage 26)	557,000	Secondary	Tornabene *et al.* 2021
19	*Limnodrilus hoffmeisteri* (Huo Fu tubifex)	96-h LC_{50}	Not reported	568,200	Primary	Yang *et al.* 2014
20	*Carassius auratus* (crucian carp)	96-h LC_{50}	Not reported	606,610	Primary	Yang *et al.* 2014
21	*Lepomis macrochirus* (bluegill sunfish)	96-h LC_{50}	Not reported	608,955 (634,000 based on PFOA ammonium salt)[b]	Secondary	Dupont Co. 1994

SSD rank order	Species	Endpoint	Life cycle stage (age)	Effect concentration (µg/L PFOA)[a]	Data categorization	Reference
22	*Physella acuta* (formerly *Physa acuta*) (snail)	96-h LC_{50}	Not reported	645,454 (672,000 based on PFOA ammonium salt)[b]	Secondary	Li 2009
23	*Oncorhynchus mykiss* (rainbow trout)	96-h LC_{50}	Not reported	679,071 (707,000, based on PFOA ammonium salt)[b]	Secondary	Colombo *et al.* 2008
24	*Anaxyrus americanus* (American toad)	96-h LC_{50}	Larvae	711,000	Secondary	Tornabene *et al.* 2021
25	*Cipangopaludina cathayensis* (mud snail)	96-h LC_{50}	Not reported	740,070	Primary	Yang *et al.* 2014
26	*Ambystoma tigrinum* (Eastern tiger salamander)	96-h LC_{50}	Larvae	752,000	Secondary	Tornabene *et al.* 2021
27	*Lithobates pipiens* (formerly *Rana pipiens*) (Northern leopard frog)	96-h LC_{50}	Larvae	752,000	Secondary	Tornabene *et al.* 2021
28	*Lithobates sylvaticus* (formerly *Rana sylvatica*) (wood frog)	96-h LC_{50}	Larvae	999,000	Secondary	Tornabene *et al.* 2021
29	*Lithobates catesbeianus* (formerly *Rana catesbeiana*) (American bullfrog)	96-h LC_{50}	Larvae	1,031,620 (geometric mean)	Secondary	Tornabene *et al.* 2021; Flynn *et al.* 2019

SSD rank order	Species	Endpoint	Life cycle stage (age)	Effect concentration (µg/L PFOA)[a]	Data categorization	Reference
30	*Ambystoma jeffersonianum* (Jefferson salamander)	96-h LC_{50}	Larvae	1,070,000	Secondary	Tornabene *et al.* 2021
31	*Lithobates clamitans* (formerly *Rana clamitans*) (green frog)	96-h LC_{50}	Larvae	1,070,000	Secondary	Tornabene *et al.* 2021

814 **Notes:**

815 SSD = species sensitivity distribution; ECx = effect concentration, meaning the concentration affecting x% of the test organisms; LCx = lethal concentration for x% of the test organisms.

816 [a] Effect concentrations are for the ionic form of PFOA unless otherwise specified.

817 [b] The original study was conducted with PFOA ammonium salt (APFO). Value in parentheses represents the effect concentration for APFO. Endpoints for ammonium salts were 818 standardized to µg/L PFOA prior to inclusion in species sensitivity distribution (see Section 9.2 for example calculation).

10.4 Derivation of a Long-term Freshwater Canadian Water Quality Guideline

Appendix C contains the full toxicity data set for PFOA, including reference information, chemical identity, test organism details, experimental conditions and design, results, and data quality classification. Endpoints for 20 species were included in the long-term SSD for freshwater (Table 8). Where multiple comparable endpoints were available for the same species, effect, life stage, exposure duration and chemical identity, a geometric mean was calculated.

The long-term SSD is preferentially derived from no-effects data for long-term effects. According to the protocol, if there is more than one long-term endpoint type (e.g., an EC_{10} and a NOEC) for a given species and effect, the most preferred endpoint will be selected for inclusion in the SSD. The preferred rank order of endpoints for a long-term SSD is as follows (CCME 2007):

1. most appropriate EC_x/IC_x representing a no-effects threshold
2. EC_{10}/IC_{10}
3. EC_{11-25}/IC_{11-25}
4. MATC
5. NOEC
6. LOEC
7. EC_{26-49}/IC_{26-49}
8. Non-lethal EC_{50}/IC_{50}

Full details of long-term endpoint selection are provided by CCME (2007).

