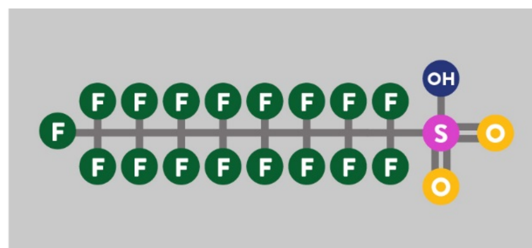
Water quality standards

December 2020

Water Quality Standards Technical Support Document: Human Health Protective Water Quality Criteria for Perfluorooctane Sulfonate (PFOS)



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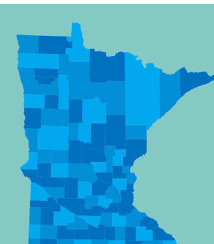

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Dr. Laura Solem and Bonnie Brooks (both formerly of the Minnesota Pollution Control Agency, Water Quality Standards Unit), with datasets and data analyses also provided by Dr. Bruce Monson and Summer Streets (MPCA), Sophie Greene (MPCA), publications support from Mary Blackstock

Adapted toxicokinetic serum model and support from Christopher Greene and Drs. Helen Goeden and James Jacobus (Minnesota Department of Health)

Photos

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Minnesota Pollution Control

Revisions

December 2020:

- The units associated with the breastmilk intake rate in Table 8-1 were corrected to mL/Kg-d from L/kg-d.
- Included additional references to Minn. R. 7052.0100 that contains methods for the development of WQC in the Lake Superior Basin.
- Fixed mistakes in how the water quality criteria were recorded in Table 8-2.

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Document number: wq-s6-61a

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Acronyms

BAF	Bioaccumulation Factor
BCC	Bioaccumulative Chemical of Concern
BW	Body Weight
CDC	Centers for Disease Control and Prevention
CC_{DFR} /CS_{DFR}	Chronic Criterion or Standard – Drinking water, fish consumption, recreation use classes
$CC_{DFR\text{-}DEV}$ / $CS_{DFR\text{-}DEV}$	Developmental endpoints/toxicity or less-than-chronic parameters are the basis for the value (also referenced as CC_{DEV} or CS_{DEV})
CC_{FT}/CS_{FT}	Chronic Criterion or Standard – Fish tissue-based
$CC_{FT\text{-}DEV}$/$CS_{FT\text{-}DEV}$	Chronic Criterion or Standard – Less-than-chronic or developmental toxicity-based, Fish tissue-based
CC_{FR}/CS_{FR}	Chronic Criterion or Standard – Fish consumption and recreation use class
$CC_{FR\text{-}DEV}$ / $CS_{FR\text{-}DEV}$	Developmental endpoints/toxicity or less-than-chronic parameters are the basis for the value (also referenced as CC_{DEV} or CS_{DEV})
CWA	Clean Water Act
DC	Domestic Consumption (Class 1 Water Quality Standard)
DWIR	Drinking Water Intake Rate
EPA	U.S. Environmental Protection Agency
FCR	Fish Consumption Rate
FCMP	Fish Contaminant Monitoring Program (interagency team with MDH and MNDNR)
FDA	U.S. Food and Drug Administration
GLI	Great lakes Initiative (Minn. R. ch. 7052)
HA	Health Advisory (Safe Drinking Water Act)
HBV	Health Based Value; developed by the Minnesota Department of Health (MDH) using the same methodologies as HRLs
HRL	Health Risk Limits; drinking water standards from MDH in Minn. R. ch. 4717
IWR	Incidental Water Intake Rate
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
Minn. R. ch.	Minnesota Rule chapter
Minn. Stat.	Minnesota Statute
NHANES	National Health and Nutrition Examination Survey
NPDES	National Pollutant Discharge Elimination System
PFAS	Per- and Polyfluoroalkyl Substances
RfD	Reference Dose for noncancer toxicants and nonlinear carcinogens
RME	Reasonable Maximum Exposure
RSC	Relative Source Contribution factor
USEPA	U.S. Environmental Protection Agency
WQC	Water Quality Criteria (developed for toxic pollutants on a site-specific basis)
WQS	Water Quality Standard (refers to a pollutant-specific numeric standard in rule; also can refer to the three elements of a WQS)
WCBA	Women of Childbearing Age

Executive summary: site-specific water quality criteria for perfluorooctane sulfonate

The Minnesota Pollution Control Agency (MPCA) has multiple programs monitoring and responding to per- and polyfluoroalkyl substance (PFAS) contamination in groundwater, surface water, and aquatic life, mainly fish. This technical support document (TSD) describes the derivation of site-specific water quality criteria (WQC) for the principal PFAS detected in Minnesota's freshwater fish at concentrations of concern for fish consumers: perfluorooctane sulfonate (PFOS).

The MPCA is the state agency responsible for setting water quality standards and criteria[1] under the Clean Water Act. Water quality standards (WQS) are used to:

- Protect water resources for uses such as source for drinking water, fishing, swimming and other aquatic recreation, and sustaining healthy communities of fish, bugs, plants, and other aquatic life.
- Identify polluted waters in need of restoration or healthy waters in need of additional protection.
- Guide the limits set on what regulated entities can discharge to surface water.

Minnesota's WQS are promulgated in Minn. R. ch. 7050 (Waters of the State), and 7052 (Lake Superior Basin Water Standards). Details of how WQS are implemented in point-source discharge permitting are contained in Minn. R. ch. 7053 (State Waters Discharge Restrictions), and parts of chapter 7052. WQS are the fundamental regulatory and policy foundation to preserve and restore the quality of all waters of the state. They consist of three elements:

- Water use classifications (beneficial uses) that identify how people, aquatic communities, and wildlife use our waters.
- Narrative and/or numeric standards to protect those uses by designating specific amount of pollutants allowed in a body of water or making statements of unacceptable conditions in and on the water.
- Antidegradation policies to maintain existing uses, protect high quality waters, and preserve waters of outstanding value.

The federal Clean Water Act requires states apply these three elements and other related protections as the framework for achieving the goals of this federal regulation.[2]

[1] *In Minnesota, the term "water quality standard" or "WQS" refers to a promulgated narrative or numeric standard. A "water quality criterion/criteria" or "WQC" is a site-specific value(s) established for a specific toxic pollutant detected in surface water, fish, or effluents that lacks a numeric standard in rule.*

[2] *In the U.S. Environmental Protection Agency (EPA) guidance the numeric values that underpin application of water quality standards are called "water quality criteria" or "National Ambient Water Quality Criteria." Minnesota's water quality standards' rules use "criterion" or "criteria" to mean numeric values not listed in Minn. R. chs 7050 or 7052, but derived by EPA-approved methods in rule.*

Minnesota's water quality rules establish the following seven beneficial uses for our waters:

Use class	Beneficial use
Class 1	Domestic consumption (i.e., drinking water and food processing)
Class 2	Aquatic life and recreation (including aquatic consumption)
Class 3	Industrial consumption
Class 4	Agricultural and wildlife
Class 5	Aesthetics and navigation
Class 6	Other uses
Class 7	Limited Resource Value Water (LRVW)

These use classes reflect the multiple beneficial uses that Minnesota's surface waters provide, and accordingly all surface waters are assigned multiple use classes. The MPCA also has the authority to protect groundwater for potable use in Minn. R. ch. 7060.[3] Nearly all surface waters are designated Class 2 and require control of pollutants so that they are safe for people recreating and eating fish affected by contamination, and, if used as source waters for drinking, are also designated Class 1 for domestic consumption as described in Minn. R. chs. 7050 and 7052.[4]

Derivation of the PFOS WQC falls under the MPCA's authorities to protect human health from adverse impacts of toxic pollutants in in Class 2 surface waters and fish. PFOS is categorized as a toxic pollutant and lacks numeric WQS in rule; therefore, the MPCA has derived site-specific WQC that are as fully enforceable as WQS after allowing for the necessary opportunities for comment. The WQC are specific to protecting human health, and include several values, each specific to the surface water's designated beneficial uses. Class 2A and 2Bd surface waters protect aquatic life (fish) consumption and recreation, but are also Class 1 waters and therefore have to account for domestic consumption uses in their final WQC. Most surface waters are designated as Class 2B and are not specifically designated for domestic consumption, so the WQC are based only on fish consumption and recreation. Class 2B WQS/WQC are also usually applied to surface waters classified as Class 2D wetlands. Protection of groundwater or downstream drinking water uses may require other considerations.

The WQC to protect human health are applied as Chronic Criteria (CC);[5] these values are developed to provide lifetime protection to people from exposure to toxic pollutants. The specific application of the different types of CC are described in Table 1-1. The MPCA developed the site-specific PFOS WQC based on the Minnesota Department of Health's (MDH) approach and toxicity value for deriving the PFOS health based guidance value for PFOS, including application of the associated Health Risk Index Endpoints for additive evaluation of pollutant mixtures (MDH 2019b). PFOS is a developmental toxicant, with prenatal and postnatal exposure, and long-biological half-life being significant factors in the derivation of the CC. Exposure rates need to specifically center on women of childbearing age (WCBA). The MPCA's review of the default fish consumption rate (FCR) for adults determined that a new interim

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[3] *The applicability of Class 1 water quality standards to groundwater is currently under review.*

[4] *The MPCA's Water Quality Standards also address impacts to aquatic life and fish-eating wildlife. Those evaluations are not covered in this TSD for human health-based WQC, but should be reviewed in the future to determine if more stringent criteria are warranted to protect ecological species.*

[5] *WQS or WQC for toxic pollutants are more specifically derived as Maximum Standard (MS) or Maximum Criterion (MC) and Chronic Standard (CS) or Chronic Criterion (CC) based on Class 2 methods Class 2 values in Minn. R. chs. 7050 and 7052).*

FCR was warranted for this subpopulation of fish consumers. The available data and information used for this FCR_{WCBA} are published in, *Interim Fish Consumption Rate for Women of Childbearing Age* (MPCA 2020a). The details of the chemical-specific derivation of the PFOS WQC are found in Section 8, with a discussion on the limitations that precluded the use of the default WQC methods in Appendix A.

The CC for PFOS applicable in surface water or fish-tissue are described in Table 1-1. The application of the site-specific WQC to specific water bodies are outlined in Appendix B and will be posted on the *Water Quality Standards: Site-Specific Criteria* webpage (https://www.pca.state.mn.us/water/site-specific-criteria). Comparison of water and fish monitoring data to the CC should follow Minn. R. chs. 7050 and 7052 and MPCA 2017 (see Section 9).

