Canadian Water Quality Guidelines for the Protection of Aquatic Life

PFOA
20XX

Perfluorooctanoic acid (PFOA) is an anthropogenic substance with a chain length of eight carbons, seven of which are perfluorinated. It has a long perfluorocarbon tail that is both hydrophobic and oleophobic, and a charged head that is hydrophilic. It belongs to the class of perfluorocarboxylic acids (PFCAs), which is under the broader class of per- and polyfluoroalkyl substances (PFAS). PFOA is an extremely stable and bioaccumulative substance found in many environmental media, including Canadian fresh and marine waters, that was determined in 2012 to meet the criteria for a toxic substance under the *Canadian Environmental Protection Act* (Environment Canada and Health Canada [EC and HC] 2012).

These water quality guidelines for PFOA considered toxicity data for the acid (CAS RN 335-67-1), its conjugate base (perfluorooctanoate or PFO) (CAS RN 45285-51-6), branched PFOA (CAS RN 90480-55-0) and PFOA's principal salt forms (various CAS RNs).

Table 1. Canadian Water Quality Guidelines (CWQGs) for the protection of aquatic life for PFOA

	Short-term benchmark (µg/L)	Long-term 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 Canadian Council of Ministers of the Environment (CCME) minimum data requirements for derivation of a short-term benchmark or long-term guideline for protection of marine life (CCME 2007).

Sources and Uses

PFOA and its salts have been used in industrial processes and as a component of aqueous firefighting foams. In addition, it has been used in the production of fluoropolymers, where it may remain as a trace contaminant when the fluoropolymer is used to manufacture commercial and consumer products such as cables and hoses, non-stick coatings on cookware, water-resistant or non-stick coatings for textiles and carpets, and personal care products. Although not known to have been manufactured in Canada, PFOA can enter through the importation of manufactured items. It can also be formed from the breakdown of precursor compounds (Agency for Toxic Substances and Disease Registry [ATSDR] 2021). Releases to the environment can occur directly from the industrial and consumer use of PFOA-containing products, including from the application of firefighting foams, from wastewater effluents and landfill leachates, or from the long-range transport of PFOA or its precursors. Aqueous film-forming foams (AFFF) containing PFAS such as PFOA are commonly used at airports and military bases to fight fires caused by flammable liquids and fuels, where it may cause the contamination of soil and water. The composition of

AFFF can vary by product, and the type of PFAS contained in foams has changed over time, with some formulations containing PFOA precursors that can degrade to PFOA (Interstate Technology Regulatory Council [ITRC] 2022). PFOA contamination can migrate offsite via groundwater, surface water and leachate to other water sources.

Environmental Fate and Behaviour

PFOA is a surfactant and tends to associate with surfaces and interfaces (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). The free acid readily dissociates to its conjugate base (i.e., ionized form) at most environmentally relevant pH values. It has high water solubility and low volatility in the ionized form, and as a result is expected to partition primarily to the aquatic environment; partitioning to sediments may occur but is not expected to be a major sink (EC and HC 2012). Organic carbon content, pH, ionic strength and salinity have all been shown to influence partitioning between water and sediment (Ahrens *et al*., 2009; 2011; Ferrey *et al.* 2012; SNC-Lavalin Environment [SNC] 2012; Wang *et al.* 2012; Xiao *et al.* 2021). PFOA is expected to be mobile in soil and can leach into groundwater (ATSDR 2021), where it could then migrate to other water sources. In the environment, 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 via ocean currents and atmospheric oxidative transformations and the subsequent wet and dry deposition of airborne precursors (Muir *et al.* 2019). PFOA has been detected in remote areas such as the Canadian Arctic (D'Agostino and Mabury 2017; Lescord *et al.* 2015; Benskin *et al.* 2012; Muir *et al*. 2015; Muir *et al.* 2019).

PFOA was found to bioaccumulate and biomagnify in terrestrial and marine mammals via protein binding rather than lipid partitioning (EC and HC 2012). It was found to have a low to moderate potential to accumulate in aquatic species (EC and HC 2012). PFOA is considered to be persistent (EC and HC 2012).

Environmental Concentrations

Concentrations of PFOA in ambient surface water in Canada 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. Freshwater sites (including reference, urban and mixed development sites as well as sites associated with municipal wastewater treatment plants) sampled across Canada between 2013 and 2020 had maximum and mean concentrations of PFOA of 24.4 and 1.52 ng/L, respectively (Lalonde and Garron 2022). Surface water sites downstream or close to areas that have used AFFF can have greatly elevated levels of PFOA (Stock *et al.* 2007; Muir *et al.* 2019; de Solla *et al.* 2012; Bhavsar *et al.* 2016). Concentrations of PFOA at contaminated sites in Canada have reached up to 11,300 ng/L (11.3 µg/L) (Moody *et al.* 2002). Available data may or may not represent the most contaminated sites as data are limited and the composition of AFFF can and has varied with time.

