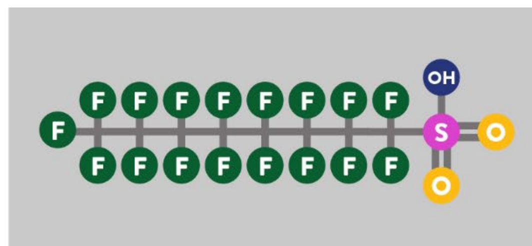
Water quality standards

May 2025

Human Health Protective Water Quality Criteria for Per- and Polyfluoroalkyl Substances (PFAS) in Mississippi River, Miles 820 to 812



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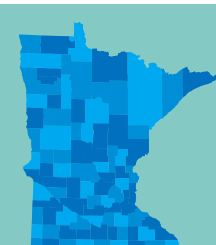

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Acronyms

ADAF	Age-Dependent Adjustment Factor
$AF_{lifetime}$	Lifetime Adjustment Factor
BAF	Bioaccumulation Factor
BCC	Bioaccumulative Chemical of Concern
CC_{FT}/CS_{FT}	Chronic Criterion or Standard – Fish tissue-based
CC_{FR}/CS_{FR}	Chronic Criterion or Standard – Fish consumption and recreation use class
CSF	Cancer Potency Slope Factor
CWA	Clean Water Act
EPA	United States Environmental Protection Agency
FCR	Fish Consumption Rate
HH-WQS	Human Health Water Quality Standards
IWR	Incidental Water Intake Rate
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
Minn. R. ch.	Minnesota Rule chapter
NLC	Nonlinear Carcinogen
NPDES	National Pollutant Discharge Elimination System
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Pefluorobutane sulfonic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFSA	Perfluorosulfonic acid
RfD	Reference Dose for noncancer toxicants and nonlinear carcinogens
ROS	Regression on Order Statistics
RSC	Relative Source Contribution factor
SSC	Site-Specific Water Quality Criteria
TSD	Technical Support Document
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 per- and polyfluoroalkyl substances

The Minnesota Pollution Control Agency (MPCA) has multiple programs monitoring and responding to per- and polyfluoroalkyl substances (PFAS) contamination in groundwater, surface water, and aquatic life. This technical support document (TSD) describes the derivation of site-specific water quality criteria (SSC) for five PFAS in the Mississippi River near Cottage Grove, Minnesota.

The MPCA is the state agency responsible for setting water quality standards and criteria[1] under the Clean Water Act (CWA). 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. Water quality standards 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 waters of the state.
- Narrative and/or numeric standards to protect those uses by designating the 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 CWA requires states to 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 "SSC" 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. 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.[3]

Derivation of the PFAS SSC falls under the MPCA's authorities to protect human health from adverse impacts of toxic pollutants in Class 2 surface waters and fish. Per- and polyfluoroalkyl substances are categorized as toxic pollutants that to date lack numeric WQS in rule; therefore, the MPCA has derived SSC that are as fully enforceable as WQS after allowing for the necessary opportunities for comment. The SSC are specific to protecting human health, and include several values, each specific to the surface water's designated beneficial uses. The SSC for five PFAS applicable in surface water and/or fish-tissue are described in Table 1-1. For purposes of this SSC derivation, the "site" is defined as the Mississippi River main channel between river miles 820 and 812.

A data reporting error was discovered that impacted several data points for some of the PFAS compounds. A subset of the data was submitted to MPCA erroneously, resulting in those data being reported as "detected" data, when they were actually below the reporting limits. The subset of erroneous data was corrected, and the data were reanalyzed. Previous versions of this SSC contained SSC for six PFAS, but after data re-evaluation, the data available for PFHxA were not robust enough to adequately calculate SSC. This is further discussed in the PFHxA section (see Section 7 of this document).

[3] 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 SSC but should be reviewed in the future to determine if more stringent criteria are warranted to protect ecological species.

Table 1-1: Derived site-specific water quality criteria for PFAS for the protection of Class 2B surface water uses in Mississippi River, Miles 820 to 812

PFAS **(CAS No. see Table 2-1)**	**Site-specific water quality criteria: Chronic Criteria (CC)**		**Health Risk Index Endpoints** **(Additive Risk)**[4]
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90^{th} percentile of 5 fish minimum per water body)	
PFOS	0.027 ng/L	0.021 ng/g	Developmental, Liver System, Immune System, Cancer
PFOA	0.039 ng/L	0.00036 ng/g	Developmental, Liver System, Immune System, Cancer
PFHxS	0.0087 ng/L	0.000085 ng/g	Liver System, Thyroid (endocrine)
PFBS	6,700 ng/L	Not applicable	Thyroid (endocrine)
PFBA	55,000 ng/L	Not applicable	Liver System, Thyroid (endocrine)
Mixtures containing PFBA and PFBS	≤ 1 (unitless) Health Risk Index	Not applicable	Thyroid (endocrine)

Definitions of CC:

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

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

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.

Water quality standards 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.

[4] When multiple chemicals are found in a water sample, those chemicals in combination may cause adverse effects that may not be equal to the effects that would be expected from exposure to a single chemical. When considering the effects from multiple chemicals, the health effects should be the same. The health risk index endpoints provided here are the currently known organ or body systems impacted by the chemical listed, that could be used to determine any additive effects of the chemicals when exposed in mixtures (MDH 2008). These endpoints are not necessarily what the CC_{FR} or CC_{FT} were based off of, though generally, at least one of the endpoints drive the criteria.

- Assessment of available pollutant-specific monitoring data in surface waters and fish for the CWA 303(d) Impaired Waters List.

Water quality standards are derived to be protective of both human health and aquatic life.[5] 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 may impact human health, and to date do not have a human health-based WQS, human health-based water quality criteria may be derived and applied at a specific site or sites, based on methods already adopted into rule and approved by the United States Environmental Protection Agency (EPA). To summarize:

- WQS: Chronic Standards (CS) – derived for Class 2 waters; pollutant-specific standards adopted into rule.
- SSC: 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).

Chronic Standards 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). Chronic Standards and CC refer to human health throughout the remainder of this document.

For purposes of SSC derivation, the "site" is defined as the Mississippi River main channel between river miles 820 and 812 (referred to collectively as Pool 2 Section 4 and Pool 3 Section 1 in 3M's Instream PFAS Characterization Study Final Report, Mississippi River, Cottage Grove, Minnesota (Weston Solutions 2023). This area is immediately adjacent to and downstream of 3M Cottage Grove manufacturing facility and impacted by discharge from 3M (Figure 1-1). Several PFAS that are indicative of 3M's Cottage Grove facility production, including PFOSA, MeFOSA, MeFOSAA, MeFOSE, EtFOSA, EtFOSAA, EtFOSE, and HQ-115 are all detected in fish and water collected in this segment of the river. Fish tissue and surface water data used for this SSC derivation were collected at the site in 2021.

[5] 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 SSC.

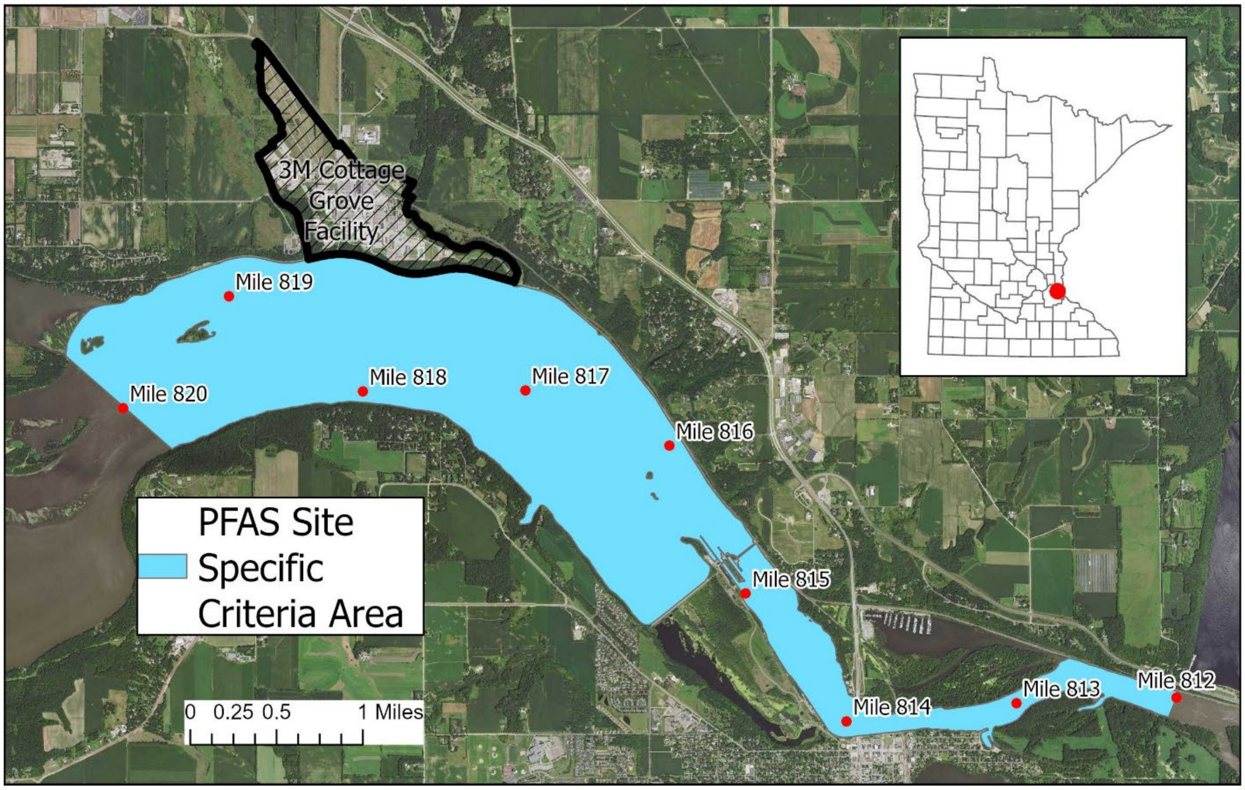

Figure 1-1: Location of site-specific water quality criteria development for Mississippi River, River Miles 820 to 812.