Table 1-1: Derived water quality criteria for PFOS for the protection of Class 1/2A or 1/2Bd or Class 2B/2D surface water uses

PFOS (CAS No. see Table 2-1)	**Site-specific water quality criteria: Chronic Criteria (CC)**			***Health Risk Index Endpoints* (Additive Risk)**
	Class 1/2A or Class 1/2Bd– drinking water, fish consumption and recreational exposure ($CC_{DFR-DEV}$) (30-day average)	**Class 2B/2D –** fish consumption and recreational exposure (CC_{FR-DEV}) (30-day average)	**Class 2 fish-tissue** (CC_{FT-DEV}) (90th percentile of 5 fish minimum per water body)	
PFOS	0.05 ng/L	0.05 ng/L	0.37 ng/g	Developmental, Adrenal (Endocrine), Hepatic (Liver) System, Immune System, Thyroid (Endocrine) (MDH 2019b)

Definitions of CC:

CC_{DFR} : Applied in Class 1/2A and Class 1/2Bd surface waters (D: Domestic Consumption, drinking water/food processing, F: Fish consumption, and R: Recreational exposure)

CC_{FR} : Applied in Class 2B surface waters (F: Fish consumption and R: Recreational exposure)

CC_{FT}: Applied for Bioaccumulative Chemicals of Concern (BCC) in fish (fillet/muscle) for all Class 2 waters (FT: fish-tissue)

$CC_{DFR-DEV}$, CC_{FR-DEV}, and CC_{FT-DEV}: Used for a pollutant with acute, short-term, or subchronic developmental (“less-than-chronic”) toxicity and higher early-life exposure rates (developmental toxicity as a Health Risk Index Endpoint)

1. Introduction

Water quality standards (WQS) provide the minimum conditions for waters of the state to meet their designated beneficial uses. Numeric standards are a key foundation for ensuring that the regulatory goals of Minnesota's water quality statutes and rules and the Clean Water Act (CWA) are met.

WQS in Minn. R. chs. 7050 and 7052 provide the foundation for:

- Effluent limits in National Pollutant Discharge Elimination System (NPDES) wastewater and stormwater permits.
- Remedial cleanup goals.
- Assessment of available pollutant-specific monitoring data in surface waters and fish for the CWA 303(d) Impaired Waters List.

WQS are derived to be protective of both human health and aquatic life.[6] Minnesota's human health-based WQS protect the beneficial uses of drinking water, fish consumption, and recreation. Human health-based WQS are adopted into rule and are applicable to Class 2 surface waters across the state. For pollutants that do not have a human health-based WQS, human health-based water quality criteria (WQC) may be derived and applied at a specific site or sites, based on methods already adopted into rule and approved by EPA. To summarize:

- WQS: Chronic Standards (CS) – derived for Class 2 waters; pollutant-specific standards adopted into rule.
- WQC: Chronic Criteria (CC) – derived and applied on a site-specific basis; based on methods adopted into rule (Minn. R. 7050.0217 to 7050.0219; 7052.0100 for the Lake Superior Basin).

CS and CC are derived based on the potential for adverse effects to human health and do not consider economic impacts or the availability of treatment technologies. Exceedance of a CS or CC is considered indicative of a polluted condition, which is actually or potentially deleterious, harmful, detrimental, or injurious with respect to the designated uses of the waters of the state (Minn. R. 7050.0150; 7050.0210, subp. 13). CS and CC refer to human health throughout the remainder of this document.

This TSD includes the derivation of a site-specific CC for perfluorooctane sulfonate (PFOS). Class 2 CC are developed for application in fish-tissue and surface waters. The CC are based on the most recent toxicity information from the Minnesota Department of Health (MDH) and MCPA's 2017 human health-based WQS/WQC derivation methods as adopted in Minn. R. chs. 7050 and 7052.

2. Problem formulation

2.1 Per-and polyfluoroalkyl substances

Per- and polyfluoroalkyl substances (PFAS) encompass a diverse suite of chemicals that are aliphatic carbon chain substances dominated by fluorine atoms in place of hydrogens (ITRC 2017). Analytical methods used by the MPCA and the MDH to detect PFAS have included the 13 PFAS listed in Table 2-1. Information regarding the environmental occurrence and toxicity of PFAS has been more readily available for PFOA and PFOS than for other PFAS included in this analytical method. The MDH has

[6] *The MPCA's Water Quality Standards also address impacts to aquatic life and fish-eating wildlife. Those evaluations are not covered in this TSD for human health-based WQC.*

developed toxicity values and health-based guidance for drinking water protection for five PFAS: PFOS, PFOA, PFHxS, PFBS, and PFBA (MDH 2017a, b, c and 2019 a, b).[7] The MPCA and MDH have detected these PFAS chemicals – as well as others from the suite of 13 PFAS monitored – in many of Minnesota's lakes and streams. PFOS and a few longer chain PFAS have also been detected in multiple fish species in these same and additional surface waters (Section 2.3). In some cases, surface waters are a conduit for these chemicals to migrate to groundwater. CC for PFAS are needed to evaluate the risk of these toxic pollutants to human health and to use as a basis to remediate and control known and potential sources of PFAS contamination to Minnesota's water resources.

Table 2-1: PFAS monitored by MPCA (Acronyms, carbon/chain lengths, and CAS numbers)

PFAS by Acronyms		Aliphatic Carbon No. (Chain length)	SGS Axys CAS No.	MDH/ITRC 2017 CAS Numbers
PFBA	perfluorobutanoic acid	4	375-22-4	375-22-4 (acid) 45048-62-2 (anion)
PFBS	perfluorobutane sulfonic acid	4	375-73-5	375-73-5 (acid) 45187-15-3 (anion)
PFPeA	perfluoropentanoic acid	5	2706-90-3	2706-90-3 (acid) 45167-47-3 (anion)
PFHxA	perfluorohexanoic acid	6	307-24-4	307-24-4 (acid) 92612-52-7 (anion)
PFHxS	perfluorohexane sulfonic acid	7	355-46-4	108427-53-8 (anion) 355-46-4 (acid) 3871-99-6 (potassium salt)
PFHpA	perfluoroheptanoic acid	7	375-85-9	375-85-9 (acid) 120885-29-2 (anion)
PFOA	perfluorooctanoic acid	8	335-67-1	45285-51-6 (anion) 335-67-1 (free acid) 335-66-0 (acid fluoride) 3825-26-1 (ammonium salt, APFO) 2395-00-8 (potassium salt) 335-93-3 (silver salt) 335-95-5 (sodium salt)
PFOS	perfluorooctane sulfonate	8	1763-23-1	45298-90-6 (anion) 1763-23-1 (acid) 29081-56-9 (ammonium salt) 70225-14-8 (diethanolamine salt) 2795-39-3 (potassium salt) 29457-72-5 (lithium salt)
PFOSA	perfluorooctane sulfonamide	8	754-91-6	Not included
PFNA	perfluorononanoic acid	9	375-95-1	375-95-1 (acid) 72007-68-2 (anion)
PFDA	perfluorodecanoic acid	10	335-76-2	335-76-2 (acid) 73829-36-4 (anion)
PFUnA (PFUnDA)	perfluoroundecanoic acid	11	2058-94-8	2058-94-8 (acid) 196859-54-8 (anion)

[7] *The MDH health-based guidance are described and found online at* *https://www.health.state.mn.us/communities/environment/risk/guidance/gw/table.html*.

PFAS by Acronyms		Aliphatic Carbon No. (Chain length)	SGS Axys CAS No.	MDH/ITRC 2017 CAS Numbers
PFDoA (PFDoDA)	perfluorododecanoic acid	12	307-55-1	307-55-1 (acid) 171978-95-3 (anion)

PFOS CC are derived based on the methods in Minn. R. chs. 7050 and 7052 for protecting human health from toxic pollutants in surface water and fish tissue.[8] The specific algorithms used and subpopulations of concern depend on the use classification of the surface water and the toxicological profile of the pollutant. Details regarding the WQC methods and how they were applied to the PFOS CC are described in Sections 3 through 8. The primary basis for concern and need for these CC is the potential for high exposure to PFOS from consuming fish caught in Minnesota's surface waters. The adverse effects of PFOS exposure includes toxicity to developmental processes. Because PFOS is a developmental toxicant and babies are born with an existing body burden based on maternal exposure, chemical-specific CC methods, in place of the default methods, are needed to fully address greater exposure and susceptibility to adverse effects in early life (see Section 3.2 and Appendix A).

The results of monitoring for PFAS in MN fish to date have indicated that other PFAS with MDH toxicity values (PFOA, PFHxS, PFBS, and PFBA) rarely exist at concentrations that are a concern to fish consumers. In a few highly contaminated water bodies, fish monitoring has shown detections of these PFAS in fish-tissue. These detections are reviewed and addressed on a site-specific basis. However, CC for all these PFAS are needed to ensure concentrations in surface water are below levels that could affect other beneficial uses: recreation in all waters and domestic consumption (drinking water and food processing) where applicable (Class 1). The CC applicable for these other uses will be published in another TSD (MPCA 2020b). As more toxicity values become available, additional PFAS WQC may be developed in the future.

2.2 Fish and water data

Many fish species present in Minnesota's surface waters have been monitored to determine if PFAS are present in fish-fillet (muscle) tissue (Table 2-2). PFAS concentrations in fish samples have been dominated by PFOS. Since monitoring began in 2004, PFOS has been detected in multiple species of Minnesota fish. PFOS is detected more frequently, at higher concentrations, and in more fish species in water bodies with known local contamination sources. However, PFOS is also commonly detected in many species of Minnesota fish from ambient environmental contamination unrelated to local sources (Table 2-2). In the most recent year of monitoring (2018), PFOS was detected in at least one species in all but five of the 75 water bodies sampled statewide.

[8] *WQS methods are described in Minn. R. 7050.0217 through 7050.0219 for statewide application and Minn. R. 7052.0110 for the Lake Superior Basin. Derived site-specific CC have the same regulatory applications as the CS listed in Minn. R. 7050.0220 through 7050.0222 or 7052.0100 after allowing for comment as specified in Minn. R. 7050.0218, subp. 2, or 7052.0110, respectively.*

Table 2-2: Minnesota fish species evaluated for PFOS

Genus:	Common name	Number of years this species was captured in a sampling event	Total number of unique water bodies sampled in those years	Percent of water bodies sampled where species had PFOS detections
Ambloplites	Rock bass	1	2	100%
	Black bullhead	6	5	60%
Ameiurus	Yellow bullhead	1	1	0%
Aplodinotus	Freshwater drum	6	2	50%
Catostomus	White sucker	2	4	75%
Coregonus	Tullibee (cisco)	1	1	100%
Cyprinus	Common carp	9	8	75%
Esox	Northern pike	9	43	72%
Ictalurus	Channel catfish	4	4	50%
	Bigmouth buffalo	2	1	100%
Ictiobus	Smallmouth buffalo	1	1	100%
	Bluegill sunfish	11	143	56%
	Hybrid sunfish	1	1	0
Lepomis	Pumpkinseed sunfish	3	3	100%
	Largemouth bass	8	63	83%
Micropterus	Smallmouth bass	12	9	100%
Morone	White bass	8	6	100%
	Golden redhorse	1	1	100%
Moxostoma	Shorthead redhorse	2	2	50%
Perca	Yellow perch	4	21	52%
	Black crappie	7	74	69%
Pomoxis	White crappie	1	6	66%
Prosopium	Round whitefish	1	1	0%
Salmo	Brown trout	1	1	100%
Salvelinus	Siscowet lake trout	1	1	100%
	Sauger	3	5	80%
Sander	Walleye	10	44	60%

Other PFAS frequently detected in fish-tissue at low concentrations include PFDA, PFUnA, and PFDoA. PFNA and PFOSA have also been detected, but less frequently. At more highly contaminated sites, like Mississippi River Pool 2, PFOA, PFHxS, PFBA, and PFBS have also been detected. There are no MDH toxicity values for PFOSA or any PFAS that has nine or more aliphatic carbons. Consideration of PFAS mixtures when applying the PFOS CC is discussed in Section 9.