The same SSD derivation methodology that was followed for the short-term benchmark in Section 10.3 was applied for the long-term guideline and the R code is provided in Appendix G. The Weibull distribution demonstrated the best fit to the long-term data with the lowest AICc criteria and the highest attributed weight, with the gamma distribution also demonstrating a high value weight (Appendix H).

The long-term SSD for freshwater is shown in Figure 3. The long-term freshwater Canadian Water Quality Guideline is **73.4 µg/L** PFOA, with 95% confidence intervals of 10.4 to 736 µg/L.

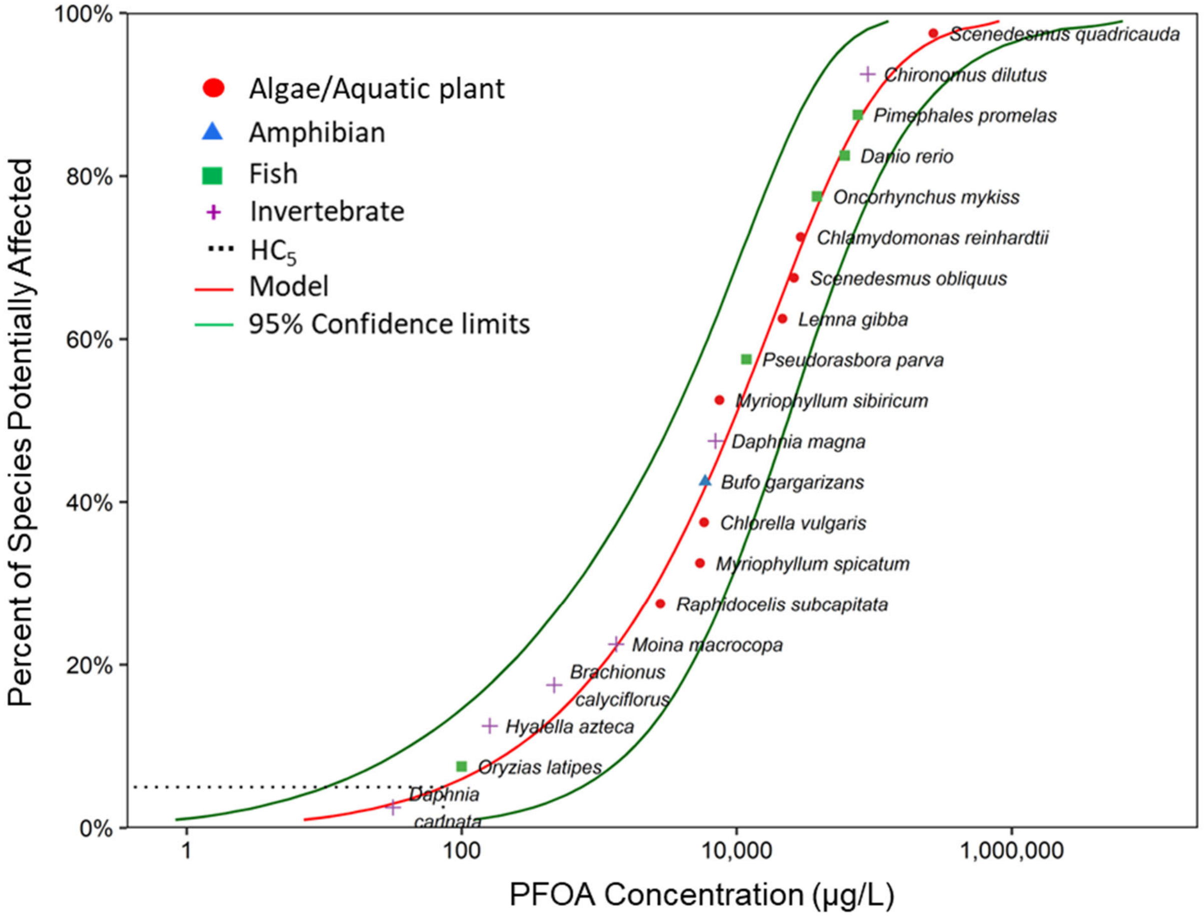


Figure 3. Long-term model-averaged species sensitivity distribution for PFOA in freshwater

Note: The HC_5 is 73.4 µg/L PFOA.