This TSD includes the derivation of a site-specific CC for perfluorobutane sulfonic acid (PFBS), perfluorobutanoic acid (PFBA), perfluorohexane sulfonic acid (PFHxS), perfluorooctanoic acid (PFOA), and perfluorooctane sulfonic acid (PFOS). Previous versions of the SSC contained a criterion for perfluorohexanoic acid (PFHxA) as well, but a data re-evaluation resulted in the inability to calculate a SSC for PFHxA, due to data limitations, as further discussed below (see Section 7). Class 2 CC are developed for application in fish-tissue and surface waters. The CC are based on the most recent toxicity information and the most recent site data, along with MPCA's 2017 human health-based WQS/SSC derivation methods as adopted in Minn. R. chs. 7050 and 7052.

Only the most recent site data were used in the SSC derivation due to fish rapidly taking up and depurating PFAS (Hassel et al. 2020), leading to relatively rapid changes in fish tissue concentrations that follow changes in water concentration. The most recent site data came from an extensive evaluation of site conditions designed to collect data needed to develop criteria based on site-specific conditions. These data are determined to be the most reliable that the MPCA had available to best reflect current site conditions.

2. Problem formulation

2.1 Per-and polyfluoroalkyl substances

Minnesota defines PFAS as a class of fluorinated organic chemicals containing at least one fully fluorinated carbon atom (Minn. Stat. § 325F.075, subd. 1.3c). Per- and polyfluoroalkyl substances are a very large and diverse class of chemicals with a range of physicochemical properties and toxicity. Extensive sampling of both fish tissue and surface water have been completed in the Mississippi River for a subset of PFAS, allowing for the calculation of SSC for PFAS with sufficient environmental data and toxicity information. Chronic Criteria 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 in the Mississippi River near Cottage Grove.

Table 2-1: PFAS evaluated for site-specific water quality criteria development for Mississippi River, Miles 820 to 812 (Acronyms, carbon/chain lengths, and CAS numbers)

PFAS by Acronyms		Aliphatic Carbon No. (Chain length)	CAS Numbers
PFBA	perfluorobutanoic acid	4	375-22-4 (acid) 45048-62-2 (anion)
PFBS	perfluorobutane sulfonic acid	4	375-73-5 (acid) 45187-15-3 (anion)
PFHxA	perfluorohexanoic acid	6	307-24-4 (acid) 92612-52-7 (anion)
PFHxS	perfluorohexane sulfonic acid	6	108427-53-8 (anion) 355-46-4 (acid) 3871-99-6 (potassium salt)
PFOA	perfluorooctanoic acid	8	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 sulfonic acid	8	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)

Per- and polyfluoroalkyl substances 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.[6] 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 SSC methods and how they were applied to the PFAS CC are described in Sections 3 through 9.

[6] 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.

2.2 Overview of fish and water data

Data used to develop the SSC were collected as part of an extensive site characterization study conducted in 2021 by 3M and its contractors at the request of MPCA (Weston Solutions 2023). The study covered roughly 41 river miles of the Mississippi River, starting upstream of the 3M Cottage Grove facility (Pool 2 Section 3, River Mile 833) and continuing downstream to River Mile 792 (Pool 4 Section 1) near Red Wing, Minnesota. Environmental samples collected included fish tissue, benthic macroinvertebrates, surface water, surface microlayer, pore water, and sediment. Concentrations of PFAS in fish tissue and surface water were used to derive the SSC. Fish tissue and surface water samples generated by this study are the most recent data available for this site and are most representative of current site contamination.

Fish tissue and surface water data used for BAF and SSC derivation were limited to the “site”, that is, the area adjacent to and immediately downstream of 3M’s Cottage Grove manufacturing facility (River Miles 820 – 812). Surface water samples collected in the main channel of the river and fish fillet samples (whole fish were excluded) were used in BAF calculation.

Table 2-2: Summary of PFAS detected and geometric mean surface water concentrations from Mississippi River, Miles 820 to 812

PFAS	Percent detected in surface water	Geometric mean detected surface water concentration (ng/L)	Percent detected in fish fillet tissue	Geometric mean detected fish fillet tissue concentration (ng/g)
PFBS	91	8.70[1]	28	0.083[1]
PFBA	97	87.8[1]	35	0.21[1]
PFHxS	97	4.77[1]	40	0.047[1]
PFHxA	100	11.2	6	0.071[1]
PFOA	86	23.1[1]	24	0.18[1]
PFOS	100	16.1	100	11.7

[1]Calculated using ½ detection limit in place of non-detects.

A data reporting error was discovered that impacted several data points for some of the PFAS compounds. A subset of the data was submitted to MPCA incorrectly, resulting in those data being reported as “detected” data, when they were actually below the reporting limits. The subset of erroneous data was corrected, and the data were reanalyzed. This reporting error did result in changes to many of the SSC, due to an alteration in the geometric mean water and fish tissue concentrations that resulted from having a greater number of non-detected data in the dataset, than had been previously reported. Some of these changes, where significant, are discussed further in the document.

3. Analysis plan: site-specific chronic criteria derivation

3.1 WQS: chronic criteria

In Class 2 designated surface waters, State and 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, fish consumption, 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.
- SSC: 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 subclass for the Mississippi River Miles 820 to 812 is Class 2B. Therefore, a CC_{FR} is derived, which includes the following exposure pathways:

- Fish consumption (F).
- Recreation, which includes an incidental water intake rate (R).

The algorithms for derivation of CC_{FR} are found in Minn. R. 7050.0219, subp. 14, and can include a noncarcinogenic value only (for noncarcinogenic chemicals or for nonlinear carcinogens (NLC)), or both a noncarcinogenic and a carcinogenic value for linear carcinogenic chemicals. When both noncarcinogenic and carcinogenic values are derived, the lowest value is used as the final CC_{FR}. All final calculations are rounded to two significant figures as the final site-specific CC.

The algorithm for noncarcinogens or NLCs for CC_{FR} in Class 2B surface waters is:

$$CC_{FR} = \frac{RfD \ast RSC \ast 1x10^{6}\, ng/mg}{\{IWR + FCR\,[(0.24 \ast BAF_{TL3}) + (0.76 \ast BAF_{TL4})]\}}$$

where: CC_{FR} = fish consumption and recreation chronic criterion in nanograms (ng) per liter (L)
RfD = reference dose in milligrams (mg) per kilogram (kg)-day (d)
RSC = relative source contribution (no units)
$1x10^6$ ng/mg = a factor used to convert milligram to nanogram; there are 1,000,000 nanograms per milligram
IWR = 0.0013 L/kg-d; assumed incidental water intake rate based on minimum chronic duration
FCR = fish consumption intake rate. For chemicals with developmental toxicity, MPCA has calculated an interim FCR for women of childbearing age of 0.00094 kg/kg-d (see Section 3.4 for further discussion)
BAF_{TL3} = final BAF for TL_3 fish in L/kg; accounts for 24 percent of fish consumed
BAF_{TL4} = final BAF for TL_4 fish in L/kg; accounts for 76 percent of fish consumed

There are two linear cancer algorithms for Class 2B surface waters (Minn. R. 7050.0219, subp. 14). One algorithm uses a lifetime adjustment factor ($AF_{lifetime}$), while the other uses age-dependent adjustment factors (ADAF). The two equations allow the user to address any age-dependent cancer risk that may be known for a given chemical. Exposure to some carcinogens pose a higher risk for cancer development in infants and children, and those higher risks are accounted for with adjustment factors. Where the exact degree of risk is unknown for a chemical, default ADAFs may be used. Alternatively, if chemical-specific data are available to estimate higher lifetime potency associated with exposure in early life stages, this additional risk is included as a single $AF_{lifetime}$. If there is no additional early-life stage susceptibility, the $AF_{lifetime}$ may equal one (MPCA 2017).

Of the PFAS chemicals being evaluated for SSC, only PFOS and PFOA have been determined to be carcinogenic by the EPA (USEPA 2024a, 2024b). The other four PFAS currently have insufficient evidence to make a determination on carcinogenicity. The EPA made the determination that for both PFOS and PFOA, these chemicals do not pose additional cancer risk for early life stages, due to no evidence of a mutagenic mode of action, and a lack of evidence to determine whether exposure during early life stages increases cancer risks. Because of this, the linear carcinogen algorithm that does not utilize ADAF was chosen to develop a CC_{FR}. Because it is assumed that there is no additional cancer risk for early life stages, a $AF_{lifetime}$ of one was chosen to represent no additional risk.