3. Analysis plan: site-specific chronic criteria derivation

3.1 WQS: chronic criteria

In Class 2 designated surface waters, State and Clean Water Act (CWA) goals are integrated as stated in 7050.0140, subp. 3:

> **Class 2 waters, aquatic life and recreation.** Aquatic life and recreation includes all waters of the state that support or may support aquatic biota, bathing, boating, or other recreational purposes

and for which quality control is or may be necessary to protect aquatic or terrestrial life or their habitats or the public health, safety, or welfare.

Development of Class 2 WQS are more specifically cited in rule as:

- WQS: Chronic Standards (CS) – derived for Class 2 waters; pollutant-specific standards adopted into rule.
- WQC: Chronic Criteria (CC) – derived and applied on a site-specific basis; based on methods adopted into rule (Minn. R. 7050.0217 to 7050.0219; 7052.0100 for the Lake Superior Basin).

Use classifications for surface water are found in Minn. R. 7050.0400 through 7050.0470. The applicable Class 2 subclass (2A, 2Bd, 2B, or 2D) determines which beneficial uses are protected and the algorithms used to address them (MPCA 2017). Class 2A and 2Bd surface waters are also designated Class 1 for domestic consumption. This additional beneficial use means those surface waters are protected as a source for drinking water and food processing (Minn. R. 7050.0221). There are three possible exposure pathways that may be included in a specific CC:

- Drinking water source.
- Recreation (incidental water intake).
- Fish consumption.

The classification of the specific water body that the CC is derived for will determine which of these exposure pathways is included.

- CC_{DFR} is derived for Class 1/2A and Class 1/2Bd waters, which include the following exposure pathways:
  - Drinking water source (D).
  - Fish consumption (F).
  - Recreation, the drinking water intake rate covers incidental ingestion exposure, but recreational exposure is considered in the relative source contribution factor (R).
- CC_{FR} is derived for Class 2B and 2D waters, which include the following exposure pathways:
  - Fish consumption (F).
  - Recreation, which includes an incidental water intake rate (R).

Two other types of CC are also derived when appropriate:

- CC_{DEV} (Developmental) is derived for less-than-chronic exposure periods (acute, short-term, subchronic) for contaminants that require the use of higher early-life exposure rates, early-life susceptibility factors, or those specific to women of child bearing age (WCBA).
  - $CC_{DFR\text{-}DEV}$ is a CC_{DFR} that was derived to address the exposure pathways described above (DFR), and also specific parameters or approaches to address developmental toxicity.
  - $CC_{FR\text{-}DEV}$ is CC_{FR} that was derived to address the exposure pathways described above (FR), and also specific parameters or approaches to address developmental toxicity.
- CC_{FT} (Fish Tissue) is derived for contaminants that are bioaccumulative contaminants of concern (BCC) to protect fish consumers. A BCC is defined as having a bioaccumulation factor (BAF)

greater than 1,000 L/kg.[11] This CC is applicable in most Class 2 waters[9], and is not based on the same subclasses as the CC described above for surface water application.

- CC_{FT-DEV} (Fish Tissue-Developmental) may be derived when less-than-chronic exposure periods (acute, short-term, subchronic) for contaminants that require the use of higher early-life exposure rates, early-life susceptibility factors, or those specific to WCBA, require lower CC than calculated for chronic exposure.

The most stringent of the CC derived (CC_{DFR} or $CC_{DFR-DEV}$; CC_{FR} or CC_{FR-DEV}; CC_{FT} or CC_{FT-DEV}) will be listed as the final applicable CC.

When surface waters are a conduit and source of PFAS contamination to groundwater (Minn. R. ch. 7060) or downstream drinking water sources (Clean Water Act), other considerations may be required to ensure protection of potable water or domestic consumption uses.

Some toxic pollutants require chemical-specific data and methods that differ from the default methods and calculations used to derive CC (or CS); Minn. R. 7050.0217 to 7050.0219 and the MPCA's *Human Health-based Water Quality Standards Technical Support Document* (Final 2017) describes when this is appropriate. Appendix A provides an overview of the limitations precluding the use of the default methods to derive WQC for PFOS. And again as noted above, to ensure protection of drinking water (domestic consumption) or potable water uses when a surface water is designated for this use (Class 1) or if the surface water influences a drinking water source or groundwater, the MPCA will also consider the need to meet the MDH health based guidance value for drinking water protection (see https://www.health.state.mn.us/communities/environment/risk/guidance/gw/table.html).

3.2 PFOS chronic criteria

The methods to develop CC assume a person that is eating fish caught from Minnesota's surface waters might also be exposed to the same pollutant through recreating (swimming, water skiing, and other full-body or primary contact activities) in those waters and from getting their drinking water from that same water body (when designated for domestic consumption). The exposure scenarios are always considered together. However, the physical-chemical properties of the toxic pollutant usually mean that only one source of exposure is the most significant. For PFOS, because of its very high bioaccumulation in fish-tissue, eating fish results in the highest potential exposure for surface water users when considered in combination with drinking water intake and recreational exposure from the same source water (assumption in CC). In general at higher concentrations of PFOS drinking water exposure can be a concern, but even extremely low concentrations of PFOS can bioaccumulate to concentrations that are, on average, over 5,000 times greater in fish tissue than in the surface waters; therefore, including drinking water or recreational (incidental) water intake is not necessary for developing protective CC. A fish-tissue based CC can be used to derive the water-based CC; this calculation is done by dividing the CC_{FT-DEV} by the PFOS BAF as described in Section 8.

PFOS has multiple characteristics that warrant the use of chemical-specific CC methods rather than the default methods (Minn. R. ch. 7050 and MPCA 2017). PFOS is a developmental toxicant with a long half-life in people. The MDH recognized that to develop a groundwater value protective of the drinking water use, a toxicokinetic serum model was warranted (Goeden et al. 2019, MDH 2019 b). The default method

[9] CC_{FT} might be different if there are site specific or other information on fish consumption rates that differ from the default values used.

for health based guidance development does not account for the transfer of chemicals from mother to fetus. The serum model is able to account for this transfer, ensuring that the most sensitive receptor, the infant, is protected from developmental effects. A toxicokinetic serum model is able to account for an infant's body burden of PFOS at birth from placental transfer and also potential high neonatal intake. The MDH modeled PFOS serum levels for both infants who were breastfed and those that were bottle-fed with formula made with contaminated tap water. This allowed the MDH to set a final guidance value that, when met, ensures infant through adult serum levels or body burdens would not exceed adverse effect levels (MDH 2019b).

The scientific foundations available to the MPCA from the MDH's publication of PFOS and other PFAS health-based guidance for drinking water protection using toxicokinetic models are available, reliable, peer-reviewed, and scientifically defensible for use in developing these human health-based CC. Using a toxicokinetic model to develop risk based guidance for environmental chemicals found in drinking water, food, and other media is recognized by the EPA and other scientists as a powerful tool to improve the accuracy of these values (Cohen Hubal et al. 2019; ITRC 2020). Use of the model also accommodates data specific to different life-stages or age ranges and subpopulations, like women of childbearing age (WCBA)(see Appendix A). Therefore, the MPCA consulted with the MDH to develop a modified model using fish consumption exposure as the basis to derive a $CC_{FT\text{-}DEV}$.

Table 3-1: Basis for Final WQC as presented in Table 1-1

PFAS	Surface Water Class	Use Protected	Criteria Application	Method	Acronym
PFOS	All Class 2 Waters	Aquatic Consumption	Fish tissue	Toxicokinetic model	$CC_{FT\text{-}DEV}$
	Class 2B/2D Waters #	Aquatic Consumption + recreation	Water column	$CC_{FT\text{-}DEV}$/BAF	$CC_{FR\text{-}DEV}$
	Class 1/2A/2Bd Waters	Aquatic consumption, recreation + domestic consumption	Water column	Most stringent value of: 1) $CC_{FT\text{-}DEV}$/BAF 2) MDH health based value	$CC_{DFR\text{-}DEV}$

When surface waters are a conduit and source of PFAS contamination to groundwater (Minn. R. ch. 7060) or downstream drinking water sources (Clean Water Act), other considerations may be required to ensure protection of potable water or domestic consumption uses.

4. Toxicokinetic serum model

4.1 MDH's drinking water health based guidance

The MDH's toxicokinetic serum model for PFOS evaluates two scenarios:

- Exclusively breastfed infant for 12 months; and
- Formula-fed infant, where formula was made using contaminated household tap water (MDH 2019b).

Both scenarios assume a "lifetime" of drinking contaminated water. The model includes the following parameters:

- Breastmilk or formula intake rates (with body weights).
- Daily drinking water intake rates (with body weights).

- Serum level corresponding to the reference dose (RfD).
- Internal or biological half-life.
- Volume of distribution.
- Clearance rates.
- Placental and breastmilk transfer factors.
- Relative source contribution (RSC) factors.

The serum model incorporates an estimated PFOS body burden from placental transfer at birth (day 0) followed by ongoing exposure to age 54.8 years (day 20,000), the duration needed to assess internal steady-state conditions (Goeden et al. 2019, MDH 2019b). The model incorporates daily adjusted fluid intake rates with body weights and clearance rates. The MDH uses the model to set final health based guidance for drinking water that limits serum concentrations below the "reference" serum concentration corresponding to the RfD. The PFOS health based value (HBV) is 15 ng/L.

4.2 MPCA's chronic criteria

The standard approach to developing the CC applicable in Class 2 surface waters (CC_{DFR} and CC_{FR}) is to use algorithms that include drinking or incidental water intake and fish consumption rates (Minn. R. 7050.0217 through 7050.0219). However, as discussed in the MDH's supporting documentation for the PFOS HBV, using a toxicokinetic serum model more accurately captures potential health risks from the high transgenerational (prenatal) and neonatal exposure and long biological half-life of PFOS. For this reason, the MPCA is using the toxicokinetic serum model to calculate CC for PFOS instead of the standard CC algorithms (Minn. R. 7050.0219, subp. 2 (A). The toxicokinetic serum model has been adjusted to consider exposure from freshwater fish consumption —the route of greatest exposure from surface water contamination when considered in combination with drinking water and recreational water intake from the same source.

Minnesota's WQS methods require the derivation of a fish-tissue (fillet) based criterion (CC_{FT}) for chemicals that are bioaccumulative contaminants of concern (BCC).[10] Having a fish-tissue based criterion is more accurate for assessing exposure to and protecting fish consumers from these kinds of surface water pollutants. In the case of PFOS, with a BAF of 7,210 L/kg (Section 6.4), calculating the $CC_{FT\text{-}DEV}$ (based on developmental toxicity) is done using a modified version of the MDH toxicokinetic serum model. The details on the toxicokinetic serum model are covered in Section 8. So for the PFOS CC:

- First, a fish-tissue CC is derived ($CC_{FT\text{-}DEV}$) using the toxicokinetic serum model.
- Second, a surface water CC is derived by dividing the fish-tissue CC ($CC_{FT\text{-}DEV}$) by the BAF.

In addition, Minnesota's human health-based WQS methods require fish-tissue datasets be used to evaluate BCCs in surface water (comparing fish monitoring datasets to the CC_{FT}). If fish-tissue datasets are not available, surface water monitoring datasets may be used for comparison to the CC_{DFR} or CC_{FR} (Minn. R. 7050.0150, subp. 7). The water column-based CC are needed to apply remedial and other treatment approaches directed at reducing PFOS in surface waters.