Effects on Aquatic Life

The mechanism of toxic action of PFAS and PFOA in aquatic organisms is an ongoing field of research. Adverse impacts of perfluoroalkyl acids (PFAAs) on aquatic organisms include disruptions to metabolism, reproduction, immune system and hormones, in addition to neuronal and developmental toxicity. Effects are initiated by the activation of various nuclear receptors or other factors, which in turn result in transcription-level changes, followed by metabolite-level and tissue-level changes (Lee *et al.* 2020). Studies with invertebrates have demonstrated signs of oxidative stress as well as effects on antioxidant defense systems (Ankley *et al.* 2020). PFOA exposure has also been associated with neurotoxic effects in invertebrate species (Ankley *et al.* 2020). In fish, studies have 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 (Benninghoff *et al.* 2011) and to activate nuclear receptors involved in lipid metabolism in fish (Ankley *et al.* 2020).

Water Quality Guideline Derivation

Both the short-term benchmark and long-term Canadian Water Quality Guidelines for PFOA for freshwater followed the derivation procedures as described in the protocol (CCME 2007). Endpoints for PFOA salts were standardized to the ionic form of PFOA prior to inclusion in guideline derivation to allow the comparison of toxicity on the same chemical basis (see CCME 20XX for details).

Short-term Freshwater Benchmark Concentration

CCME derives short-term benchmark concentrations using severe effects data (such as lethality) for defined short-term exposure periods. These benchmarks are estimators of severe effects to the aquatic ecosystem and are intended to give guidance on the impacts of severe but transient situations, such as spill events and inappropriate use or disposal. Short-term benchmark concentrations do not provide guidance for protective levels of a substance in the aquatic environment, as they are levels that do not protect against adverse effects.

CCME minimum data requirements were met for the Type A (Species Sensitivity Distribution (SSD)) approach for short-term freshwater exposure, and data for 31 species were included in the SSD (Figure 1; Table 1) following criteria outlined by CCME (2007). Where multiple comparable endpoints were available for the same species, effect, life stage, exposure duration and chemical identity, a geometric mean was calculated. A model averaged SSD and associated statistics were generated using ssdtools and R software (Thorley and Schwarz 2018; Dalgarno 2018). The short-term benchmark concentration is the hazard concentration for the fifth percentile (HC_5) from the short-term SSD and is 93,800 μg/L PFOA.