The algorithm for linear carcinogenic chemicals with a lifetime $AF_{lifetime}$ for Class 2B surface waters:

$$CC_{FR} = \frac{CR\ (1x10^{-5})}{CSF\ x\ AF_{lifetime}} * \frac{1x10^{6}\ ng/mg}{\{IWR\ + FCR\ [(0.24 * BAF_{TL3}) + (0.76 * BAF_{TL4}\ )]\}}$$

where: CC_{FR} = fish consumption and recreation chronic criterion in micrograms (ng) per liter (L)
CR = cancer risk level or an additional excess cancer risk equal to 1 x 10^{-5}
AF = lifetime adjustment factor (no units)
CSF = cancer potency slope factor in $(mg/kg\text{-}d)^{-1}$
Other factors are as described above

In addition to a CC_{FR}, a fish tissue-based CC (CC_{FT}) is derived for contaminants that are bioaccumulative contaminants of concern (BCC) to protect fish consumers. The Rule language in 7052.0010, subp. 4, describes a BCC as:

> *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*

While the mean PFOS BAF at this site, which is based on a relatively small set of site data, is less than 1,000 L/kg for trophic levels 3 and 4, individuals and certain species in the dataset exhibited PFOS BAFs greater than 1,000 L/kg. Furthermore, PFOS is widely recognized as a bioaccumulative chemical of concern as demonstrated by the development of fish consumption guidance in many states (including Minnesota), presence in 100% of fish at this site, and published BAFs that can be greater than 7,000 L/kg (Burkhard 2021, ITRC 2018, UNEP 2007, UNEP 2017, UNEP 2018). Because of this, a CC_{FT} was developed for PFOS.

Fish tissue-based SSC were also derived for PFHxS and PFOA. While the mean BAFs for PFHxS and PFOA were less than 1,000 L/kg at this site, one black crappie fish tissue sample (measured at 15.2 ng/g) in the dataset used to determine the current SSC (Weston 2023) exceeded the BAF of 1,000 for PFHxS. Additionally, both PFOA and PFHxS have demonstrated BAFs > 1,000 L/kg in fish in other field studies (ITRC 2018). Both PFHxS and PFOA are known to be highly bioaccumulative in humans with long half-lives (5.3 years and 2.7 years, respectively) (Li et al., 2018), and exhibit potential toxic effects at exceptionally low concentrations. In addition, PFHxS and PFOA were detected in at least 40% and 24% of fish fillets at this site, respectively, presenting a route of exposure for people consuming fish collected in this area. The detection percentage of PFOA is likely an underestimate, however, due to elevated reporting limits for a subset of samples (see Section 5 of this document for further discussion).

Both PFOA and PFHxS have the potential to cause adverse effects in humans (as further discussed in Sections 5 and 6 of this document), but have physiochemical properties that are unique from other bioaccumulative chemicals. Both PFOA and PFHxS are water soluble, and rather than partitioning to lipid tissue in aquatic organisms (as is typical of most bioaccumulative compounds), they bind to proteins in blood and liver and are expected to be excreted through the fish's gills during respiration. Aquatic organisms are less likely to accumulate PFOA and PFHxS, when compared to terrestrial animals (ECHA 2017). The Rule language in 7052.0010, subp. 4 allows for the consideration of metabolism and other physiochemical properties of the chemicals. The unique properties of these chemicals, which create an inhibition of bioaccumulation due to metabolism and excretion of these chemicals in aquatic organisms, should be considered alongside the knowledge about the accumulation in humans, because the purpose of the fish tissue criteria is to protect human health. If the narrow definition of having a BAF of > 1,000 in aquatic organisms is only considered, this can underestimate the exposure to humans via the route of fish consumption.

Bioaccumulation factors are not generally calculated for terrestrial organisms, but determination of chemical half-lives is often used instead, as an indication of how long a chemical will remain in the body. Both PFOA and PFHxS have very long half-lives in humans (5.3 and 2.7 years, respectively; Li et al. 2018), and both have demonstrated long half-lives in other terrestrial organisms as well. Perfluorohexane sulfonic acid has a half-life of nearly 2 years in pigs (which exceeds the half-life of PFOS in pigs; Numata et al., 2014), and nearly 5 months in monkeys (ECHA 2017). Perfluorooctanoic acid has a half-life in pigs of nearly 8 months (Numata et al. 2014). Due to the long half-lives of these chemicals, they will accumulate in human blood, because each new exposure (via water, fish, etc.) will add to what is already in the body. The tissue criteria values are important to ensure protection of human consumers because many fish at this site already contain PFOA and/or PFHxS at concentrations that exceed the calculated fish tissue values. Perfluorooctane sulfonic acid, PFOA and PFHxS are entering the fish and accumulating to levels that can cause adverse effects to vulnerable human populations (such as women of childbearing age, subsistence fishing populations, etc.).

Many fish at the site had detectable levels of PFOA and PFHxS (24% and 40% of filets, respectively). The detection and reporting limits for the two chemicals are higher than their calculated CC_{FT} values. This means that potentially, additional fish could contain the chemicals at concentrations higher than the CC_{FT}. Because the chemicals elicit adverse effects at very low concentrations, and take years to be eliminated from the body, consumption of fish could be a significant exposure route, even with lower BAFs. The intent of fish tissue criteria is to protect human health from significant exposures to toxic chemicals, when exposure via fish may be an important route of exposure (MPCA 2014). Even though PFOA and PFHxS do not consistently result in BAFs in fish that exceed the > 1000 threshold, their properties still cause a significant exposure route for humans, given their low toxicological values and very long half-lives in humans.

This waterbody is not classified as a drinking water source, so incidental ingestion and fish consumption are the two routes of exposure to consider for criteria development. Fish consumption is the more likely exposure route, as incidental ingestion occurs infrequently, and in small quantities. A key aspect of HH-WQS is to maintain fish tissue concentrations below levels that adversely impact human health. Including fish tissue criteria for chemicals that accumulate in humans is a more accurate HH-WQC than criteria in water (MPCA 2014). Criteria based on water concentrations can be influenced by BAFs, which are inherently variable due to variations in BAFs within individuals, between species, and over time, and dependent upon variable water concentrations. Fish tissue criteria are a direct link between consumption and adverse impacts, while water-based criteria include a translation into a water concentration, via the BAF, which is a variable factor. Additionally, when water concentrations are below the detection limit, the MPCA cannot assess the water body as impaired when the criteria are well below the detection limit. This could result in the water not being assessed as impaired, even though there are high enough concentrations in fish to impact human health. Having fish tissue criteria give MPCA another route to determine if the water body is impaired due to PFAS concentrations exceeding levels that impact human health.

Additionally, governing bodies have determined that PFOA and PFHxS are bioaccumulative. The European Chemicals Agency (ECHA) determines that chemicals are bioaccumulative when they have a BAF of >2,000, which is higher than Minnesota Rule. However, when the ECHA's member state committee evaluated PFOA and PFHxS, the weight-of-evidence was high enough to designate these chemicals bioaccumulative, even without an aquatic organism dataset with BAFs over 2,000. The ECHA also considered the unique physiochemical properties of PFOA and PFHxS, which inhibit bioaccumulation in aquatic organisms, alongside available information about terrestrial organisms and humans. The ECHA determined that these compounds should be designated as bioaccumulative under their framework (ECHA 2013, ECHA 2017). The EPA has also recently added a group of PFAS, including PFOA and PFHxS, to their list of recommended contaminants to monitor for purposes of developing fish consumption advisories. The EPA has encouraged states and tribes to monitor specific contaminants to "protect people from eating potentially harmful concentrations of contaminants." Their documentation asserts that the lists they have developed contain contaminants that "have been found to occur in the edible tissue of fish and shellfish at concentrations that may be of concern for human health" after comparing fish tissue data to toxicity information (USEPA 2024e). This demonstrates a concern from EPA about the accumulation of these contaminants in fish tissue to levels that could impact human health.

Due to the information presented above, MPCA determined that fish tissue criteria for PFOS, PFOA and PFHxS were needed to protect human health. The algorithm for Class 2 noncarcinogens or NLCs for CC_{FT} is:

$$CC_{FT} = \frac{RfD * RSC * 1x10^6 \, ng/mg}{FCR}$$

where: CC_{FT} = fish consumption and recreation chronic criterion in nanograms (mg) per kilogram (kg)
Other factors are as described above

The algorithm for linear carcinogenic chemicals with lifetime adjustment factors ($AF_{lifetime}$) applicable to class 2 waters to calculate CC_{FT} is:

$$CC_{FT} = \frac{CR \, (1x10^{-5})}{CSF \; x \; AF_{lifetime}} * \frac{1x10^6 \, ng/mg}{FCR}$$

where: CC_{FT} = fish consumption and recreation chronic criterion in nanograms (mg) per kilogram (kg)
Other factors are as described above

3.2 Reference dose and cancer potency slope factor

Minn. R. 7050.0219, subp. 4, states that the toxicological values (RfD and CSF) to be used in criteria calculation are obtained from MDH or developed according to Minn. R. 4717.7820, subp. 5 and 21, and 7050.0218, subp. 3.

The toxicological values chosen for use in these criteria calculations were taken from the EPA's most recent evaluations of PFAS data. Over time, the toxicological values for PFAS have decreased as more information is learned about their effects on human health. For this reason, the most recent evaluation of data was desired. The EPA had recently released updated reviews of these chemicals, so the EPA toxicological information was used in place of the MDH values. The EPA-derived RfD and CSF values meet the requirements in Minn. R. 7050.0219, subp. 4, because they were developed according to Minn. R. 4717.7820, subp. 5 and 21, and 7050.0218, subp. 3, as further described below.

The RfD for a chemical is defined in Minn. R. 7050.0218, subp. 3, and in Minn. R. 4717.7820, subp. 21, as:

> *An 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 definitions in Minn. R. 7050.0218, subp.3 and in Minn. R. 4717.7820, subp. 21 both then describe five divisors, or uncertainty factors (UFs), that are applied to the dose level to account for uncertainty in the dataset and both require that the product of all applied UFs cannot exceed 3,000.

The EPA's reference doses are calculated following these rules. The methodology that MDH utilizes is based on standard EPA methodology (MDH 2008), and MPCA adopted their methodology from MDH, and thus MPCA's rules are also based on EPA methods. Because of this, utilizing toxicological values developed by EPA will follow Minnesota Rule, because those rules are based on EPA methodology.