[10] *A BCC is defined as toxic pollutant with a bioaccumulation factor (BAF) > 1,000 L/kg.*

5. Toxicity values and health risk index endpoints

The MPCA used the MDH toxicity values for PFOS (MDH 2019b) (Table 5-1).

Table 5-1 PFOS Toxicity values and health endpoints

PFAS	MDH RfD (Duration)	MDH-derived comparable RfD in serum	Health Risk Index Endpoints	Reference
PFOS	0.0000031 mg/kg-d (short-term to chronic)	24 µg/L (Dong et al. 2011*, Archives of Toxicology* 85: 1235-44)	Developmental, Adrenal (E), Hepatic (Liver) System, Immune System, Thyroid (E)	MDH 2019b
Key: (E) stands for endocrine and means a change in circulating hormone levels or interactions with hormone receptors, regardless of the organ or organ system affected (Minn. R. 7050.0218, subp. 3 (X), based on 4717.7820, subp. 10)				

Use of these additivity endpoints for mixtures analyses is further described in Section 9.

6. Exposure factors

6.1 Drinking water intake rate

As stated previously, a CC_{DFR} or $CC_{DFR\text{-}DEV}$ is derived for Class 1/2A and Class 1/2Bd waters and typically includes the following exposure pathways:

- Drinking water source (D).
- Fish consumption (F).
- Recreation (R).

This CC usually is based on a drinking water intake rate (DWIR)(assumed to incorporate the relatively smaller incidental ingestion rate used for recreational exposure) that is added to a fish consumption rate (FCR) multiplied by the BAF; however, because PFOS concentrations in fish are so much higher than concentration in surface water, starting with $CC_{FT\text{-}DEV}$ based on the modified toxicokinetic serum model and dividing this criterion by the BAF, gives a more defensible CC for application in surface waters than use of the standard algorithms. This approach to CC development is fully protective of all beneficial uses, including drinking water and recreational exposures.

The MPCA considered adjusting the toxicokinetic serum model to consider exposure from drinking water and fish consumption, but preliminary calculations indicated that adding the exposure term for drinking water would have negligible influence on the final criteria values; this more complicated model would still have resulted in a $CC_{FT\text{-}DEV}$ driven by fish consumption exposure, with formula or drinking water exposure negligible if added into the model. A comparable exposure in liters per kilogram of body weight each day (L/kg-d) from consuming fish can be calculated to compare to the default DWIR to demonstrate the relative exposure differences to PFOS. Using the fish consumption intake rate (FCR_{WCBA}) of 0.00094 kg/kg-d and multiplying it by the BAF for PFOS of 7,210 L/kg (BAF) results in an equivalent fish-consumption intake of PFOS at 6.78 L/kg-d. The default chronic DWIR in the WQS methods is 0.043 L/kg-d. Comparing the potential exposure from consuming fish harvested in contaminated surface water to potential exposure from consuming contaminated drinking water shows that potential PFOS exposure from eating fish is over 150 times greater than from consuming drinking water at the same surface water concentration. In other words, drinking water exposure would account for less than 1% of the combined exposure to PFOS from eating fish and drinking water at these intake rates.

The CC are numeric goals for surface water to meet to ensure drinking water, recreation, and fish consumption exposure does not contribute to a person's total exposure above the RfD (or level associated with adverse effects). Surface waters, and groundwater influenced by surface waters in areas of PFAS contamination, have PFOS (and/or PFOA, because of additive toxicity) concentrations greater than the $CC_{DFR\text{-}DEV}$ applicable in water (0.05 ng/L). When concentrations are closer to or above the MDH drinking water guidance for PFOS of 15 ng/L then drinking water exposure would not be considered negligible. The CC takes such actual exposures to people into account in the relative source contribution (RSC) factor. The details for how the MPCA developed the fish-tissue based toxicokinetic serum model and how it is also protective for drinking water exposure are described in Section 8.

6.2 Incidental water intake

For calculating a $CC_{FR\text{-}DEV}$ for Class 2B surface waters for PFOS, only the fish consumption pathway was necessary to develop $CC_{FR\text{-}DEV}$ protective of people eating fish from and recreating in the same surface water. As with drinking water intake, the potential exposure from incidental water is negligible and not necessary to include in the model. The $CC_{FT\text{-}DEV}$ divided by the BAF will also be applied as the $CC_{FR\text{-}DEV}$ (see Section 8).

6.3 Fish consumption rates

The WQS methods include default fish consumption rates (FCR) for the general adult population of 0.43 g/kg-d (30 grams of fish consumed per day with an average 70 kg body weight) and children ages 1 through 5 of 0.86 g/kg-d (based on intake per kg of body weight, approximately twice that of adults). The basis for these rates and their use in Class 2 CS (CC) is described in Minn. R. 7050.0218 to 7050.0219 and MPCA 2017.

Because PFOS is a developmental toxicant with a long half-life (3.4 year-mean)(MDH 2019b), PFOS exposure from fish consumption includes prenatal or transgenerational exposure. The resultant body burden at birth, when paired with ongoing indirect exposure through high fluid intake from breastmilk after birth, leads to the first year of life being the age range of greatest exposure. To ensure that exposure during this window of time remains below the determined risk threshold established by the MDH "reference" serum concentration (based on the RfD), it is critical to use the toxicokinetic serum model to develop the $CC_{FT\text{-}DEV}$. When accounting for exposure from fish consumption only, the PFOS exposure profile demonstrates a peak serum level at the end of year one (when breastfeeding ceases). The relatively high indirect exposure to the infant from the mother's body burden (based on her fish consumption rates from her birth through breastfeeding) results in higher serum levels in the breastfed infant than in a formula-fed infant who begins fish consumption at age one (Figure 1). This is true even with the assumption that formula for a bottle-fed infant was reconstituted with PFOS contaminated tap water at the level of the CC_{DFR_DEV}. In the formula-fed infant exposure scenario, the peak serum concentration occurs from ages 40 to 50 years.

PFOS has Developmental Health Endpoints, so appropriate FCR are needed for women of childbearing age (WCBA) – the fish consumers whose exposure is directly related to transgenerational (prenatal) to postnatal (breastfeeding) exposure. The MPCA developed the adult and child rates to reflect upper percentile recreational or sport-caught fish consumption rates from regional survey results. The MPCA has established that the cultural importance and popularity of fishing warrants a high level of protection for Minnesota's fish consumers (MPCA 2017). The adult FCR, however, was not based on data specific to

WCBA. The EPA defines WCBA as women between the ages of 13 to 50 (USEPA 2014). As specified in the WQS technical support document, if a pollutant affects development and *in utero* or prenatal through postnatal exposure is relevant to the toxicity, the MPCA will review available survey and exposure data to ensure the adult FCR is representative of WCBA (MPCA 2017). The WQS rules allow for the application of chemical-specific data (Minn. R. 7050.0219, subp 2(A)). WCBA are an important subpopulation of fish consumers because their environmental pollutant exposure directly influences fetal development, growth, and health outcomes; thus, a significant amount of study and outreach has been directed at understanding their patterns of fish and shellfish consumption (USEPA and FDA 2017). It is important to note that both pregnant women and those considering pregnancy are encouraged to consume fish and shellfish because of the many beneficial nutrients these foods provide, especially for neurodevelopment and cardiovascular health. Ensuring freshwater fish are not a significant source of toxic pollutants is the goal of WQC.

An interim FCR for WCBA (FCR_{WCBA}) of 66 g/d using a 70 kg body weight (0.94 g/kg-d)[11] will be applied to account for reasonable maximum exposure (RME)[12] for WCBA in Minnesota that consume freshwater fish caught in Minnesota. This FCR is based on the MDH's *Fish is Important to Superior Health* (FISH) survey of North Shore Minnesotans (MDH 2017d), and also reflects similar rates found in other surveys of Minnesota's WCBA (see MPCA 2020a). The detailed FISH survey was conducted in clinical settings in Grand Portage and Grand Marias, MN, with trained health professionals supporting accurate data collection on almost 500 Minnesotan WCBA (MDH 2017d). This FCR will be an interim rate used in CC for pollutants characterized as developmental toxicants to ensure reasonable maximum protection from adverse health effects in developing babies whose mothers eat fish and shellfish as part of a healthy and balanced diet. Future plans include broader review and outreach on available fish consumption surveys and rates, especially for future CC developed for the Lake Superior basin. Tribal Authorities with Treatment as a State for water quality standards in the Lake Superior Basin include the Fond du Lac Band of Lake Superior Chippewa, who use a FCR of 60 g/d, and the Grand Portage Band of Lake Superior Chippewa, who use 142.5 g/d as their FCR.

6.4 Bioaccumulation factors

A bioaccumulation factor (BAF) is the ratio of a toxic pollutant's concentration in fish tissue to its concentration in ambient surface water at steady-state (in L/kg), and is used to set water column values (CC_{DFR} /CC_{FR}) that if met, will also result in compliance with the fish-tissue criterion (CC_{FT}). The methods and data needs for developing a BAF are described in Minn. R. 7050.0219 and MPCA 2017. The preferred procedure for developing a BAF is the use of field studies. The general approach to developing a BAF for application in CC is as follows:

- Internal review of quality assurance and control information provided by the lab.

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[11] While EPA has recommended use of a higher body weight from NHANES for developing water quality criteria or standards (USEPA 2015) and the latest NHANES time weighted averages body weight for ages 16 to 50 is 74 kg (Table 8-5, USEPA 2011). However, these rates are not specific to fish consumers. The use of the standard 70 kg body weight is used for assigning portion sizes of 227 g to statistical estimates of fish meal size and is used in development of the interim FCR (MPCA 2020a).
[12] In the EPA's human health guidance for Superfund sites, reasonable maximum exposure (RME) is defined as the highest exposure that is reasonably expected to occur at a site. The estimate considers current and future exposure scenarios (USEPA 1989).

- Consolidate paired surface water and fish datasets.
- Develop geometric mean water concentrations for a specific water body (lake or river segment).
- Calculate BAF for each individual fish by dividing reported concentrations in fillet tissue by water concentration. Combine BAF for geometric means for each species in a water body (if data warrant, there may be BAF by trophic level 3 and 4).
- Evaluate these BAF to develop the final site-BAF (a "site" may be defined as narrowly as a single water body or as broadly as all statewide surface waters), typically the geometric mean of all the species- or water body-geometric means.

An important aspect to developing a BAF is the physical-chemical characteristics of the pollutant. PFOS is an ionic, organic chemical commonly detected across fish species in Minnesota. CC needs to accurately account for bioaccumulation of PFOS in many species of fish caught and consumed in Minnesota. Minnesota state agencies have been monitoring for the thirteen PFAS found in Table 2-1 in fish and surface water since 2004 and 2006, respectively. Monitoring was initially conducted with MPCA funding and goals, and later through collaboration with the interagency Fish Contaminant Monitoring Program (FCMP), a team that includes the MDH and the Minnesota Department of Natural Resources (MNDNR). PFOS water and fish monitoring data from the water bodies being evaluated included the following datasets from the last 10 years: 2009, 2012, 2013, 2016, and 2018.

After review of the MPCA's field monitoring datasets and consideration of some changes in PFOS concentrations in surface waters over time, the paired PFOS datasets from 18 water bodies collected in 2016 and 2018 are being used to develop a reliable and scientifically defensible interim statewide BAF.