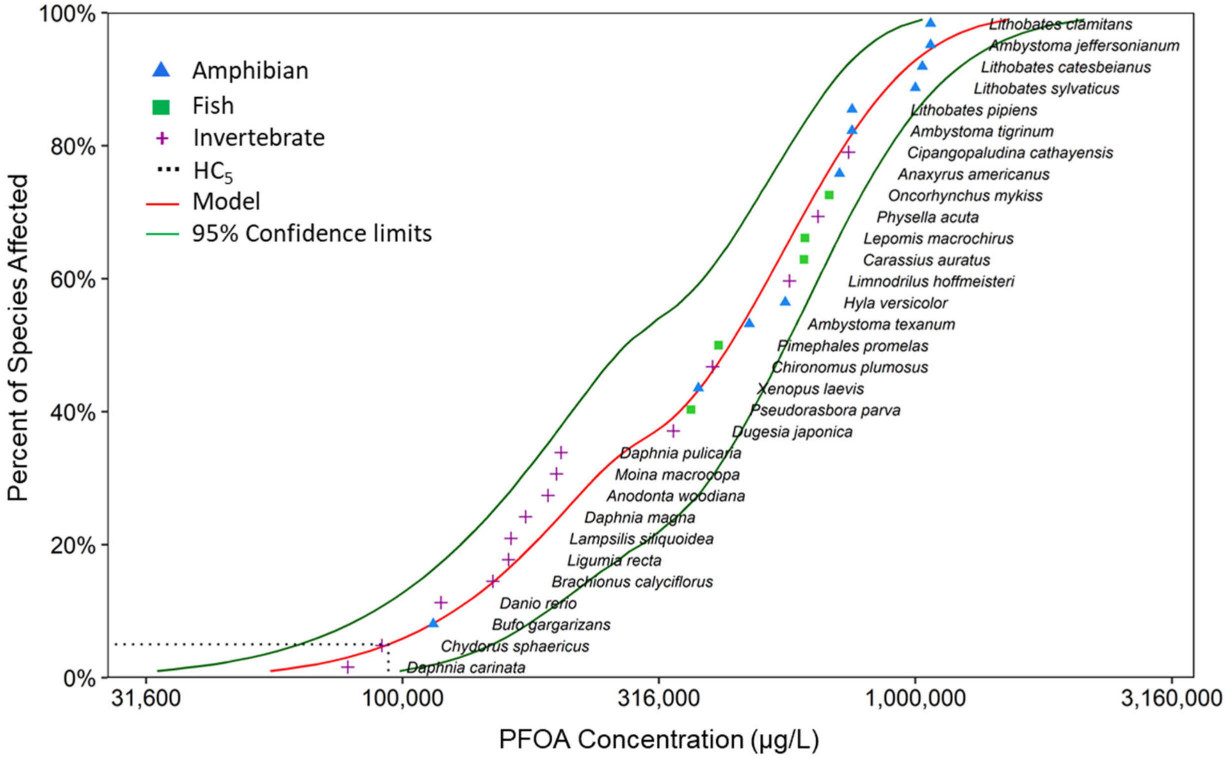

Figure 1. Short-term model-averaged species sensitivity distribution (SSD) for PFOA in freshwater

Note: The HC5 is 93,800 μg/L PFOA.

Table 1. Endpoints used to determine the short-term freshwater benchmark concentration for perfluorooctanoic acid (PFOA)

SSD rank	Species	Endpoint	Concentration (μg/L PFOA)[a]
1	*Daphnia carinata* (water flea)	48-h EC_{50}	78,200
2	*Chydorus sphaericus* (cladoceran)	48-h EC_{50}	91,100
3	*Bufo gargarizans* (Asiatic toad)	96-h LC_{50}	114,740
4	*Danio rerio* (zebrafish)	96-h LC_{50}	118,820
5	*Brachionus calyciflorus* (rotifer)	24-h LC_{50}	150,000
6	*Ligumia recta* (black sandshell)	24-h EC_{50}	161,000
7	*Lampsilis siliquoidea* (fatmucket)	48-h EC_{50}	162,600
8	*Daphnia magna* (cladoceran)	48-h LC_{50}	173,762[b]
9	*Anodonta woodiana* (Chinese pond mussel)	48-h LC_{50}	192,083
10	*Moina macrocopa* (cladoceran)	48-h EC_{50}	199,510
11	*Daphnia pulicaria* (cladoceran)	48-h EC_{50}	203,722
12	*Dugesia japonica* (dugesiid)	96-h LC_{50}	337,200[b,c]
13	*Pseudorasbora parva* (topmouth gudgeon)	96-h LC_{50}	365,020
14	*Xenopus laevis* (South African clawed frog)	96-h LC_{50}	377,466
15	*Chironomus plumosus* (midge)	96-h LC_{50}	402,240
16	*Pimephales promelas* (fathead minnow)	96-h LC_{50}	413,200
17	*Ambystoma texanum* (small-mouthed salamander)	96-h LC_{50}	474,000
18	*Hyla versicolor* (gray treefrog)	96-h LC_{50}	557,000
19	*Limnodrilus hoffmeisteri* (Huo Fu tubifex)	96-h LC_{50}	568,200
20	*Carassius auratus* (crucian carp)	96-h LC_{50}	606,610
21	*Lepomis macrochirus* (bluegill sunfish)	96-h LC_{50}	608,955[c]
22	*Physella acuta* (formerly *Physa acuta*) (snail)	96-h LC_{50}	645,454[c]

SSD rank	Species	Endpoint	Concentration (µg/L PFOA)[a]
23	*Oncorhynchus mykiss* (rainbow trout)	96-h LC_{50}	679,071[c]
24	*Anaxyrus americanus* (American toad)	96-h LC_{50}	711,000
25	*Cipangopaludina cathayensis* (mud snail)	96-h LC_{50}	740,070
26	*Ambystoma tigrinum* (Eastern tiger salamander)	96-h LC_{50}	752,000
27	*Lithobates pipiens* (Northern leopard frog)	96-h LC_{50}	752,000
28	*Lithobates sylvaticus* (wood frog)	96-h LC_{50}	999,000
29	*Lithobates catesbeianus* (American bullfrog)	96-h LC_{50}	1,031,620[b]
30	*Ambystoma jeffersonianum* (Jefferson salamander)	96-h LC_{50}	1,070,000
31	*Lithobates clamitans* (green frog)	96-h LC_{50}	1,070,000

Notes:
EC_x = effect concentration, meaning the concentration affecting x% of the test organisms; LC_x = lethal concentration for x% of the test organisms
[a] Effect concentrations are for the ionic form of PFOA.
[b] Based on geometric mean of multiple comparable values.
[c] The original study was conducted with PFOA ammonium salt (APFO). Endpoint was standardized to µg/L PFOA for inclusion in species sensitivity distribution (see CCME 20XX for details).