The EPA estimated PFAS doses that would result in little risk of adverse effects over a lifetime of exposure and evaluated multiple toxicological endpoints. The EPA considered vulnerable subgroups, such as early life stages, and conducted statistical evaluations to calculate the appropriate dose, compared to the control group, that would lead to minimal impacts. The UFs the EPA uses in their evaluations are the same UFs described in Minn. R. 7050.0218, subp. 3 and in Minn. R. 4717.7820, subp. 21., and are applied to the no effect doses that the EPA calculated. No UFs used exceeded 3000.

The CSF for a chemical is defined in Minn. R. 7050.0218, subp. 3 as:

> *A factor indicative of a chemical's human cancer causing potential and an upper-bound estimate of cancer risk per increment of dose that can be used to estimate cancer risk probabilities for different exposure levels.*

A carcinogen is defined in Minn. R. 4717.7820, subp. 5 as a chemical that is a human carcinogen when it meets the requirements set out in at least one of three different guidelines. One of those guidelines, the "Guidelines for Carcinogenic Risk Assessment" (USEPA 2005), was used by the EPA in their assessment of the carcinogenic status of PFOS and PFOA (USEPA 2024a, USEPA 2024b). The determination of PFOS and PFOA as carcinogenic therefore follows the rule language in 4717.7820, subp. 5. The methodology of deriving the CSF values was also conducted using the same EPA 2005 guidelines. The CSF is defined by the EPA as "a plausible upper bound lifetime cancer risk from chronic ingestion of a chemical" and is calculated from exposure to different chemical doses (USEPA 2024b). This methodology for calculating the CSF, therefore, also meets the rule language in Minn. R. 7050.0218, subp. 3.

3.3 Bioaccumulation factor derivation

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). The BAF is used to set water column values (CC_{FR}) that if met, will also result in compliance with the fish-tissue criterion (CC_{FT}). The methods and data needed 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 data collected from field studies, rather than using literature data. 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 that analyzed the field-collected samples.

- Consolidate paired surface water and fish datasets.
- Develop geometric mean water concentrations for a specific water body (lake, river segment, or site-specific area).
- Calculate BAF for each individual fish collected by dividing reported concentrations in fillet tissue by the associated surface 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 portion or stretch of a single water body or as broadly as all statewide surface waters), which is typically the geometric mean of all the species- or water body-geometric means.

Bioaccumulation factors are the ratio of the contaminant concentration in fish to the contaminant concentration in water (Minn. R. 7050.0219, subp. 8):

$$measured\ BAF = C_t/C_w$$

where: BAF = field-measured bioaccumulation factor based on total concentration in tissue and water (L/kg)
C_t = total concentration of the chemical in the specified wet tissue (µg/kg)
C_w = total concentration of the chemical in water (µg/L)

Bioaccumulation factors were calculated for fish collected at the site using the geometric mean concentration of PFAS in fish fillets from trophic levels 3 and 4 (Appendix A, Table 6). Most of the PFAS had at least one measured sample that was below the reporting limit (non-detection). These non-detection samples must be addressed before calculating geometric means. For compounds with 100% detection (such as PFOS), a geometric mean was calculated using all of the data points for either surface water or tissue samples. To try to account for non-detects, Regression on Order Statistics (ROS) were used to calculate a geometric mean. With the current dataset, the fish tissue geometric means calculated from ROS were over-inflated when compared to other substitution methods (such as substituting the detection limit or half of the detection limit for any data points that are non-detects; see Appendix A for additional information). This is likely due to the amount of non-detections in the dataset. The data from the surface water samples did not have enough non-detections to use the ROS method. The Kaplan-Meier methodology can also be used to address non-detects. Geometric means using this technique were not able to be determined because it is not possible with negative values, which result when using log-transformed data in geometric mean calculations (see Appendix A for additional information on non-detection analysis). Because the available data did not meet the criteria for ROS or Kaplan-Meier, ½ the detection limit was used for non-detects in geometric mean calculation. The MPCA conducted an evaluation of multiple approaches to mean calculation, demonstrating that using ½ the detection limit in place of non-detects is a reasonable approach to geometric mean calculation (Appendix A). The evaluated methods are also generally accepted as reasonable approaches for addressing non-detect data in environmental datasets (Mikkonen et al. 2018, USEPA 1991). The R script for mean calculation used in BAF development are available in the MPCA's document "Human health protective water quality criteria for PFAS in Mississippi River, Miles 820 to 812, Supplemental Data" (MPCA 2024b).

3.4 Fish consumption rate

The human health WQS (HH-WQS) methods include a default fish consumption rate (FCR) for adults (Minn. R. 7050.0219), but this rate was not based on data specific to women of child-bearing age (WCBA). The HH-WQS TSD states that if a pollutant affects development and prenatal to postnatal (gestational to lactational) exposure is relevant to the toxicity profile of the pollutant, the MPCA will review available fish consumption survey and exposure data to determine if the default adult FCR was representative of WCBA, or if an alternative rate is needed (MPCA 2017). Minnesota Rule allows for consideration of other scientifically defensible algorithms on a chemical-specific basis for evaluating developmental susceptibility to toxic pollutants in fish tissue (Minn. R. 7050.0219, subp. 2A). Perfluorooctane sulfonic acid, PFOA and PFHxA have direct evidence of developmental toxicity (Table 1-1). PFHxS, PFBS and PFBA demonstrate thyroid toxicity (Table 1-1). Thyroid hormones are critical to fetal brain development, metabolism, and oxygen consumption (Bernal 2022; Forhead and Fowden 2014; Liu et al., 2023). Therefore, all five PFAS for which SSC were derived are determined to have developmental impacts, so this chemical-specific consideration should be factored into the SSC via the FCR.

Using the best available and reliable data for this limited review to meet MPCA and EPA's protective goals for HH-WQS, an interim FCR for WCBA (FCR_{WCBA}) of 66 g/d and 70 kg bodyweight (0.94 g/kg-d or 0.00094 kg/kg-d) will be applied to account for reasonable maximum exposure to WCBA (ages 16 to 50) in Minnesota that consume freshwater fish. This FCR is based on the Minnesota Department of Health (MDH) Fish are Important for Superior Health (FISH) survey of North Shore Minnesotans (MDH 2017) and reflects similar rates found in other surveys of Minnesotan WCBA.

Women of Childbearing Age can be considered the most vulnerable population, due to the developmental effects on the unborn child, and this population is often advised to eat fish to support developing pregnancies. The recommended amount given by the FDA is 8 to 12 oz per week, which translates to 32 to 49 g/day, which is in excess of the FCR in rule (30 g/d) in Minnesota. WCBA are encouraged to consume more than what is in rule, making the non-specific FCR in Rule inappropriate for this vulnerable population.

Additionally, the North Shore FISH survey did include indigenous women as part of the cohort, but the percentage of that population is not known, due to privacy given to the study participants. Indigenous populations have cultural practices that lead to consumption of larger quantities of harvested fish, which is accounted for in EPA's use of a subsistence fish consumption rate of 142.4 g/d. Prairie Island Indian Community is downstream of this discharge, and their WCBA may be at greater risk of excess exposure due to the additional fish consumption. Tribal members fish throughout Pools 2 and 3 and they consume whole fish in multiple ways that may increase their exposure to PFAS. It is critically important that MPCA consider this consumption, so that residents of the Prairie Island Community can safely enjoy eating fish taken from the river and fulfill their traditional practices. Using MPCA's interim FCR of 66 g/d is not unreasonable to ensure better protection of WCBA that may be consuming more fish to ensure a healthy pregnancy, based on current federal advice and/or cultural practices.

The data collected on the North Shore was the most robust dataset in Minnesota that evaluated WCBA, who are the most vulnerable population within the Cottage Grove site-specific area. The FCR is chemical-specific, due to the developmental toxicity of the PFAS evaluated for this SSC. This makes the rate site-specific because the chemicals being released at this site are developmental toxicants. Using the interim FCR_{WCBA} is more appropriate to ensure women's health is protected, rather than using the base FCR in rule, which was not calculated with the intent to protect vulnerable populations. Using a FCR that was calculated with consumption patterns of indigenous populations and WCBA helps protect the Prairie Island Indian Community that live and recreate in the area.

Further description of the interim FCR for WCBA and its applicability is included in the MPCA document number wq-s6-60, *Interim fish consumption rate for women of childbearing age* (2022).

3.5 Incidental intake rate

The incidental ingestion exposure parameter applies for human health standards or criteria developed for waters not designated as sources of drinking water, where the beneficial uses are narrowed to fish consumption and recreation, which applies to the Mississippi River, Miles 820 to 812 (Class 2B). The incidental intake rate of 0.0013 L/kg-d was used as the exposure factor in the calculation of the chronic criteria for the PFAS evaluated. This value is presented in Minnesota Rule 7050.0219, subp. 14 for Class 2B waters.

3.6 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.

Use of an 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 and can include: availability of biomonitoring datasets, food and environmental media monitoring, physical-chemical properties, and fate and transport of the pollutant (USEPA 2000a).

For the PFAS in these SSC, the evidence available supports use of 0.2 as the RSC in the CC_{FR}. The MPCA determined that exposure from incidental ingestion and eating freshwater fish should be limited to 20% of total exposure due to the presence of these PFAS and their precursors in other environmental media, food, drinking water, and consumer products.

4. SSC: Perfluorooctane sulfonic acid (PFOS)

Perfluorooctane sulfonic acid is an eight-carbon chemical with a sulfonate functional group. Perfluorooctane sulfonic acid has a long half-life and transgenerational transfer, even short durations of exposure can lead to significant increases in chronic duration or lifetime body burdens (Goeden et al. 2019, MDH 2022b).