- The 18 water bodies included those with local PFAS source contamination and those away from known contamination or remediation areas.
- The species of fish targeted for monitoring in a water body were chosen based on which species historically show higher PFOS levels, a desire to represent different trophic levels or habitat preferences, and a desire to represent regularly caught and consumed species; however, those species that are actually collected can differ from the targeted list. Therefore, combining BAF results from multiple water bodies is more likely to capture the targeted mix of fish species and the resulting BAFs will more accurately represent the distribution of potential exposure.
- Combining species' BAF by water body better represents BAF for PFOS, because even small differences in surface water concentrations have a significant influence on the BAF. Combining datasets by water body geometric means vs. species across water bodies better addresses this issue.
- Applying different site-specific BAF by water body to develop CC is not defensible for addressing PFOS because having different CC among water bodies is not in the best interest of clear communication to the public or for regulators needing to implement control plans (as described in Section 8).

Use of this recent dataset supports the goal of ensuring protection to fish consumers from health effects associated with toxic pollutants found in Minnesota fish. As the FCMP collects more paired datasets, the PFOS interim statewide BAF can be further reviewed.

The development of a BAF for PFOS followed the general approach for developing field-based BAF. PFOS results reported below the reporting limit were not used in the BAF calculations; therefore, no substitution method was needed to estimate fish-tissue or water results below the reporting limits. The datasets used to calculate the BAFs are summarized in Table 6-1.

Table 4-1: Summary of water body-specific BAFs and Final 90th percentile BAF for PFOS

WATER BODY Year of dataset is 2018, unless listed as 2016 (MNDNR Lake ID or DOWID)	BAFs Species Minimum (L/kg)	BAFs Species Maximum (L/kg)	BAFs, geometric means based on geo-means for all species (L/kg)
BDE MAKA SKA 2016	3,000	5,220	3,960
BDE MAKA SKA (27003100)	2,910	7,570	4,330
CLEAR (82016300)	6,560	9,260	7,620
CRYSTAL (27003400)	1,330	1,680	1,490
ELMO 2016	5,340	8,040	6,870
ELMO (82010600)	1,250	12,420	5,110
FISH (DAKOTA) (19005700)	1,460	4,760	2,940
GERVAIS (62000700)	5,440	14,450	8,250
HARRIET 2016	2,740	6,540	4,170
HARRIET (27001600)	4,200	8,270	5,940
ISLES 2016 (2700400)	4,680	10,010	6,550
JOHANNA 2016 (62007800)	4,000	10,130	6,870
JOSEPHINE (62005700)	7,170	7,170	7,170
MCCARRON (62005400)	4,440	11,680	7,210
OWASSO (62005600)	2,820	5,980	4,110
REBECCA (19000300)	960	3,530	1,840
SNELLING (27000100)	1,500	1,500	1,500
TANNERS (82011500)	4,230	12,590	6,360
TWIN 2016	1,950	2,960	2,300
TWIN (27004200)	3,550	4,370	3,640
WILD RICE RESERVOIR (69037100)	2,760	5,410	3,990
WINONA (21008100)	2,380	4,530	3,280
GEOMEAN			4,289
COUNT (N):			22
FINAL BAF (90th percentile)			7,206 **7,210** **(3 significant figures)**

Some species of fish consistently have higher fillet-tissue PFOS concentrations than others: bass (white, smallmouth, and largemouth), black crappie, walleye, northern pike, and bluegill sunfish. Because a mean or median BAF would not be sufficiently protective across fish species regularly caught and consumed in Minnesota, the selected final BAF to calculate the CCFT is the 90th percentile value of the pooled water body-specific final geometric means.13 In other words, to ensure most fish species meet

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[13] *The MPCA BAF review did not focus on detailed analyses of trophic level 3 and 4 differences, and instead is basing a defensible BAF on a higher percentile value across species and waterbody characteristics. Additional review of other studies examining the mechanisms behind PFOS trophic level bioaccumulation and biomagnification may provide evidence for other approaches to address PFOS bioaccumulation, which distributes more on the basis of biological proteins versus lipids (ITRC 2020).*

the CCFT-DEV the interim statewide BAF needs to reflect the BAF of those species that accumulate PFOS to higher concentrations than the average species- or water body- specific BAF when setting the protective water column criteria (CCDFR-DEV and CCFR-DEV).

7. Relative source contribution

The RSC factor is used to account for exposures to the same toxic pollutant from other sources unrelated to those addressed by the CC. Methods in Minn. R. 7050.0219, subp. 5 indicate that the RSC should be a default value of 0.2 (20%) for most pollutants, unless:

A. There are no significant known or potential sources other than those addressed for the designated use (then 0.5 must be used).
B. Sufficient exposure data are available to support an alternative pollutant-specific value between 0.2 and 0.8.

The RSC is intended to estimate the percent of a person's total exposure that can be attributed to surface water sources including water consumption from drinking water with a surface water supply, water consumption from incidental ingestion during recreational activities, and consumption of fish harvested in surface water. Use of a RSC of 20% assumes that 20% of a person's exposure to a specific chemical comes from the exposure pathways used to derive the CC, while the other 80% of the person's exposure to that pollutant comes from other sources. The RSC methods in Minn. R. 7050.0219 follow the EPA's RSC Decision Tree for deriving the RSC as described in MPCA 2017. Multiple lines of evidence are used to develop RSCs: availability of biomonitoring datasets, food and environmental media monitoring, physical-chemical properties, and fate and transport of the pollutant (USEPA 2000).

For PFOS, the evidence available supports use of 0.2 as the RSC in the $CC_{FT\text{-}DEV}$. The MPCA determined that exposure from eating freshwater fish should be limited to 20% of total exposure because of the presence of PFOS and its precursors in other environmental media, food, and consumer products. The CC RSC methods require use of the 0.2 RSC if there are other significant sources of exposure to the toxic pollutant. The use of a 20% RSC applies for all life-stages in the modified toxicokinetic serum model. An overview of the PFOS sources and routes of exposure considered in developing the RSC are summarized in Table 7-1.

Table 7-1: Relative source contribution factor considerations

Sources of exposure	Routes of exposure	Comments
Groundwater or surface water	Drinking water Ingestion/drinking water intake	Included in RSC
	Drinking water Cooking, showering, bathing, etc. Inhalation, dermal contact	Dermal exposure is not expected to be a significant PFOS is not considered volatile from water, but could be aerosolized on particulates Included in RSC
	Irrigation of gardens	Included in RSC
Surface water only	Recreational Ingestion from suspended sediment/particulates, inhalation, dermal contact	Potential ingestion of suspended sediments included in RSC
Estuarine and marine fish and shellfish	Ingestion of contaminated fish and shellfish from restaurants, grocery stores, etc. that are not included in the freshwater fish consumption rates used to develop CC	Included in RSC Limited studies of PFAS in commercial fish and shellfish sold in the United States; PFOS, PFOA have been detected
Food other than fish and shellfish	Ingestion of commercial food and drinks	Included in RSC Multiple studies detected PFOS and other PFAS in food packaging and food and drink items
Residential and business indoor air and dust	Ingestion, inhalation, and dermal contact	Included in RSC Multiple studies have detected PFOS and other PFAS, including precursors, in indoor air and dust samples Some researchers estimate indoor dust is a significant route of exposure for children
Outdoor air	Inhalation	Included in RSC Studies detect PFAS, particularly volatile precursor substances
Key references: Health Canada (2018), ITRC (2018a; 2020), MDH (2019b, c,), Scher et al. 2018, USEPA (2106 a,b), Vedagiri et al. (2018), and Young et al. (2013)		

PFOS also has a long biological half-life and persists in people to levels much higher than in the media to which people are exposed. Just from PFOS exposure through drinking water intake, studies have found a 200-fold increase in people's serum levels over the drinking water concentrations (ITRC 2020). U.S.

population-level biomonitoring results for many PFAS are available from NHANES and demonstrate detection of PFOS in the serum of most Americans three years old and older (USEPA 2016a; CDC 2017; Ye et al. 2018). The MDH used this biomonitoring data to develop RSC for their drinking water guidance (MDH 2019b). The MDH's evaluation of the relatively high population-level serum concentrations of PFOS, as compared to the corresponding serum "reference" concentration, determined that exposure from drinking water intake should be limited to 20% of total PFOS exposure for long-term adult steady-state (MDH 2019b). For infants and young children, the MDH used a 50% RSC. The MDH based the higher RSC on comparisons of national biomonitoring data and upper percentile PFOS exposure to three to five year olds from the Ye et al. 2018 study.

The MPCA is not aware of studies that specifically address the relative portion of total PFOS exposure expected to derive from fish consumption in regions with surface water contamination. In this scenario, the EPA's RSC Decision Tree also supports use of 0.2 for the RSC. Considering that in several of the regions where Minnesota's surface waters may be contaminated with PFOS, the PFOS concentrations in groundwater-supplied drinking water are near the HBV set by the MDH, exposure from non-surface water sources could remain significant (MDH 2019b). It is not public health protective to add to existing PFOS body burdens from ongoing freshwater fish consumption. The application of a 20% RSC for all life-stages is warranted to ensure total serum PFOS (and PFOA, based on the same Health Risk Index Endpoints and long serum half-life) do not exceed adverse effect thresholds (see Figure 1). Use of the default WQC methods could not ensure that early-life exposure would be below this critical threshold (Appendix A).

8. Chronic criteria derivation

8.1 Class 2 fish tissue-based chronic criterion

The MDH's single-compartment toxicokinetic serum model is used to derive the $CC_{FT\text{-}DEV}$ for PFOS. Details of the MDH model parameters used to develop a HBV (applicable to groundwater) are found in MDH 2019b. The model is also described in detail as initially developed for PFOA in Goeden et al. 2019. The MPCA replaced drinking water exposure with fish consumption for two versions of the model:

- In the bottle-fed infant model, PFOS intake from formula was not included and direct fish consumption exposure began at age one (with the use of the 20% RSC accounting for exposure from formula made with contaminated tap water)
- In the model based on exclusive breastmilk intake for the first year of life, indirect exposure based on the estimated body burden of a 30-year old, nursing female and direct exposure based on fish consumption starting at age one; the maternal body burden at time zero (birth) was based on a time-weighted average FCR from birth to age 30 with the PFOS concentration at the CC level of 0.37 ng/g (the model is iterative and different PFOS fish-tissue concentrations are used in the model until the birth to 54.8 years of age serum levels remain below 20% of the "reference" serum concentration based on the RfD).