Table 8. Toxicity data points used in the long-term species sensitivity distribution to determine the Canadian Water Quality Guideline for PFOA in freshwater

SSD rank order	Species	Endpoint	Life cycle stage (age)	Effect concentration (µg/L PFOA)[a]	Data categorization	Reference
1	*Daphnia carinata* (water flea)	21-day MATC (reproduction, offspring)	Neonate	31.6	Secondary	Logeshwaran *et al.* 2021
2	*Oryzias latipes* (Japanese ricefish (medaka))	28-day post hatch LOEC (survival in F1)[b]	F0 adult; F1 egg	100	Secondary	Ji *et al.* 2008
3	*Hyalella azteca* (amphipod)	42-day EC_{10} (growth)	2–9 days old	160	Primary	Bartlett *et al.* 2021
4	*Brachionus calyciflorus* (rotifer)	Life cycle EC_{10} (intrinsic rate of natural increase)	Neonate	471	Secondary	Zhang *et al.* 2013
5	*Moina macrocopa* (cladoceran)	7-day EC_{10} (reproduction, number of young per adult)	Not reported	1,330	Secondary	Ji *et al.* 2008
6	*Raphidocelis subcapitata* (green algae)	10-day EC_{10} (growth, cell count)	Not reported	2,785 (2,900 based on PFOA ammonium salt)[c]	Secondary	Elnabarawy 1981
7	*Myriophyllum spicatum* (aquatic macrophyte)	21-day EC_{10} (plant length)	Apical shoots	5,413 (5,700 based on PFOA sodium salt)[d]	Secondary	Hanson *et al.* 2005
8	*Chlorella vulgaris* (green algae)	96-h IC_{10} (growth inhibition)	Not reported	5,797	Secondary	Boudreau 2002
9	*Bufo gargarizans* (Asiatic toad)	30-day EC_{10} (longevity)	Tadpole	5,890	Primary	Yang *et al.* 2014

SSD rank order	Species	Endpoint	Life cycle stage (age)	Effect concentration (µg/L PFOA)[a]	Data categorization	Reference
10	*Daphnia magna* (water flea)	21-day EC$_{10}$ (total number of spawning events)	<24 h	7,020	Primary	Yang *et al.* 2014
11	*Myriophyllum sibiricum* (aquatic macrophyte)	21-day EC$_{10}$ (dry mass)	Apical shoots	7,502 (7,900 based on PFOA sodium salt)[d]	Secondary	Hanson *et al.* 2005
12	*Pseudorasbora parva* (topmouth gudgeon)	30-day EC$_{10}$ (longevity)	Not reported	11,780	Primary	Yang *et al.* 2014
13	*Lemna gibba* (duckweed)	7-day IC$_{10}$ (growth inhibition)	Not reported	21,532	Secondary	Boudreau 2002
14	*Scenedesmus obliquus* (green algae)	96-h IC$_{10}$ (growth inhibition)	Exponential growth phase	26,100	Secondary	Hu *et al.* 2014
15	*Chlamydomonas reinhardtii* (green algae)	96-h IC$_{10}$ (growth inhibition)	Exponential growth phase	29,200	Secondary	Hu *et al.* 2014
16	*Oncorhynchus mykiss* (rainbow trout)	85-day NOEC (mortality, growth)	Fertilized eggs	≥38,420[e] (≥40,000 based on PFOA ammonium salt)[c]	Secondary	Colombo *et al.* 2008
17	*Danio rerio* (zebrafish)	7-day LC$_{10}$ (mortality)	Embryos	61,128	Secondary	Stinckens *et al.* 2018
18	*Pimephales promelas* (fathead minnow)	21-day NOEC (growth)	Egg to larvae	>76,000[f]	Secondary	Bartlett *et al.* 2021
19	*Chironomus dilutus* (midge)	19-day EC$_{10}$ (survival)	Larvae	89,800	Primary	McCarthy *et al.* 2021
20	*Scenedesmus quadricauda* (green algae)	96-h EC$_{50}$ (growth inhibition)	Logarithmic growth	269,630	Primary	Yang *et al.* 2014

Notes:

PFOA = perfluorooctanoic acid; SSD = species sensitivity distribution; ECx = effect concentration, meaning the concentration affecting x% of the test organisms; ICx = inhibitory concentration, meaning the concentration causing x% inhibition; LCx = lethal concentration for x% of the test organisms; LOEC = lowest observed effect concentration; NOEC = no observed effect concentration; MATC = maximum acceptable toxicant concentration (geometric mean of the NOEC and LOEC)

[a] Effect concentrations are for the ionic form of PFOA unless otherwise specified.