4.1 Toxicological values and health risk index endpoints

The MPCA used the 2024 EPA RfD and CSF for PFOS in calculating the SSC (USEPA 2024a) (Table 4-1).

Table 4-1: PFOS Toxicity values and health endpoints

PFAS	RfD or CSF	Health Risk Index Endpoints	Reference
PFOS RfD	1×10^{-7} mg/kg-d	Developmental, Liver System, Immune system	USEPA 2024a, MDH 2024b
PFOS CSF	39.5 $(mg/kg\text{-}d)^{-1}$	Cancer	USEPA 2024a

Use of these additivity endpoints for mixture analyses is further described in Section 10.2.

4.2 Exposure factors

Exposure factors are based on the algorithms in Minn. R. 7050.0219. Because PFOS is characterized for CC as a developmental toxicant (USEPA 2024a), higher intake rates need to be applied to protect developmental life stages (MPCA 2017).

Table 4-2: PFOS Exposure parameters

Exposure parameter	Rate or value	Basis
IWR	0.0013 L/kg-d	The default WQS incidental water intake rate is applied. The rate is based on children ages one through eight.
FCR	0.00094 kg/kg-d	The most stringent RfD is based on developmental impacts affecting prenatal to neonatal health endpoints (USEPA 2024a). Because of this, the use of the interim FCR_{WCBA} for this subpopulation of fish consumers is warranted and is also protective of other Minnesota fish consumers.
BAF_{TL3}	661.1 L/kg	Paired fish fillet and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. PFOS was detected in each surface water and fish tissue sample, so BAFs were calculated without need of statistical consideration of non-detect samples.
BAF_{TL4}	834.0 L/kg	Paired fish fillet and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. PFOS was detected in each water and fish tissue sample, so BAFs were calculated without need of statistical consideration on non-detect samples.
RSC	0.2	For the CC_{FR}, the default RSC is 0.2 because routes of exposure other than recreation and freshwater fish consumption are significant to people's total exposure to PFOS. Aside from other sources, drinking water is a known source, with several drinking water sources in Minnesota having detectable levels of PFOS (USEPA 2024d).
$AF_{lifetime}$	1	The EPA determined that PFOS does not pose additional cancer risk for early life stages. Because it is assumed that there is no additional cancer risk for early life stages, a $AF_{lifetime}$ of one was chosen to represent no additional risk.

4.3 Chronic criteria calculation

Perfluorooctane sulfonic acid is a carcinogen (USEPA 2024a) and is evaluated using both the noncarcinogenic and linear carcinogenic algorithms for that toxicological profile in Minn. R. 7050.0219, as described previously. The fish consumption and recreational exposure (CC_{FR}) values use the RfD and CSF in Table 4-1 paired with the exposure factors in Table 4-2.

Noncarcinogenic CC_{FR} calculation:

$$CC_{FR} = 0.027\, ng/L = \frac{1\ x\ 10^{-7} * 0.2\ * 1x10^{6}\ ng/mg}{\{0.0013\ + 0.00094\ [(0.24 * 661.1) + (0.76 * 834.0)]\}}$$

Linear carcinogenic CC_{FR} calculation:

$$CC_{FR} = 0.35\ ng/L = \frac{CR\ (1x10^{-5})}{39.5\ x\ 1} * \frac{1x10^{6}\ ng/mg}{\{0.0013\ + 0.00094\ [(0.24 * 661.1) + (0.76 * 834.0)]\}}$$

The noncarcinogenic CC_{FR} is more protective than the linear carcinogenic CC_{FR}, therefore, the noncarcinogenic CC_{FR} is the site-specific fish consumption and recreational exposure criterion.

In addition to a CC_{FR}, a fish-tissue based CC (CC_{FT}) was derived for PFOS due to its bioaccumulation potential. The fish tissue (CC_{FT}) values use the RfD and CSF in Table 4-1 paired with the exposure factors in Table 4-2.

Noncarcinogenic CC_{FT} calculation:

$$CC_{FT} = 21\ ng/kg = \frac{1\ x\ 10^{-7} * 0.2 * 1x10^{6}\ ng/mg}{0.00094}$$

Linear carcinogenic CC_{FT} calculation:

$$CC_{FT} = 269\ ng/kg = \frac{1x10^{-5}}{39.5\ x\ AF_{lifetime}} * \frac{1x10^{6}\ ng/mg}{0.00094}$$

The noncarcinogenic CC_{FT} is more protective than the linear carcinogenic CC_{FT}, therefore, the noncarcinogenic CC_{FT} is the site-specific fish consumption and recreational exposure criterion. Calculations were rounded to two significant figures.

Table 4-3: Derived site-specific water quality criteria for PFOS for the protection of Class 2B surface water uses in Mississippi River, Miles 820 to 812

PFAS (CAS No. see Table 2-1)	**Site-specific water quality criteria: Chronic Criteria (CC)**		**Health Risk Index Endpoints** (Additive Risk)
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90th percentile of 5 fish minimum per water body)	
PFOS	0.027 ng/L	0.021 ng/g	Developmental, Liver System, Immune System (MDH 2023a)

Definitions of CC:

CCFR: Applied in Class 2B surface waters (F: Fish consumption and R: Recreational exposure)

CCFT: Applied as a wet weight concentration for Bioaccumulative Chemicals of Concern (BCC) in fish (fillet/muscle) for all Class 2 waters (FT: fish-tissue

5. SSC: Perfluorooctanoic acid (PFOA)

Perfluorooctanoic acid is an eight-carbon chemical with a carboxylate (oxygen) functional group. Perfluorooctanoic acid has a long half-life and transgenerational transfer, even short periods of exposure can lead to significant increases in chronic duration or lifetime body burdens (Goeden et al. 2019, MDH 2024a).

5.1 Toxicological values and health risk index endpoints

The MPCA used the current 2024 EPA RfD and CSF values for PFOA in calculating the SSC (USEPA 2024b) (Table 5-1).

Table 5-1: PFOA Toxicity values and health endpoints

PFAS	RfD or CSF	Health Risk Index Endpoints	Reference
PFOA RfD	3 x 10^{-8} mg/kg-d	Developmental, Liver System, Immune system	USEPA 2024b, MDH 2024a
PFOA CSF	29,300 $(mg/kg\text{-}d)^{-1}$	Cancer	USEPA 2024b

Use of these additivity endpoints for mixture analyses is further described in Section 10.2.

5.2 Exposure factors

Exposure factors are based on the algorithms in Minn. R. 7050.0219. Because PFOA is characterized for CC as a developmental toxicant (USEPA 2024b), higher intake rates need to be applied to protect developmental life stages (MPCA 2017).

There were some data quality issues with the PFOA data, due to contamination of the blank, in a subset of the data, which resulted in elevated reporting limits for PFOA in that subset of data. These samples had reporting limits up to nearly 3 ng/g, which is two orders of magnitude higher than the lowest reporting limit for PFOA data (0.044 ng/g). Having elevated reporting limits increases the likelihood of false negatives - determining that a chemical is not present, when it is actually present. Evaluating the PFOA dataset, most fish samples that had reportable concentrations fell between 0.05 and 0.5 ng/g (only three reported values exceeded these concentrations). When the reporting limit is orders of magnitude higher than the likely concentrations of the compound, it is harder to assert that those samples did not contain PFOA. This leaves some uncertainty in the data for PFOA because there are about 20% of the samples that have reporting limits greater than 1 ng/g (which is about 22 times higher than the lowest reporting limit). Those samples likely have a mix of data that would and would not be reportable data, if the typical, lower reporting limits were used. This was demonstrated in the subset of samples that were analyzed by both 3M's Global EHS lab and SGS AXYS Analytical Services, Ltd. (AXYS). For the fish tissue samples that were used for SSC calculation, AXYS had lower detection limits than the 3M lab, and thus detected PFOA in 35% of the subset that they analyzed, while 3M only detected PFOA in 25% of the same samples (3M 2025).

As mentioned previously, there was also a data reporting error that was discovered that impacted several data points. A subset of the data was submitted to MPCA incorrectly, resulting in those data being reported as "detected" data, when they were actually below the reporting limits. The subset of erroneous data was corrected, and these values became data characterized as being below the reporting limit. The data containing elevated reporting limits due to blank contamination (and mostly non-reportable data) was 80% trophic level 4 fish. Because of this, the percentage of trophic level 4 fish that had reportable concentrations of PFOA decreased considerably (to 8% detected) when the reporting error was fixed. Given the fact that likely some of those fish actually do have reportable levels of PFOA, but were impacted by the elevated detection limits, the trophic level 4 fish samples likely have a higher percentage of detected concentrations, if the blank contamination issue had been resolved and samples re-run, with a lower reporting limit. The trophic level 3 fish had a greater percentage detected (35%), for a combined detection percentage of 24% (for both trophic levels). While MPCA would typically want to base the BAFs on greater detection frequency, using the available data, with its known uncertainties (that would likely increase detections if the data issues were resolved) will ensure protection of fish consumers, since the data show that PFOA does show up in fish tissue and can contribute to an individual's exposure to PFOA.