The MPCA used the MDH's model approach and parameters, except as described in Table 8-1:

Table 8-1: Toxicokinetic serum model exposure parameters

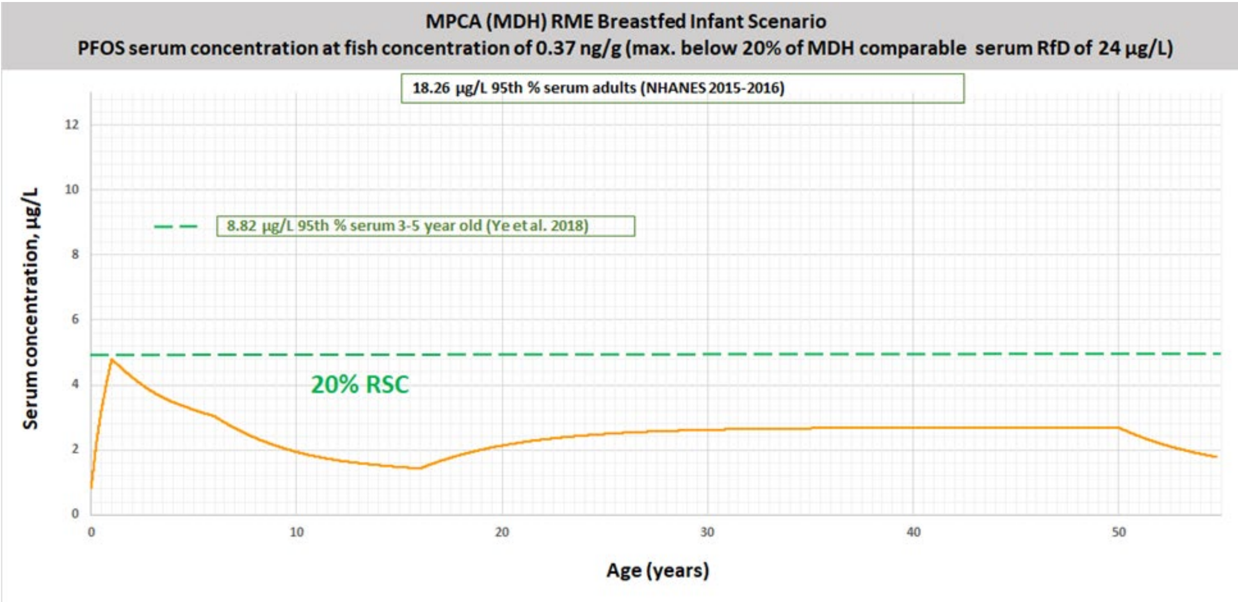
Model parameters	Values used and descriptions (Sources: MPCA or MDH 2019b)	
Half-life	1,241 days	Mean value for all ages, Li et al 2018 (5th to 95th percentile range: 803 – 2263 days)(MDH)
Volume of distribution (Vd)	0.23 L/kg	Consistent with extracellular fluid as volume of distribution. (MDH) Ratio of distribution of PFOS in body fluids to that in serum.
Vd age adjustment factor	Early-life stages are known to have higher body water content per unit weight than adults. The midpoint in time for each age group was set equal to the age group value. Daily intake (and corresponding body weight) between midpoint and the next were calculated by linear interpolation to avoid abrupt changes from age group to age group. (MDH)	
	Age ranges	**Vd age adjustment factor**
	0-1 day of age	2.4
	1-30 days	2.1
	1-3 months	1.7
	3-6 months	1.6
	6-12 months	1.5
	1-3 years	1.4
	3-5 years	1.1
	5-10 years	1.2
	>10 years	1
Clearance rate (CR)	0.00013 L/kg-d	Calculated from Vd x (Ln 2/half-life)(MDH)
Placental transfer factor ***(% of maternal serum level)***	40%	Mean of mean paired maternal:cord blood ratios reported in the literature. (Range of mean values 30 – 60%.) (Mean 95th percentile value 81%, range 70 – 106%.) (MDH)
Breastmilk transfer factor ***(% of maternal serum level)***	1.7%	Mean of mean paired maternal serum:breastmilk ratios reported in the literature. (Range of mean values 1 – 3 %.)(No 95th percentile values reported in literature.) (MDH)
Gastrointestinal absorption factor	100%	Acidic conditions used in PFOS analytical methods (extraction) support this bioavailability factor from the stomach/intestines into circulation (MPCA)
Fish consumption rates (FCR) and body weights[14]	Upper percentile FCR; The use of the default 70 kg body weight to develop the adult and interim WCBA FCRs are specific to these parameters and not used to estimate actual serum levels in the model scenarios. (MPCA) Body weights are means for female and males for age groups from age 1 to 16 years from Table 8-1 and Table 8-3 for adults age 50 to 54.8 years in EPA's Exposure Factors Handbook (2011). For application for WCBA, ages 16 to 50 years, mean body weights for females are from Table 8-5. Some of the body weights used are Time Weighted averages (TWA), and applied in the models as daily adjusted value for the age groupings.[14] (MPCA)	

Model parameters	Values used and descriptions (Sources: MPCA or MDH 2019b)		
	Age ranges	**Fish consumption rates (g/kg-d)**	**Body weights (kg)**
	Birth	0	N/A
	Birth to <1 month	0	4.8
	1 to <3 months	0	5.9
	3 to <6 months	0	7.4
	6 to <11 months	0	9.2
	1 to <2 years	0.86	11.4
	2 to <3 years	0.86	13.8
	3 to <6 years	0.86	18.6
	6 to <11 years	0.43	31.8
	11 to <16 years	0.43	56.8
	16 to <18 years	0.94	65.9
	18 to <21 years	0.94	65.9
	21+ to <50 years	0.94	74.7
	50 to 54.8 years	0.43	83.4
	Women of Childbearing Age (16 to <50 years)	0.94	73.3
	Birth (0) to < 30 years	0.725	N/A
Breastmilk intake rates and body weights	Upper percentile exclusively breast-fed infants (Table 15-1, USEPA 2011) Breastfed intake rates used from birth to 12 months of age. (MDH)		
	Age ranges	**Breastmilk Intake rates (mL/kg-d)**	**Body weights (kg)**
	Birth	N/A	3.38
	Birth to <1 month	220	4.3
	1 to <3 months	190	5.2
	3 to <6 months	150	6.7
	6 to <12 months	130	7.7

The toxicokinetic serum model is run in Excel as described in Goeden et al. 2019. To obtain the fish-tissue criterion ($CC_{FT\text{-}DEV}$), candidate PFOS concentrations are tested in the model until the maximum serum concentrations were at the 20% RSC (4.8 µg/L) threshold from birth to 54.8 (20,000 days) years of age. Maintaining PFOS body burdens from freshwater fish consumption at this low level will help ensure total PFOS exposure does not exceed the serum level associated with adverse effects based on the MDH RfD. The model begins with an estimated value of maternal steady-state serum (birth to age 30 years). The PFOS serum concentration is used to estimate placental transfer (initial body burden at birth) and then run for formula-fed and breastfed scenarios. The MPCA determined that breastfeeding could result in a higher body burden; therefore, protecting infants under this scenario is the basis for developing the final CC. As shown in Figure 1, protection is achieved for breastfed infants as long as a PFOS fish-tissue concentration of 0.37 ng/g is not exceeded in fish tissue. For the formula-fed scenario, this level of protection was achieved as long as a PFOS concentration of 0.66 ng/g is not exceeded.

The Final PFOS $CC_{FT\text{-}DEV}$ applicable to Class 2 surface waters is 0.37 ng/g in fish-fillet (muscle) tissue. The Health Risk Index Endpoints for evaluating additive toxicity are developmental, adrenal (endocrine), hepatic (liver) system, immune system, and thyroid (endocrine) (MDH 2019b).

Figure 1: Estimated PFOS serum concentration based on using fish consumption in a modified version of the MDH toxicokinetic serum model (MDH 2019b)



8.2 Class 1/2A, Class 1/2Bd, Class 2B, and Class 2D water column chronic criteria

While fish tissue concentrations are important for human health, most regulatory and remediation programs are designed to look at the concentrations of pollutants in water. This requires the derivation of criteria for the water column. The water concentration based CC ($CC_{DFR\text{-}DEV}$ and $CC_{FR\text{-}DEV}$) are derived from the $CC_{FT\text{-}DEV}$ by dividing by the PFOS BAF. The $CC_{FT\text{-}DEV}$ of 0.37 ng/g is first converted to 370 ng/kg and then divided by the interim statewide PFOS BAF of 7,210 L/kg. As described in Section 6.4, using this 90th percentile BAF based on paired fish and water datasets from 18 water bodies (four with two years of recent data for a final total of 22 water body-specific BAF) will ensure most species of fish will meet the $CC_{FT\text{-}DEV}$ when or if PFOS concentrations in surface water fall below the water column $CC_{DFR\text{-}DEV}$. This approach leads to a $CC_{DFR\text{-}DEV}$ of 0.05 ng/L.

The $CC_{DFR\text{-}DEV}$ is compared to a surface water concentration. Use of the $CC_{DFR\text{-}DEV}$ for surface water is intended to ensure PFOS does not bioaccumulate to concentrations greater than 0.37 ng/g in most species of fish. The $CC_{DFR\text{-}DEV}$ of 0.05 ng/L is more stringent than the MDH's PFOS health based guidance value for drinking water of 15 ng/L, so the final $CC_{DFR\text{-}DEV}$ for Class 1/2A or Class 1/2Bd is 0.05 ng/L (see Table 7-1).

The same value of 0.05 ng/L is also applied as the $CC_{FR\text{-}DEV}$ for Class 2B and 2D surface waters, since it is more stringent than what is needed to address recreational exposure to PFOS.

As shown in Table 8-2 the $CC_{DFR\text{-}DEV}$ and $CC_{FR\text{-}DEV}$ applied in surface water will be protective for all the beneficial uses relevant to people's exposure. These CC have the same Health Risk Index Endpoints for evaluating additive toxicity as the $CC_{FT\text{-}DEV}$: developmental, adrenal (endocrine), hepatic (liver) system, immune system, and thyroid (endocrine)(MDH 2019b).

Table 8-2: PFOS water quality criteria for the protection of Class 1/2A,1/2Bd, or Class 2B/2D surface water uses

PFOS (CAS No. see Table 2-1)	**MDH Health-based guidance**	**Site-specific water quality criteria: Chronic Criteria (CC)**			***Health Risk Index Endpoints*** **(Additive Risk)**
	HBV (2019)	**Class 1/2A or Class 1/2Bd**– drinking water, fish consumption and recreational exposure ($CC_{DFR-DEV}$) (30-day average)	**Class 2B/2D** – fish consumption and recreational exposure (CC_{FR-DEV}) (30-day average)	**Class 2 fish-tissue** (CC_{FT-DEV}) (90th percentile of 5 fish minimum per water body)	
PFOS	15 ng/L	0.05 ng/L	0.05 ng/L	0.37 ng/g	Developmental, Adrenal (Endocrine), Hepatic (Liver) System, Immune System, Thyroid (Endocrine) (MDH 2019b)

Description of CC:

CC_{DFR} : Applied in Class 1/2A and Class 1/2Bd surface waters (D: Domestic Consumption, drinking water/food processing, F: Fish consumption, and R: Recreational exposure)

CC_{FR} : Applied in Class 2B surface waters (F: Fish consumption and R: Recreational exposure)

CC_{FT}: Applied for Bioaccumulative Chemicals of Concern (BCC) in fish (fillet/muscle) for all Class 2 waters (FT: fish-tissue)

$CC_{DFR-DEV}$, CC_{FR-DEV}, and CC_{FT-DEV}: Used for a pollutant with acute, short-term, or subchronic developmental ("less-than-chronic") toxicity and higher early-life exposure rates (developmental toxicity as a Health Risk Index Endpoint)

If more than one CC can be developed for a pollutant (e.g., for a pollutant with a chronic RfD and a less-than-chronic RfD or a chronic RfD and linear cancer slope factor), the more stringent CC by use classification and media (CC_{DFR} /$CC_{DFR-DEV}$, CC_{FR} / CC_{FR-DEV}, or CC_{FT}/CC_{FT-DEV}) will be listed as the final applicable WQC. For PFOS, the most stringent CC are based on the developmental life-stages.
Note on reporting limits (RL) from SGS Axys Analytical, British Columbia, for PFOS:
Datasets used in developing WQC (RL: 2 ng/g in fish and 5 ng/L in water); new methods in 2019 (RL: 0.2 ng/g and 0.8 ng/L, respectively)

8.3 Uncertainty

The development of WQC are based on recently updated human health-based methods in Minn. R. chs. 7050 and 7052. In addition, specifically, development of CC for PFOS is based on the most currently available, reliable, and scientifically defensible toxicological and exposure information and monitoring data. As fully described in the MPCA's 2017 *Human Health-based Water Quality Standards Technical Support Document*, there can be uncertainty in exposure factors, toxicity values, and risk characterization. The chemical-specific methods for the PFOS CC improve the accuracy of these regulatory values (see Appendix A).