[b] Transgenerational study; F0 (parental generation) exposed to 100 µg/L for 14 days, F1 (progeny generation) exposed to 100 µg/L and mortality assessed at 28 days post-hatch.

[c] The original study was conducted with PFOA ammonium salt (APFO). Value in parentheses represents the effect concentration for APFO. Endpoints for ammonium salts were standardized to µg/L PFOA prior to inclusion in species sensitivity distribution (see Section 9.2 for example calculation).

[d] The original study was conducted with PFOA sodium salt. Value in parentheses represents the effect concentration for the sodium salt form. Endpoints for sodium salts were standardized to µg/L PFOA prior to inclusion in species sensitivity distribution (see Section 9.2 for example calculation).

[e] Value plotted as 38,420 µg/L in species sensitivity distribution.

[f] Value plotted as 76,000 µg/L in species sensitivity distribution.

10.5 Assessing the Protection of the Long-term Freshwater Canadian Water Quality Guideline

To determine whether the long-term PFOA guideline is sufficiently protective (meaning that it meets CCME's guiding principle), a protectiveness assessment was completed using results of acceptable aquatic toxicity studies (i.e., all acceptable acute and chronic data from Appendix C). Any toxic effects observed at concentrations below the long-term PFOA guideline value were examined to determine if the protection clause was applicable (CCME 2007). The CCME (2007) protocol includes the following section regarding the protection clause, which applies only to the long-term guideline:

> The protection clause may be invoked if an acceptable single (or, if applicable, geometric mean) no-effect or low-effect level endpoint (e.g., ECx for growth, reproduction, survival, or behaviour) for a species at risk (as defined by the Committee on the Status of Endangered Wildlife in Canada [COSEWIC]) is lower than the proposed guideline (i.e., is below the 5th percentile intercept to the fitted curve), then that endpoint becomes the recommended guideline value. If this endpoint is a moderate- or severe-effect level endpoint for a species at risk (i.e., ECx x≥ 50%, or a lethality endpoint [LCx]), then the guideline value shall be determined on a case-by-case basis (e.g., by using an appropriate safety factor) (Chapman et al. 1998).
>
> Similarly, if an acceptable single (or, if applicable, geometric mean) lethal-effects endpoint (i.e., LCx, where x is ≥ 15%) for any species is lower than the proposed guideline (i.e., is below the 5th percentile intercept to the fitted curve), then that endpoint becomes the recommended guideline value.
>
> Furthermore, special consideration will be required if multiple endpoints for a single taxon (e.g., fish, invertebrates, or plant/algae) and/or an elevated number of secondary studies are clustered around the 5th percentile. Best scientific judgment should be used in deciding whether this situation is present (e.g., due consideration should be given to the percentage of data points in question to the whole data set) and in determining the best path forward to address this situation. (CCME 2007, p. 5–6)

Three endpoints were below the CWQG for PFOA, including a 21-day NOEC and 21-day MATC for reproduction for *Daphnia carinata* and a 42-day EC_{10} for reproduction for *Hyalella azteca*. None of these endpoints that fell below the guideline were for a species at risk or for lethal effects equal to or above a level of 15%. For *Daphnia carinata,* the 21-day MATC that was below the guideline was included in the long-term SSD for PFOA as it was the most preferred endpoint for this species. Additionally for this species, a 21-day LOEC for reproduction as well as two EC_{50} values for immobility were available and appear above the guideline. For *Hyalella azteca*, 49 other acceptable chronic and sub-chronic endpoints were available for this species that appear above the guideline. The 42-day EC_{10} for reproduction for *H. azteca* was not included in the long-term SSD as the 42-day EC_{10} for growth for *H. azteca* was preferred due to variability in the reproduction endpoint and the determination that the endpoint for growth was more reliable (Bartlett *et al.* 2021). No acceptable data from the short-term data set were below the long-term CWQG. Overall examination of the data suggests that the long-term freshwater PFOA CWQG is protective and that the protection clause is not applicable.