Table 5-2: PFOA Exposure parameters

Exposure parameter	Rate or value	Basis
IWR	0.0013 L/kg-d	The default WQS incidental water intake rate is applied. The rate is based on children ages one through eight.
FCR	0.00094 kg/kg-d	The most stringent RfD is based on developmental impacts affecting prenatal to neonatal health endpoints (USEPA 2024b). Because of this, the use of the interim FCR_{WCBA} for this subpopulation of fish consumers is warranted and is also protective of other Minnesota fish consumers.
BAF_{TL3}	7.5 L/kg	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for trophic level 3. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit (see discussion in Section 3.2, and analyses in Appendix A).
BAF_{TL4}	8.0 L/kg	Paired fish and surface water samples from the Mississippi River Miles 820 to 812 yielded a small dataset to develop BAFs for trophic level4. As discussed above, the uncertainty with the data led MPCA to calculate a BAF with limited data to ensure protection of fish consumers. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
RSC	0.2	For the CC_{FR}, the default RSC is 0.2 because routes of exposure other than recreation and freshwater fish consumption are significant to people's total exposure to PFOA. Aside from other sources, drinking water is a known source, with several drinking water sources in Minnesota having detectable levels of PFOA (USEPA 2024d).
$AF_{lifetime}$	1	The EPA determined that PFOA does not pose additional cancer risk for early life stages. Because it is assumed that there is no additional cancer risk for early life stages, a $AF_{lifetime}$ of one was chosen to represent no additional risk.

5.3 Chronic criteria calculation

Perfluorooctanoic acid is a carcinogen (USEPA 2024b) and so is evaluated using both the noncarcinogenic and linear carcinogenic algorithms for that toxicological profile in Minn. R. 7050.0219, as described earlier. The CC_{FR} values use the RfD and CSF in Table 5-1 paired with the exposure factors in Table 5-2.

Noncarcinogenic CC_{FR} calculation:

$$CC_{FR} = 0.69\, ng/L = \frac{3\ x\ 10^{-8} * 0.2\ * 1x10^{6}\ ng/mg}{\{0.0013\ + 0.00094\ [(0.24 * 7.5) + (0.76 * 8.0)]\}}$$

Linear carcinogenic CC_{FR} calculation:

$$CC_{FR} = 0.039\,ng/L = \frac{CR\ (1x10^{-5})}{29{,}300\ x\ 1} * \frac{1x10^{6}\ \ ng/mg}{\{0.0013\ + 0.00094\,[(0.24 * 7.5) + (0.76 * 8.0)]\}}$$

The linear carcinogen CC_{FR} is more protective than the noncarcinogenic CC_{FR}, therefore, the carcinogenic CC_{FR} is the site-specific fish consumption and recreational exposure criterion.

In addition to a CC_{FR}, a fish-tissue based CC (CC_{FT}) was derived for PFOA due to its bioaccumulation potential. The fish tissue (CC_{FT}) values use the RfD and CSF in Table 5-1 paired with the exposure factors in Table 5-2.

Noncarcinogenic CC_{FT} calculation:

$$CC_{FT} = 6.4\,ng/kg = \frac{3\ x\ 10^{-8} * 0.2 * 1x10^{6}\ ng/mg}{0.00094}$$

Linear carcinogenic CC_{FT} calculation:

$$CC_{FT} = 0.36\,ng/kg = \frac{1x10^{-5}}{29{,}300\ x\ 1} * \frac{1x10^{6}\ ng/mg}{0.00094}$$

The noncarcinogenic CC_{FT} is more protective than the linear carcinogenic CC_{FT}, therefore, the carcinogenic CC_{FT} is the site-specific fish consumption and recreational exposure criterion. Calculations were rounded to two significant figures.

Table 5-3: Derived site-specific water quality criteria for PFOA for the protection of Class 2B surface water uses in Mississippi River Miles 820 to 812

PFAS (CAS No. see Table 2-1)	**Site-specific water quality criteria: Chronic Criteria (CC)**		**Health Risk Index Endpoints (Additive Risk)**
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90th percentile of 5 fish minimum per water body)	
PFOA	0.039 ng/L (Cancer)	0.00036 ng/g (Cancer)	Developmental, Thyroid (E), Cancer (MDH 2024b)

Definitions of CC:

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

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

6. SSC: Perfluorohexane sulfonic acid (PFHxS)

Perfluorohexane sulfonic acid is a six-carbon chemical with a sulfonate functional group. Perfluorohexane sulfonic acid is characterized as a long-chain PFSA, with similar properties to PFOS. Perfluorohexane sulfonic acid has a long half-life and transgenerational transfer, so even short periods of exposure can lead to significant increases in chronic duration body burdens (MDH 2020a).

6.1 Toxicological values and health risk index endpoints

The MPCA used the current 2023 EPA RfD value for PFHxS in calculating the SSC (USEPA 2023a) (Table 6-1). The 2023 EPA RfD is a draft value, but it is the most recent evaluation of the data that was available, and was conducted using EPA methodology. The external peer review of the draft document was generally supportive of EPA's methodology (ERG 2024). More recent evaluations of PFAS toxicity data have tended to result in lower toxicity values. So, to best ensure protection of human health, the most recent evaluation of the PFHxS toxicological information was used.

Table 6-1: PFHxS Toxicity values and health endpoints

PFAS	RfD	Health Risk Index Endpoints	Reference
PFHxS	4×10^{-10} mg/kg-d	Liver System, Thyroid (E)	USEPA 2023a, MDH 2023b

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 mixture analyses is further described in Section 10.2.

6.2 Exposure factors

Exposure factors are based on the algorithms in Minn. R. 7050.0219. Perfluorohexane sulfonic acid is characterized for CC as a developmental toxicant based on short-term effects to the thyroid including effects on offspring during gestational studies and developmental immune responses (USEPA 2023a). Perfluorohexane sulfonic acid has a very long half-life in humans, so exposure at birth is influenced by the lifetime exposure of the mother. Higher intake rates need to be applied to protect developmental life stages when exposure to a toxic pollutant is greater on a per body weight basis (MPCA 2017).

Table 6-2: PFHxS Exposure parameters

Exposure parameter	Rate or value	Basis
IWR	0.0013 L/kg-d	The default WQS incidental water intake rate is applied. The rate is based on children ages one through eight.
FCR	0.00094 kg/kg-d	The toxicological profile of PFHxS demonstrated evidence of developmental impacts, including effects to thyroid in offspring after gestational exposure. Because of this, the use of the interim FCR_{WCBA} for this subpopulation of fish consumers is warranted and is also protective of other Minnesota fish consumers.
BAF_{TL3}	12.4 L/kg	Paired fish and water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
BAF_{TL4}	7.1 L/kg	Paired fish and water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
RSC	0.2	For the CC_{FR}, the default RSC is 0.2 because routes of exposure other than recreation and freshwater fish consumption are significant to people's total exposure to PFHxS. Aside from other potential sources, drinking water is a known source, with several drinking water sources in Minnesota having detectable levels of PFHxS (USEPA 2024d).

6.3 Chronic criteria calculation

The EPA has concluded that there is inadequate information to assess carcinogenic potential for PFHxS (USEPA 2023a). For development of these site-specific criteria, it is considered a noncarcinogen, and is evaluated using the noncarcinogenic algorithms for that toxicological profile in Minn. R. 7050.0219, as described earlier. The CC_{FR} uses the RfD (Table 6-1) paired with the exposure factors in Table 6-2.

$$CC_{FR} = 0.0087\, ng/L = \frac{4\, x\, 10^{-10} * 0.2 * 1x10^{6}\, ng/mg}{\{0.0013 + 0.00094\, [(0.24 * 12.4) + (0.76 * 7.1)]\}}$$

In addition to a CC_{FR}, a fish-tissue based CC (CC_{FT}) was derived for PFHxS due to its bioaccumulation potential. The fish tissue (CC_{FT}) values use the RfD and CSF in Table 6-1 paired with the exposure factors in Table 6-2.

Noncarcinogenic CC_{FT} calculation:

$$CC_{FT} = 0.085\, ng/kg = \frac{4\, x\, 10^{-10} * 0.2 * 1x10^{6}\, ng/mg}{0.00094}$$

Table 6-3: Derived site-specific water quality criteria for PFHxS for the protection of Class 2B surface water uses in Mississippi River Miles 820 to 812

PFAS (CAS No. see Table 2-1)	Site-specific water quality criteria: Chronic Criteria (CC)		Health Risk Index Endpoints (Additive Risk)
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90th percentile of 5 fish minimum per water body)	
PFHxS	0.0087 ng/L	0.000085 ng/g	Liver System, Thyroid (E) (MDH 2023b)

Definitions of CC:

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

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

7. SSC: Perfluorohexanoic acid (PFHxA)

Perfluorohexanoic acid is a six-carbon chemical with a carboxylate (oxygen) functional group. Perfluorohexanoic acid has characteristics similar to PFBA and is described as a short-chain PFAS. Perfluorohexanoic acid has shorter half-lives in people and laboratory animals than PFOA (MDH 2021).

7.1 Toxicological values and health risk index endpoints

The MPCA used the current 2023 EPA RfD values for PFHxA in calculating the SSC (USEPA 2023b) (Table 7-1).

Table 7-1: PFHxA Toxicity values and health endpoints

PFAS	RfD	Health Risk Index Endpoints	Reference
PFHxA	5×10^{-4} mg/kg-d	Developmental, Thyroid (E)	USEPA 2023b, MDH 2023c

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)

7.2 Exposure factors

Exposure factors are based on the algorithms in Minn. R. 7050.0219. Because PFHxA is characterized for CC as a developmental toxicant (USEPA 2023b), higher intake rates need to be applied to protect developmental life stages (MPCA 2017).