Another area of uncertainty and ongoing research are the other PFAS being detected in fish-fillet (muscle) tissue. Monitoring of fish tissue by the MPCA and the interagency FCMP has detected PFAS chemicals that lack MDH toxicity values. PFAS detected at relatively lower concentrations include PFDA, PFUnA, and PFDoA, and, less frequently, PFNA and PFOSA. As new analytical methods are developed or detection limits lowered, there may be other PFAS in fish that will need WQC. However, PFOS in fish tissue is a known health risk. And at this point, relying on a PFOS criterion – particularly given its very stringent level – to help address these other PFAS in fish tissue is a defensible approach because focusing on PFOS as a basis for best management practices, source control, and treatment technology will result in cleanup or reduction in wastewater discharges of other PFAS. The MPCA has significant ongoing remediation efforts to continue to limit and cleanup water resource contamination. Continued monitoring of the most common PFAS in fish can demonstrate where technology or other practices are working or not to remove the longer chain PFAS in addition to PFOS. These efforts include water treatment systems that remove many PFAS, because of some similarity in physical-chemical properties.

And in regards to pollution prevention, the EPA has put restrictions on the use and import of longer carbon length PFAS, specifically PFOA and other eight and longer carbon chain perfluoroalkyl carboxylic acids and six and longer carbon chain perfluoroalkane sulfonates, including PFOS, thereby contributing greatly to reducing the future concentrations and presence of those PFAS in fish (USEPA 2018).

9. Risk characterization

9.1 Application

It is appropriate to use the PFOS CC in the following ways:

- $CC_{FT\text{-}DEV}$: compare to concentration of PFOS in fish-tissue to evaluate potential risks at those water bodies for which this site-specific CC was derived.
- $CC_{DFR\text{-}DEV}$: compare to PFOS concentrations in Class 1/2A/2Bd surface waters to evaluate potential risks at those water bodies for which this site-specific CC was derived.
- $CC_{FR\text{-}DEV}$: compare to PFOS concentrations in Class 2B/2D surface waters to evaluate potential risks at those water bodies for which this site-specific CC was derived.

The application of the CC in regards to comparing to water and fish monitoring data to the level of the CC must include sufficient samples. The $CC_{DFR\text{-}DEV}$ and $CC_{FR\text{-}DEV}$ of 0.05 ng/L is applied as a 30-day average concentration that should not be exceeded more than once in a three-year window. The $CC_{FT\text{-}DEV}$ requires at least five fish from a water body and calculation of a 90th percentile PFOS concentration in the fillet tissue for comparison to 0.37 ng/g. These details are found in the assessment methods in Chapter 6: Aquatic consumption and drinking water of the most recent MPCA *Guidance Manual for Assessing the Quality of Minnesota Surface Waters for Determination of Impairment: 305(b) and 303(d) List* (2020).

A key aspect to assessing PFOS, because it is a BCC, is the comparison of fish-tissue monitoring data to the $CC_{FT\text{-}DEV}$; this is the most accurate way to determine if PFOS is at concentrations affecting the beneficial use of fish consumption in a water body (Minn. R. 7050.0150, subp. 7). A fish-tissue based CC_{FT} or $CC_{FT\text{-}DEV}$ has less uncertainty than water column CC. The CC_{FT} is calculated without a BAF, an exposure parameter that can be quite variable. The application of an upper percentile BAF based on paired fish and water datasets from 18 water bodies in two years (2016 and 2018) increases the certainty that meeting the water-based $CC_{DFR\text{-}DEV}$ or $CC_{FR\text{-}DEV}$ (0.05 ng/L) will reduce PFOS below concentrations of concern in fish tissue. However, again the fish-tissue $CC_{FT\text{-}DEV}$ will be of greater value, because new analytical methods have detection limits below 0.37 ng/g for fish-tissue. Analytical methods for water do not have detection limits below the 0.05 ng/L water-based CC. The expected detection limit available to the MPCA for PFOS is 0.2 ng/g and 0.8 ng/L, respectively (SGS Axys Analytical).

In addition, not all PFAS can be detected at this time due to analytical method limitations. The methods to protect human health do incorporate additive risk from mixtures of two or more toxic pollutants in fish or water samples. Additive risks for noncancer effects are based on toxic pollutants that have numeric WQS or WQC and the same Health Risk Index Endpoints (MPCA 2017).

9.2 Additive risks

Methods to develop CC require evaluation of additive risk when more than one toxic pollutant is present in surface water or fish tissue (Minn. R. 7050.0222, subp. 7 D). Additive risks are evaluated for both noncancer and cancer effects. The PFOS CC is derived based on noncancer effects. To evaluate additive risks from noncancer effects, hazard quotients are calculated by dividing the site fish-tissue concentration by the CC for each individual contaminant present. All of the hazard quotients for individual chemicals that affect the same Health Endpoint are summed to calculate a hazard index. If the hazard index is equal to or less than 1, it is not likely that exposure to those contaminants involved in the evaluation will lead to a health risk (Equation 1). Concentrations above would exceed the WQC for mixtures.

$$Noncancer\ Health\ Risk\ Index\ by\ Common\ Health\ Risk\ Index\ Endpoint = \frac{C_1}{CC_1} + \frac{C_2}{CC_2} + \cdots + \frac{C_n}{CC_n} \leq 1$$

Where:

$C_1 \ldots C_n$ - surface water concentrations (as a 30-day average) or fish-tissue concentrations for the first through the n^{th} noncancer pollutant with the same Health Risk Index Endpoints. These health endpoints for PFOS are found in Table 7-1.

$CC_1 \ldots CC_n$ - CC for surface water or fish tissue concentrations for the first to the n^{th} noncancer pollutant.

Equation 1. Additive risks

9.3 Tribal and Environmental Justice communities

Fishing patterns and fish consumption from Minnesota's water bodies are likely not the same among all populations living within the borders of Minnesota. Fortunately, the MDH has conducted or partnered with many researchers, communities, and healthcare providers to gain important information on Minnesota and Great Lakes regional fish consumers and provide guidance to ensure balanced and healthy fish consumption (MDH 2020).

In developing WQS for pollutants in fish, the MPCA considers the need to address subsistence fishing by communities or populations and to ensure those populations are adequately protected. The MDH FISH study was specifically used as the basis for an interim FCR for WCBA because it was conducted in communities on the North Shore of Minnesota with a high rate of freshwater fishing (MDH 2017d). Specific demographics of the women that participated were kept confidential, except for the age range for participation of 16 to 50 years; the survey results indicated that 73% of the women consumed freshwater-caught fish. By contrast, most surveys of Minnesota as a whole estimate consumption for WCBA at around 40%. Because more research and outreach is needed to finalize a FCR for WCBA, the rate being used for WQC is considered "interim."

Tribal nations have reserved fishing rights in many water bodies across the state, and therefore members of Tribal nations are important fish consumers. They are likely to consume fish at higher rates than the "average" Minnesotan. For water bodies in the Lake Superior Basin, there are Tribal Water Quality Standards that have different human health-based methods and intake rates. For example, the Fond du Lac Band of Lake Superior Chippewa use a FCR of 60 g/d and Grand Portage Band of Lake Superior Chippewa use a FCR of 142.5 g/d. These rates have provided important context to the MPCA's decision on an interim FCR. If the MPCA considers a statewide WQS for PFOS in fish tissue, or develops criteria for water resources that are important tribal fisheries, the MPCA will engage with affected Tribes to consider the appropriate fish consumption rates.

The MPCA also has a published story map of areas of potential environmental justice concern in the state–areas where the number of people of color exceed 50% and/or more than 40% of the households have a household income of less than 185% of the federal poverty level (MPCA 2019b). The map also includes Tribal areas. As PFAS CC are applied on a site-specific basis, information specific to environmental justice areas will be considered, particularly specific to exposure parameters.

Environmental justice also considers populations that may be more susceptible to adverse effects from environmental pollutants, or may be more highly exposed. For PFOS, the combination of bioaccumulation, developmental toxicity, and high exposure during infancy means protecting these early-life stages is dependent on a mother's lifetime body burden. The foundation of the toxicokinetic serum models developed by the MDH and modified by the MPCA is the use of exposure rates specific to WCBA and nursing mothers. The MDH has also provided practical health recommendations to women and their families with elevated exposure, and still recommends breastfeeding as the best nutritional support to infants.

10. Definitions

Definitions and abbreviations pertinent to the TSD are listed below; for a complete list of definitions see Minn. R. 7050.0218.

Adverse effect – A biochemical change, functional impairment, or pathologic lesion that affects the performance of the whole organism or reduces an organism's ability to respond to an additional environmental challenge.

Available and reliable scientific data – The information derived from scientific literature including: published literature in peer reviewed scientific journals, USEPA ambient water quality criteria documents, and other reports or documents published by the USEPA or other governmental agencies.

Bioaccumulation factor (BAF) – The concentration of a pollutant in one or more tissues of an aquatic organism, exposed from any source of the pollutant but primarily from the water column, diet, and bottom sediments, divided by the average concentration in the solution in which the organism had been living, under steady state conditions.

Bioaccumulative chemical of concern (BCC) – Any chemical that has the potential to cause adverse effects which, upon entering the surface waters of the state, by itself or as its toxic transformation product, accumulates in aquatic organisms by a human health bioaccumulation factor (BAF) greater than 1,000, after considering metabolism and other physiochemical properties that might enhance or inhibit bioaccumulation, in accordance with the methodology in part 7052.0110, subpart 3.

Chronic toxicity – A stimulus that lingers or continues for a long period of time, often one-tenth the life span or more. A chronic effect can be mortality, reduced growth, reproduction impairment, harmful changes in behavior, and other non-lethal effects.

Chronic criterion (CC) and chronic standard (CS) – The highest water concentration or fish tissue concentration of a toxicant or effluent to which aquatic life, humans, or wildlife can be exposed indefinitely without causing chronic toxicity. CC represents a site-specific chronic criterion developed based on this part (7050.0218) and 7050.0219 or 7052.0110. CS represents a chronic standard listed in parts 7050.0220 and 7050.0222 or in Minn. R. 7052.0100.

Developmental health endpoint or developmental toxicity – An adverse effect on the developing organism that may result from parental exposure prior to conception, maternal exposure during prenatal development, or direct exposure postnatally until the time of sexual maturation. Developmental toxicity may be detected at any point in the lifespan of the organism. The major manifestations of developmental toxicity include: A. Death of developing organism, B. Structural abnormality, C. Altered growth, and/or D. Functional deficiency (Minn. R. 4717.7820, subp.8).

Duration – The time over which the instream concentration of a pollutant is averaged for comparison with the standard or criterion.