Long-term Freshwater Canadian Water Quality Guideline

Long-term exposure guidelines identify waterborne concentrations intended to protect all forms of aquatic life for indefinite exposure periods. These guidelines are preferentially derived using no-effects data for long-term effects. CCME minimum data requirements were met for the Type A (SSD) approach for long-term freshwater exposure, and data for 20 species were included in the SSD (Figure 2; Table 2) following criteria outlined by CCME (2007). Where multiple comparable endpoints were available for the same species, effect, life stage, exposure duration and chemical identity, a geometric mean was calculated. A model averaged SSD and associated statistics were generated using ssdtools and R software (Thorley and Schwarz 2018; Dalgarno 2018). The long-term freshwater Canadian Water Quality Guideline is the HC_5 value from the long-term SSD and is 73.4 µg/L PFOA.

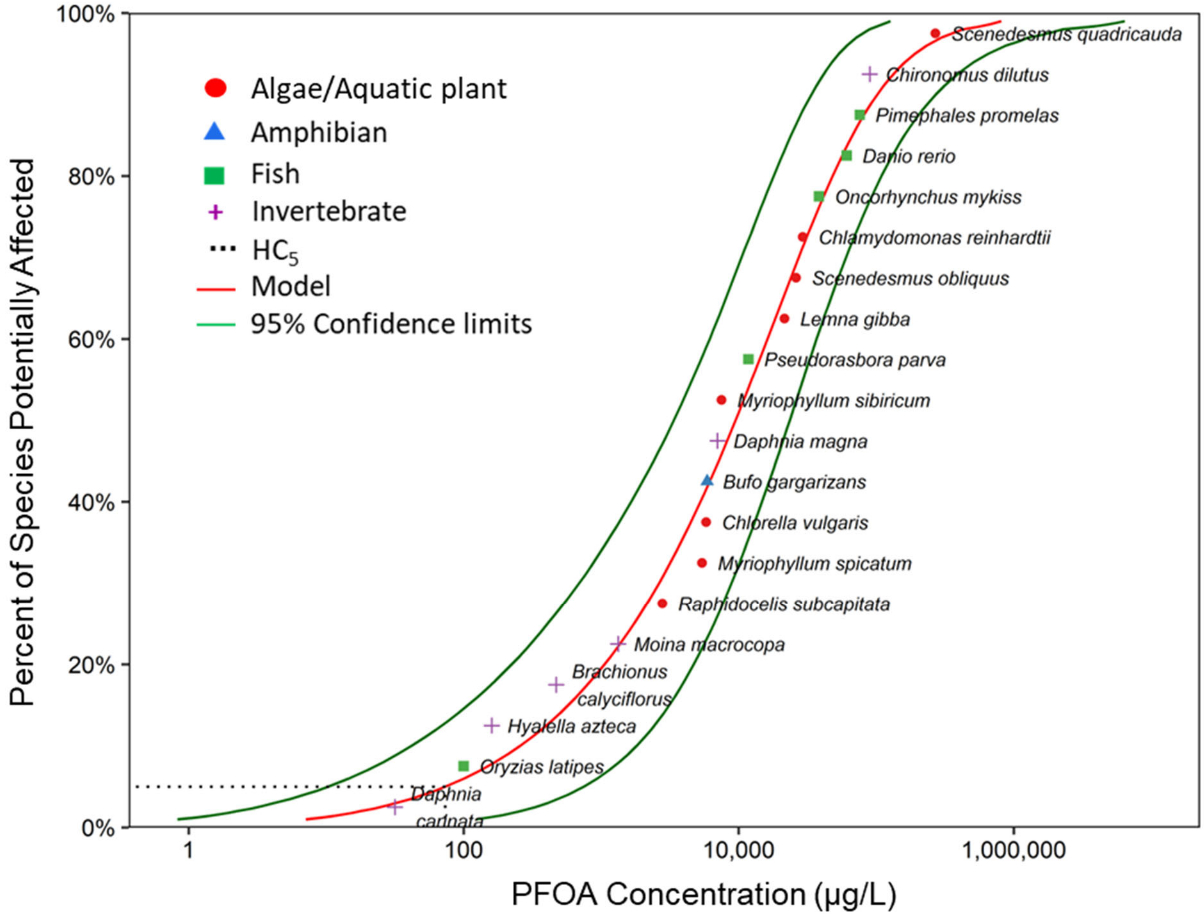

Figure 2. Long-term model-averaged species sensitivity distribution (SSD) for PFOA in freshwater

Note: The HC_5 is 73.4 µg/L PFOA.