Table 7-2: PFHxA Exposure parameters

Exposure parameter	Rate or value	Basis
IWR	0.0013 L/kg-d	The default WQS incidental water intake rate is applied. The rate is based on children ages one through eight.
FCR	0.00094 kg/kg-d	The most stringent RfD is based on developmental impacts affecting prenatal to neonatal health endpoints (USEPA 2024a). Because of this, the use of the interim FCR_{WCBA} for this subpopulation of fish consumers is warranted and is also protective of other Minnesota fish consumers.
BAF_{TL3}	Not calculable	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 did not yield sufficient data to develop BAFs for either trophic level. There were very few detections of PFHxA in trophic level 3 fish – only six of 80 fish had detected levels of PFHxA.
BAF_{TL4}	Not calculable	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 did not yield sufficient data to develop BAFs for either trophic level. There were very few detections of PFHxA in trophic level 4 fish – only two of 60 fish had detected levels of PFHxA.
RSC	0.2	For the CC_{FR}, the default RSC is 0.2 because routes of exposure other than recreation and freshwater fish consumption are significant to people's total exposure to PFHxA. Aside from other potential sources, drinking water is a known source, with drinking water sources in Minnesota having detectable levels of PFHxA (USEPA 2023b).

7.3 Chronic criteria calculation

A data reporting error was discovered that impacted several data points for some of the PFAS compounds. A subset of the data was submitted to MPCA incorrectly, resulting them in being reported as "detected" data, when they were actually below the reporting limits. The subset of erroneous data was corrected, and the data were reanalyzed. Some PFAS were more affected by this data error, with PFHxA having a large portion of data being misrepresented as detectable data. Because of this data correction, the number of reportable data was minimal, leaving few datapoints to use to calculate BAFs for PFHxA. Of the 140 fish analyzed, only eight fish had reportable levels of PFHxA (6% of fish had reportable levels of PFHxA). With the limited data available, BAFs were not calculated, which resulted in the inability to calculate a SSC. Therefore, no SSC for PFHxA is available for this site.

The water-based criteria are calculated to prevent concentrations of the contaminant accumulating to levels in fish that would cause impacts to human health, when those fish are consumed. Because it is rarely detected in fish, and at low levels, the more likely route of exposure would be through water consumption. However, this reach of the Mississippi River is not designated as a drinking water source, so a drinking water exposure criterion cannot be calculated. PFHxA was detected in 100% of water samples, but only 6% of fish tissue samples. The highest detection in water was 42 ng/L in the main channel in the site characterization study (Weston 2023), which is well below the estimated SSC that was previously calculated (11,000 ng/L) to protect human health from fish tissue consumption. Current water concentrations should not cause accumulation of PFHxA into fish at levels that would impact human health, based on current toxicological knowledge.

Table 7-3: Derived site-specific water quality criteria for PFHxA for the protection of Class 2B surface water uses in Mississippi River Miles 820 to 812

PFAS (CAS No. see Table 2-1)	**Site-specific water quality criteria: Chronic Criteria (CC)**		**Health Risk Index Endpoints (Additive Risk)**
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90th percentile of 5 fish minimum per water body)	
PFHxA	Not calculable	Not applicable	Developmental, Thyroid (E) (MDH 2023c)

Definitions of CC:

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)

8. SSC: Perfluorobutane sulfonic acid (PFBS)

Pefluorobutane sulfonic acid is characterized as a four-carbon chain PFAS or short-chain perfluorosulfonic acid (PFSA) based on its carbon number and sulfonate (sulfur and oxygen) functional group. Perfluorooctane sulfonic acid is also a PFSA but has different characteristics than PFBS mainly due to its longer carbon chain and more hydrophobic properties. Pefluorobutane sulfonic acid has shorter half-lives in people and laboratory animals than PFOS (MDH 2023a).

8.1 Toxicological values and health risk index endpoints

The MPCA used the current 2024 EPA RfD values for PFBS in calculating the SSC (USEPA 2021, 2024c) (Table 8-1).

Table 8-1: PFBS Toxicity values and health endpoints

PFAS	**RfD**	**Health Risk Index Endpoints**	**Reference**
PFBS	3×10^{-4} mg/kg-d	Thyroid (E)	USEPA 2021, USEPA 2024c, MDH 2023a

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 mixture analyses is further described in Section 10.2.

8.2 Exposure factors

Exposure factors are based on the algorithms in Minn. R. 7050.0219. Because the EPA determined that evidence supports PFBS as a developmental toxicant (USEPA 2021), higher intake rates need to be applied to protect developmental life stages (MPCA 2017).

Table 8-2: PFBS Exposure parameters

Exposure parameter	Rate or value	Basis
IWR	0.0013 L/kg-d	The default WQS incidental water intake rate is applied. The rate is based on children ages one through eight.
FCR	0.00094 kg/kg-d	The toxicological profile of PFBS demonstrated evidence of developmental impacts, including effects to thyroid function. Because of this, the use of the interim FCR_{WCBA} for this subpopulation of fish consumers is warranted and is also protective of other Minnesota fish consumers.
BAF_{TL3}	12.3 L/kg	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
BAF_{TL4}	6.8 L/kg	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
RSC	0.2	For the CC_{FR}, the default RSC is 0.2 because routes of exposure other than recreation and freshwater fish consumption are significant to people's total exposure to PFBS. Aside from other potential sources, drinking water is a known source, with several drinking water sources in Minnesota having detectable levels of PFBS (MDH 2022b).

8.2 Chronic criteria calculation

The EPA has concluded that there is inadequate information to assess carcinogenic potential for PFBS (USEPA 2022). For development of these site-specific criteria, it is considered a noncarcinogen, and is evaluated using the noncarcinogenic algorithms for that toxicological profile in Minn. R. 7050.0219, as described earlier. The CC_{FR} uses the RfD (Table 8-1) paired with the exposure factors in Table 8-2.

$$CC_{FR} = 6{,}717\, ng/L = \frac{3x10^{-4} * 0.2 * 1x10^{6}\, ng/mg}{\{0.0013 + 0.00094\, [(0.24 * 12.3) + (0.76 * 6.8)]\}}$$

Calculations were rounded to two significant figures for setting the CC_{FR}.

Table 8-3: Derived site-specific water quality criteria for PFBS for the protection of Class 2B surface water uses in Mississippi River Miles 820 to 812

PFAS (CAS No. see Table 2-1)	Site-specific water quality criteria: Chronic Criteria (CC)		Health Risk Index Endpoints (Additive Risk)
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90th percentile of 5 fish minimum per water body)	
PFBS	6,700 ng/L	Not applicable	Thyroid (endocrine) (MDH 2023a)

Definitions of CC:

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)

9. SSC: Perfluorobutanoic acid (PFBA)

Similar to PFBS, PFBA is also a four-carbon or short-chain PFAS with a carboxylate (oxygen) functional group (ITRC 2020c). This category of PFAS, perfluoroalkyl carboxylates or carboxylic acids (PFCA) also includes PFOA. Perfluorobutanoic acid has shorter half-lives in people and laboratory animals than PFOA (MDH 2018).

9.1 Toxicological values and health risk index endpoints

The MPCA used the current 2022 EPA RfD values for PFBA in calculating the SSC (USEPA 2022) (Table 9-1).

Table 9-1: PFBS Toxicity values and health endpoints

PFAS	RfD	Health Risk Index Endpoints	Reference
PFBA	1×10^{-3} mg/kg-d	Liver System, Thyroid (E)	USEPA 2022, MDH 2018

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 mixture analyses is further described in Section 10.2.

9.2 Exposure factors

Exposure factors are based on the algorithms in Minn. R. 7050.0219. Because PFBA is characterized for CC as a developmental toxicant (USEPA 2022), higher intake rates need to be applied to protect developmental life stages (MPCA 2017).

Table 9-2: PFBA Exposure parameters

Exposure parameter	Rate or value	Basis
IWR	0.0013 L/kg-d	The default WQS incidental water intake rate is applied. The rate is based on children ages one through eight.
FCR	0.00094 kg/kg-d	The subchronic RfD is based on developmental impacts affecting prenatal to neonatal health endpoints (USEPA 2022). Because of this, the use of the interim FCR_{WCBA} for this subpopulation of fish consumers is warranted and is also protective of other Minnesota fish consumers.
BAF_{TL3}	2.3 L/kg	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
BAF_{TL4}	2.5 L/kg	Paired fish and surface water samples from the Mississippi River, Miles 820 to 812 yielded sufficient data to develop BAFs for two trophic levels. Non-detect values in fish tissue and surface water samples were substituted using ½ of the detection limit. (see discussion in Section 3.2, and analyses in Appendix A).
RSC	0.2	For the CC_{FR}, the default RSC is 0.2 because routes of exposure other than recreation and freshwater fish consumption are significant to people's total exposure to PFBA. Aside from other potential sources, drinking water is a known source, with several drinking water sources in Minnesota having detectable levels of PFBA (MDH 2022a).

9.3 Chronic criteria calculation

The EPA has concluded that there is inadequate information to assess carcinogenic potential for PFBA (USEPA 2022). For development of these site-specific criteria, it is considered a noncarcinogen, and is evaluated using the noncarcinogenic algorithms for that toxicological profile in Minn. R. 7050.0219, as described earlier. The CC_{FR} uses the RfD (Table 9-1) paired with the exposure factors in Table 9-2.

$$CC_{FR} \; = 55{,}480\, ng/L = \frac{1\;x\;10^{-3}\; *0.2\; * 1x10^{6}\; ng/mg}{\{0.0013\; + 0.00094\;[(0.24*2.3)+(0.76*2.5)]\}}$$

Calculations were rounded to two significant figures for setting the CC_{FR}.