10.6 Protection of Marine Life

There were insufficient data to meet CCME's minimum data requirements for the derivation of a short-term benchmark or long-term guideline for the protection of marine life. Available marine toxicity data are included in Appendix C. It is not appropriate to apply the freshwater PFOA guidelines in a marine environment as there appears to be a difference in toxicity between freshwater and marine organisms based on the available data (Appendix C; Hayman *et al*. 2021). This may be due to differences in the sensitivity of marine species to PFOA compared to freshwater species, or to greater bioavailability of PFOA in the more saline marine water compared to freshwater (Hayman *et al.* 2021).

11.0 CONSIDERATIONS FOR USES OF THE SHORT-TERM BENCHMARK CONCENTRATION AND THE LONG-TERM CANADIAN WATER QUALITY GUIDELINE

The short-term benchmark concentration and the CWQG provide guidance for both short-term and long-term exposures, respectively. The short-term exposure value is intended to protect a specified fraction of individuals from severe effects such as lethality for a defined short-term exposure period. The short-term benchmark is intended to give guidance on impacts of severe but transient events such as spills or inappropriate use or disposal of the substance in question. Long-term guidelines are intended to protect the most sensitive species and life stage indefinitely. Aquatic life may be chronically exposed to a substance as a result of gradual release from soils or sediments and gradual entry through groundwater or runoff, emissions from industrial processes and long-range transport. There is potential for PFOA present at contaminated sites to migrate through groundwater, surface water and leachate to off-site water sources away from contaminated sites.

Before using the PFOA short-term benchmark concentration or the long-term CWQG, it should be taken into consideration that they are both based on existing scientific information. The short-term benchmark concentration and CWQG for PFOA are two of many tools for the assessment and interpretation of PFOA monitoring data in surface water. Although this guideline does not apply to precursors of PFOA, consideration should be given to the potential for precursors to degrade into PFOA and cause accumulation in the environment. The effect of PFOA on aquatic organisms may vary among sites because the species composition, physicochemical characteristics and presence of other toxicants that could interact additively or synergistically with PFOA may differ through ecosystems (CCME 2007). For example, other PFAS are often present with PFOA, especially with applications of AFFF. Additionally, the CCME (2007) protocol does not address exposure through food or bioaccumulation to higher trophic levels. As such, aquatic life that is exposed to PFOA primarily through food may not be adequately protected. Furthermore, the guidelines for PFOA may not prevent the accumulation of PFOA in aquatic life. Therefore, this document may be used as a basis for the derivation of site-specific guidelines and objectives when needed. For more information on site-specific water quality guideline derivation procedure, please refer to the CCME guidance document (2003).

12.0 GUIDELINE SUMMARY

The short-term benchmark and long-term CWQG for PFOA are summarized in Table 9.

Table 9. Short-term benchmark and long-term Canadian Water Quality Guideline for PFOA (µg/L) for the protection of aquatic life

	Short-term benchmark (µg/L)	**Long-term Canadian Water Quality Guideline (µg/L)**
Freshwater	93,800	73.4
Marine	NRG[a]	NRG[a]

Notes:

The derivation of the PFOA short-term benchmark and long-term Canadian Water Quality Guideline followed the CCME Protocol for Derivation of Water Quality Guidelines for the Protection of Aquatic Life (CCME 2007).

NRG = no recommended guideline

[a] Insufficient data were available to meet CCME minimum data requirements for the derivation of a short-term benchmark or long-term guideline for protection of marine life (CCME 2007).

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APPENDIX A: PHYSICAL AND CHEMICAL PROPERTIES OF PFOA

(Separate Excel file)

APPENDIX B: CONCENTRATIONS OF PFOA IN SURFACE WATER

(Separate Excel file)

APPENDIX C: FULL SHORT-TERM AND LONG-TERM AQUATIC TOXICITY DATA SET

(Separate Excel file)

APPENDIX D: RATIONALE FOR SURROGATE SPECIES

(Separate Excel file)

APPENDIX E: R CODE FOR SHORT-TERM SPECIES SENSITIVITY DISTRIBUTION

(Separate Excel file)

APPENDIX F: GOODNESS-OF-FIT STATISTICS FOR SHORT-TERM SPECIES SENSITIVITY DISTRIBUTION

(Separate Excel file)

APPENDIX G: R CODE FOR LONG-TERM SPECIES SENSITIVITY DISTRIBUTION

(Separate Excel file)

APPENDIX H: GOODNESS OF FIT STATISTICS FOR LONG-TERM SPECIES SENSITIVITY DISTRIBUTION

(Separate Excel file)