Table 2. Endpoints used to determine the long-term freshwater Canadian Water Quality Guideline for perfluorooctanoic acid (PFOA)

SSD rank	Species	Endpoint	Concentration (µg/L PFOA)[a]
1	*Daphnia carinata* (water flea)	21-day MATC (reproduction, offspring)	31.6
2	*Oryzias latipes* (Japanese ricefish (medaka))	28-day post-hatch LOEC (survival in F1)[b]	100
3	*Hyalella azteca* (amphipod)	42-day EC_{10} (growth)	160
4	*Brachionus calyciflorus* (rotifer)	Life-cycle EC_{10} (intrinsic rate of natural increase)	471
5	*Moina macrocopa* (cladoceran)	7-day EC_{10} (reproduction, number of young per adult)	1,330
6	*Raphidocelis subcapitata* (green algae)	10-day EC_{10} (growth, cell count)	2,785[c]
7	*Myriophyllum spicatum* (aquatic macrophyte)	21-day EC_{10} (plant length)	5,413[d]
8	*Chlorella vulgaris* (green algae)	96-h IC_{10} (growth inhibition)	5,797
9	*Bufo gargarizans* (Asiatic toad)	30-day EC_{10} (longevity)	5,890
10	*Daphnia magna* (water flea)	21-day EC_{10} (total number of spawning events)	7,020
11	*Myriophyllum sibiricum* (aquatic macrophyte)	21-day EC_{10} (dry mass)	7,502[d]

SSD rank	Species	Endpoint	Concentration (µg/L PFOA)[a]
12	*Pseudorasbora parva* (topmouth gudgeon)	30-day EC_{10} (longevity)	11,780
13	*Lemna gibba* (duckweed)	7-day IC_{10} (growth inhibition)	21,532
14	*Scenedesmus obliquus* (green algae)	96-h IC_{10} (growth inhibition)	26,100
15	*Chlamydomonas reinhardtii* (green algae)	96-h IC_{10} (growth inhibition)	29,200
16	*Oncorhynchus mykiss* (rainbow trout)	85-day NOEC (mortality, growth)	≥38,420[c,e]
17	*Danio rerio* (zebrafish)	7-day LC_{10} (mortality)	61,128
18	*Pimephales promelas* (fathead minnow)	21-day NOEC (growth)	>76,000[f]
19	*Chironomus dilutus* (Midge)	19-day EC_{10} (survival)	89,800
20	*Scenedesmus quadricauda* (green algae)	96-h EC_{50} (growth inhibition)	269,630

Notes:
EC_x = effect concentration, meaning the concentration affecting x% of the test organisms; IC_x = inhibitory concentration, meaning the concentration causing x% inhibition; LC_x = 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.
[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). Endpoint was standardized to µg/L PFOA for inclusion in species sensitivity distribution (see CCME 20XX for details).
[d] The original study was conducted with PFOA sodium salt. Endpoint was standardized to µg/L PFOA for inclusion in species sensitivity distribution (see CCME 20XX for details).
[e] Value plotted as 38,420 µg/L in species sensitivity distribution.
[f] Value plotted as 76,000 µg/L in species sensitivity distribution.

A protectiveness assessment was completed for the long-term CWQG (CCME 20XX), which found that it achieved the intended level of protection as per the protocol (CCME 2007).

Marine Water Quality Guideline

There were insufficient data to meet CCME minimum data requirements for derivation of a short-term benchmark or long-term guideline for the protection of marine life. 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, with at least marine invertebrates appearing to be more sensitive to PFOA (CCME 20XX; Hayman *et al*. 2021).

Implementation and Other Considerations

A short-term benchmark concentration and the CWQG provide guidance for short-term and long-term exposures, respectively. 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.

This guideline does not apply to intact (i.e., not degraded) precursors of PFOA; however, consideration should be given to the potential for precursors to degrade into PFOA and cause accumulation in the environment. Additionally, the guideline does not address exposure through food or bioaccumulation to higher trophic levels. The effect of PFOA on aquatic organisms may vary among sites due to species composition, physicochemical characteristics and presence of other toxicants (CCME 2007). For example, other PFAS are often present with PFOA, especially with applications of AFFF. Therefore, this document may be used as a basis for the derivation of site-specific guidelines and objectives when needed (CCME 2003).

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