Endocrine (E) – A change in circulating hormone levels or interactions with hormone receptors, regardless of the organ or organ system affected. Health Endpoints with or without the (E) designation are deemed equivalent, for example, thyroid (E) = thyroid, and must be included in the same Health Risk Index Equation (Minn. R. 4717.7820, subp. 10).

Frequency – The number of times a standard can be exceeded in a specified period of time without causing acute or chronic toxic effects on the aquatic community, human health, or fish-eating wildlife.

Health risk index – Sum of the quotients calculated by identifying all chemicals that share a common Health Endpoint or are based on linear carcinogenicity and dividing the water or fish tissue concentration for each chemical (measured or statistically derived) by its applicable chronic standard or chronic criterion (Minn. R. 4717.7820, subp. 11). To meet the objectives in part 7050.0217, the health risk index must not exceed a value of one.

Health risk index endpoint or health endpoint – General description of toxic effects used to group chemicals for the purpose of calculating a Health Risk Index (Minn. R. 4717.7820, subp. 12).

Intake rate (IR) – Rate of ingestion, inhalation, or dermal contact, depending on the route of exposure, expressed as the amount of media taken in, on a per body weight and daily basis, for a specified duration.

Magnitude – The acceptable amount of a toxic pollutant in water or fish tissue expressed as a concentration.

Reference dose (RfD) – Estimate of a dose for a given duration to the human population, including susceptible subgroups such as infants, that is likely to be without an appreciable risk of adverse effects during a lifetime. It is derived from a suitable dose level at which there are few or no statistically or biologically significant increases in the frequency or severity of an adverse effect between the dosed population and its associated control group.

The RfD includes one or more divisors, applied to the suitable dose level, accounting for: (i) uncertainty in extrapolating from mammalian laboratory animal data to humans; (ii) variation in toxicological sensitivity among individuals in the human population; (iii) uncertainty in extrapolating from effects observed in a short-term study to effects of long-term exposure; (iv) uncertainty in using a study in which health effects were found at all doses tested; and (v) uncertainty associated with deficiencies in the available data (Minn. R. 4717.7820, subp. 21). The product of the divisors is not to exceed 3,000 in an RfD used for a chronic standard. The RfD is expressed in units of daily dose as milligrams of chemical per kilogram of body weight-day or mg/kg-day.

Relative source contribution factor (RSC) – Percentage or apportioned amount (subtraction method) of the Reference Dose (RfD) for a pollutant allocated to surface water exposures from drinking or incidental water ingestion and fish consumption. In the absence of sufficient data to establish a pollutant- or chemical-specific RSC value, the default RSC is 0.2 and 0.5 as described in part 7050.0219, subpart 5.

Time-weighted average (TWA) – When quantifying a measurement that varies over time, such as water intake, a time-weighted average takes measured intakes, which may occur at unevenly spaced intervals, and multiplies each measurement by the length of its interval. These individual weighted values are then summed and divided by the total length of all of the individual intervals. The result is an average of all of the measurements, with each measurement carrying more or less weight in proportion to its size.

Toxic effect – Observable or measurable adverse biological event in an organ, tissue, or system. The designation of health endpoints does not exclude other possible observable or measurable biological events. For the purpose of grouping chemicals and creating a health risk index when multiple chemicals are present, toxic effects may be ascribed to more general health risk index endpoints or health endpoints (Minn. R. 4717.7820, subp. 24).

Toxic pollutant – Pollutants, or combinations of pollutants, including disease-causing agents, which after discharge and upon exposure, ingestion, inhalation or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, will, on the basis of information available to the MPCA, cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions, including malfunctions in reproduction, or physical deformation, in such organisms or their offspring (Minnesota Statutes Chapter 115.01).

Toxicokinetics – Determination and quantification of the time course of adsorption, distribution, metabolism, and excretion of chemicals (sometimes referred to as pharmacokinetics)(USEPA 2000).

Trophic level – The food web level in an ecosystem that is occupied by an organism or group of organisms because of what they eat and how they are related to the rest of the food web. For example, trophic level 3 in an aquatic ecosystem consists of small fish such as bluegills, crappies, and smelt and trophic level 4 consists of larger carnivorous fish such as walleye, northern pike, and most trout species.

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Appendix A. Limitations of the default water quality criteria methods for perfluorooctane sulfonate (a developmental toxicant)

The MPCA's scientific review of the default methods in Minn. R. ch. 7050 and supporting technical information (MPCA 2017) determined that chemical-specific parameters and approaches are available, reliable, and scientifically defensible for use in developing WQC for PFOS. As described in this TSD the MPCA based the PFOS $CC_{FT\text{-}DEV}$ on the MDH toxicokinetic serum model developed for health based drinking water guidance (MDH 2019b). Use of the model for developing a fish-tissue based CC for PFOS has multiple benefits including:

- Accounting for health risks from the high transgenerational (prenatal) and neonatal exposure and long biological half-life of PFOS.
- Developing and applying exposure parameters by life-stage.
- Improving estimates of internal doses.
- Ensuring serum concentrations remain below the 20% RSC threshold to limit total lifetime body burdens of PFOS from all sources below the "reference" serum concentration corresponding to adverse health effects.

The default algorithm for developing a Class 2 fish-tissue based CC for a noncarcinogen or nonlinear carcinogen is found in Minn. R. 7050.0219, subp. 15 (A).

Beneficial use classification

Class 2A, 2Bd, 2B (2D): Fish consumption, pollutant with a final BAF > 1,000, CS_{FT} or CC_{FT} (mg/kg)

$$= \frac{RfD_{Chronic}\ (mg/kg-d)\ x\ RSC\ (no\ units)\ or - RSC\ (mg/kg-d)}{FCR_{Adult}\ (kg/kg-d)}$$

Toxicity Value and Health Endpoints	Reference Dose (RfD) designed for chronic durations (> 10% of lifetime); comparable to 1990 RfD definition.	Pollutant-specific in mg/kg-d (sources: MPCA, MDH and EPA)
Fish Exposure	Fish Consumption Rate (FCR): adult	0.00043 kg/kg-d (0.43 g/kg-d) (default) (Review would be conducted to determine if an alternate FCR is needed for developmental toxicants. MPCA 2017)
Relative Source Contribution (RSC)	Based on EPA 2000 Exposure Decision Tree: Accounts for exposures other than ingestion of fish; as with other RSC applications, can include percentage or subtraction approach. Subtraction was used for the 2008 fish tissue-based mercury CS_{FT}	Pollutant-specific or more often: 0.2 or 0.5 (defaults) (sources: MPCA and EPA)

The limitations to developing a $CC_{FT\text{-}DEV}$ for PFOS using the default approach include the need for a new interim FCR for women of childbearing age (FCR_{WCBA}). PFOS is a developmental toxicant, so requires exposure parameters that are representative of prenatal to postnatal exposure. The development of the new FCR_{WCBA} of 0.00094 kg/kg-d or 0.94 g/kg-d is described in MPCA 2020a. The other significant limitation is the ability to account for its long biological half-life and transgenerational exposure *in utero* and potentially from breastfeeding. Using the modified MDH toxicokinetic serum model allows for an evaluation of the protectiveness of the $CC_{FT\text{-}DEV}$ using the default algorithm.

Beneficial Use Classification

Class 2A, 2Bd, 2B (2D): Fish Consumption, pollutant with a final BAF > 1,000, CC_{FT} (mg/kg)

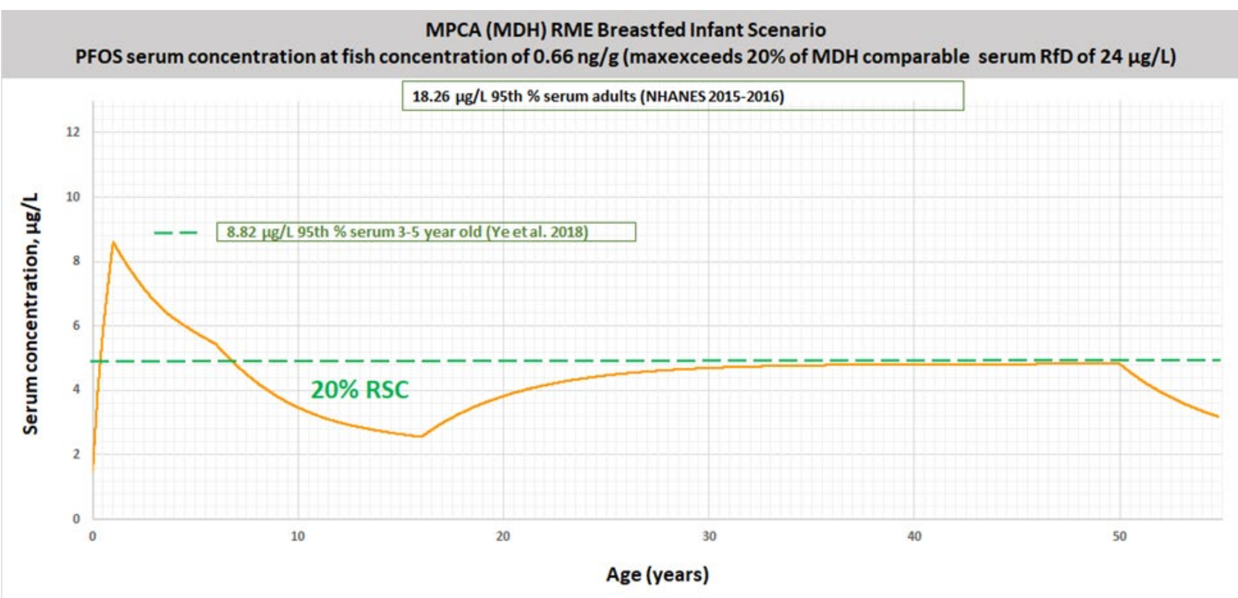
$$= \frac{RfD_{Chronic}\,(mg/kg-d)\ x\ RSC\ (no\ units)}{FCR_{Adult}\,(kg/kg-d)}$$

$$CC_{FT-DEV}\ (ng/g) = \frac{RfD_{Short-term\ to\ Chronic}\ (0.0000031\ mg/kg-d)\ x\ RSC\ (0.2)\ x\ 1{,}000{,}000\ ng/mg}{FCR_{WCBA}\ (0.94\ g/kg-d)} = 0.66$$

Toxicity value and health endpoints	$RfD_{Short\text{-}term\ to\ chronic}$ Developmental, Adrenal (Endocrine), Hepatic (Liver) System, Immune System, Thyroid (Endocrine)	0.0000031 mg/kg-d (source: MDH 2019b)
Fish exposure	FCR_{WCBA}	0.00094 kg/kg-d (0.94 g/kg-d) (source: MPCA 2020a)
Relative Source Contribution (RSC)	Default: multiple other routes/sources of exposure	0.2 (source: MPCA)

Like MDH's health based guidance approach, the MPCA used this value in the toxicokinetic serum model to determine if the estimated serum level of PFOS would remain below 20% of the comparable "reference" serum concentration of 24 µg/L. The 20% threshold of 4.80 µg/L is exceeded from approximately age 4.4 months to 6.9 years in the breastfed infant scenario. The elevation of PFOS serum levels for a six year window, especially during early life, does not meet the health protective goals of WQC.

Figure 2 PFOS serum concentrations at a fish-tissue concentration of 0.66 ng/g (default algorithm)



Appendix B. Application of perfluorooctane sulfonate water quality criteria to specific water bodies.

https://www.pca.state.mn.us/sites/default/files/wq-s6-61b.pdf