Table 9-3: Derived site-specific water quality criteria for PFBA for the protection of Class 2B surface water uses in Mississippi River Miles 820 to 812

PFAS (CAS No. see Table 2-1)	Site-specific water quality criteria: Chronic Criteria (CC)		Health Risk Index Endpoints (Additive Risk)
	Class 2B – fish consumption and recreational exposure (CC_{FR}) (30-day average)	**Class 2 fish-tissue** (CC_{FT}) (90^{th} percentile of 5 fish minimum per water body)	
PFBA	55,000 ng/L	Not applicable	Liver System, Thyroid (E) (MDH 2018)

Definitions of CC:

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)

10. Risk characterization

10.1 Application

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

- CC_{FT}: compare to PFAS concentrations in fish-tissue to evaluate potential risks in those water bodies for which this site-specific CC was derived.
- CC_{FR}: compare to PFAS concentrations in Class 2B surface waters to evaluate potential risks in those water bodies for which this site-specific CC was derived.

A sufficient number of samples should be used when comparing water and fish monitoring data to the CC. The CC_{FR} is applied as a 30-day average concentration that should not be exceeded more than once in a water body in a three-year window. The CC_{FT} requires at least five fish of the same species or a lesser number of fish from at least three species from a water body. The CC_{FT} is compared to the 90^{th} percentile PFAS concentration in fillets by species. These details are found in the assessment methods in the most recent MPCA *Guidance for Assessing the Quality of Minnesota Surface Waters for Determination of Impairment: 305(b) and 303(d) Impaired Waters List* (MPCA 2024a).

In addition, not all PFAS can be evaluated at this time due to analytical method limitations or lack of available toxicological values. The methods to protect human health do incorporate additive risk from mixtures of two or more toxic pollutants in fish or surface water samples. Additive risks for noncancer effects are based on toxic pollutants that have numeric WQS or SSC and the same Health Risk Index Endpoints (Section 10.2, MPCA 2017).

10.2 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. 7D). Additive risks are evaluated for both noncancer and cancer effects. The PFAS CC presented in this document are derived based on noncancer effects (except for PFOA). Perfluorobutanoic acid, PFBS, and PFHxS all impact the thyroid health endpoint. Perfluorohexanoic acid, PFOS, and PFOA all impact the developmental health endpoint.

Perfluorooctane sulfonic acid and PFOA both impact the immune health endpoint. Perfluorobutanoic acid, PFHxS, PFOA, and PFOS all impact the liver health endpoint.

To evaluate additive risks from noncancer effects, hazard quotients are calculated by dividing a water 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 health risk index. If the health risk 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. Concentrations above 1 would exceed the SSC 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:

$C_1 \ldots C_n$ is the concentration in water (as a 30-day average) for the first through the n^{th} noncancer pollutant with the same health risk index endpoints. These health endpoints for PFAS are found in Table 1-1.

$CC_1 \ldots CC_n$ is the fish consumption and recreation chronic criteria for the first to the n^{th} noncancer pollutant.

Perfluorooctane sulfonic acid, PFOA, and PFHxS share health risk index endpoints with the remaining two PFAS. But, including PFOS, PFOA and PFHxS in the health risk index presents challenges, due to the low concentrations of the CC for these chemicals. Reporting limits do not allow for quantification of PFOS, PFOA and PFHxS down to the levels where toxic effects may be seen (the CC), so including them in the equations is problematic. The equation requires the determination of the concentration of each chemical in a surface water sample. If concentrations are below the level of quantification, the hazard quotients of the three chemicals cannot be calculated to be included in the additivity equation.

If either PFOS, PFOA or PFHxS were measured at quantifiable levels, the CC would be exceeded, because the CC are below the limits of quantification. The resulting health risk index would automatically exceed a value of 1, due to the exceedance of the CC. The concentrations of the remaining chemicals in the mixture would not matter, because the exceedance of the CC results in an exceedance of the health risk index value of 1. Any restrictions on the effluent discharge would then be related to the PFAS that caused the exceedance (PFOS, PFOA or PFHxS in that case), because that chemical alone caused the exceedance of the health risk index. Perfluorooctane sulfonic acid, PFOA and PFHxS will be restricted down to the reporting limit, so exceedances of the permitted limits would already have occurred from that chemical being above the reporting limit.

Additivity and health risk index calculation can be considered for PFBA and PFBS, which have CC above their respective detection limits and share the thyroid health endpoint. The equation to apply the health risk index to these PFAS is:

$$\frac{C_{PFBA}}{55{,}000\ ng/L} + \frac{C_{PFBS}}{6{,}700\ ng/L} \leq 1$$

10.3 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 2017). Specific demographics of the women that participated were kept confidential, except for the age of the participants which ranged from 16 to 50 years. The survey results indicated that 73% of the women consumed freshwater-caught fish. By contrast, most statewide surveys of Minnesota estimate consumption for WCBA at around 40%. More research and outreach is needed to finalize a FCR for WCBA, therefore the rate being used for SSC is considered "interim" and applicable to current site conditions, as described previously.

Tribal nations have reserved fishing rights in many water bodies across the state, and members of Tribal nations are important fish consumers. They are likely to consume fish at higher rates than most non-tribal Minnesotans. 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 PFAS 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 2019). The map also includes Tribal areas. The location of this SSC does not contain identified areas of potential environmental justice concerns, but it is upstream of a tribal community. The interim FCR used for this SSC, as described above, considered the context of increased tribal consumption.

Environmental Justice also considers populations that may be more susceptible to adverse effects from environmental pollutants or may be more highly exposed. For PFOS, PFHxS, and PFOA the combination of bioaccumulation, developmental toxicity, cancer risk, and high exposure during infancy means protecting these early-life stages is dependent on a mother's lifetime body burden.

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Appendix A – Summary of PFAS data and non-detection analysis

In order to determine PFAS site-specific criteria for the Mississippi River, Miles 820 to 812, the Minnesota Pollution Control Agency (MPCA) calculated bioaccumulation factors (BAFs) with PFAS surface water and fish measurements from the Mississippi River near Cottage Grove, MN. Bioaccumulation factor calculation requires geometric means per PFAS for surface water and fish. Since some measurements are less than the reported quantification limit of the analytical method, the MPCA applied non-detection analyses to the data.

The 3M Instream PFAS Characterization Study Final Report, (Weston Solutions 2023) did not provide method detection limits (MDL) for the study, but included lower limits of quantitation (LLOQ), which 3M's Global EHS Laboratory calculates using the lowest calibration standard producing a signal-to-noise ratio of at least 2 times the peak area of a blank sample (3M 2025)[7]. There are multiple ways to typically calculate a MDL, but one way is to use a signal-to-noise ratio of 3 to 5 (40 CFR Part 136, Appendix B). Because 3M's LLOQs are calculated more stringently than some MDLs, the LLOQs are low enough to be an estimation of a MDL, and thus were used when data were reported as "non-detect" in the characterization study. The following discussion describes the non-detection analysis conducted on the fish and surface water data. Where "non-detect" or "detection limit" are referenced, it means the data are lower than the LLOQs reported by 3M, or refers to the LLOQ as being the detection limit.

The data were processed prior to calculating PFAS surface water and fish means and BAFs. Data were converted to be in a consistent unit (ng/L and ng/g), measurements from quality control samples were removed, data resulting from a single analytical method (method 537.1 and ETS-8-045 for surface water and fish samples, respectively) were retained, and duplicate data were addressed.

Geometric means for PFAS were calculated with five different non-detection methods. The methods are described in Table A-1. Means were not calculated via the Kaplan-Meier and Regression on Order Statistics (ROS) for PFAS when certain criteria were not met: (1) two or fewer values in the given dataset were detected or (2) two or fewer values in the given dataset were not detected. Application of the Kaplan-Meier or ROS methods is not appropriate when datasets are composed of nearly all detected or non-detected measurements. Geometric means were not determined via the Kaplan-Meier technique since it is not possible with negative values, which results when using log-transformed data in geometric mean calculations. All data processing and statistical calculations were performed in R statistical software (2024).[8] R scripts and raw data used for this analysis are available upon request.

[7] 3M (2025). Estimation of Analytical Method Detection Limit (MDL) for ETS-8-045 Based on Evaluation of Laboratory Control Spike (LCS) Data from the 2021 IPCS Fish Analytical Results.

[8] R Core Team (2024). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Table A-1: Non-detection analyses.

Method	Description
Raw	Geometric mean of raw data with non-detection values excluded
Detection limit	Geometric mean of data with non-detection values replaced with the reported detection limit
Half detection limit	Geometric mean of data with non-detection values replaced with half of the reported detection limit
ROS	Semi-parametric method for calculating a probability distribution and estimating statistics, including means; utilizes the detection limit dataset
Kaplan-Meier	Nonparametric method for calculating a probability distribution and estimating statistics, including means; utilizes the detection limit dataset

Surface water PFAS data

For surface water data, calculated geometric means are comparable between all non-detection methods (Table A-2 and Figure A-1). For PFOS and PFHxA, means for raw, detection limit, and half detection limit methods are equivalent since the dataset for the given PFAS contains only detected values (Tables A-2 and A-3). For most PFAS in surface water, means have not been calculated with the Kaplan-Meier or ROS methods since the datasets contained too few non-detection values (Table A-3).

Table A-2. Surface water geometric means (ng/L) per PFAS.

Method	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
Raw	91.0	10.7	11.2	5.00	26.6	16.1
Detection limit	89.4	9.23	11.2	4.86	25.5	16.1
Half detection limit	87.7	8.70	11.2	4.77	23.1	16.1
ROS	NA	8.79	NA	NA	23.7	NA
Kaplan-Meier	NA	NA	NA	NA	NA	NA

Table A-3. Surface water sample composition. *ND* abbreviates *non-detected*.

	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
Total count	35	35	35	35	35	35
ND count	1	3	0	1	5	0
Percent ND (%)	2.9	8.6	0	2.9	14.3	0

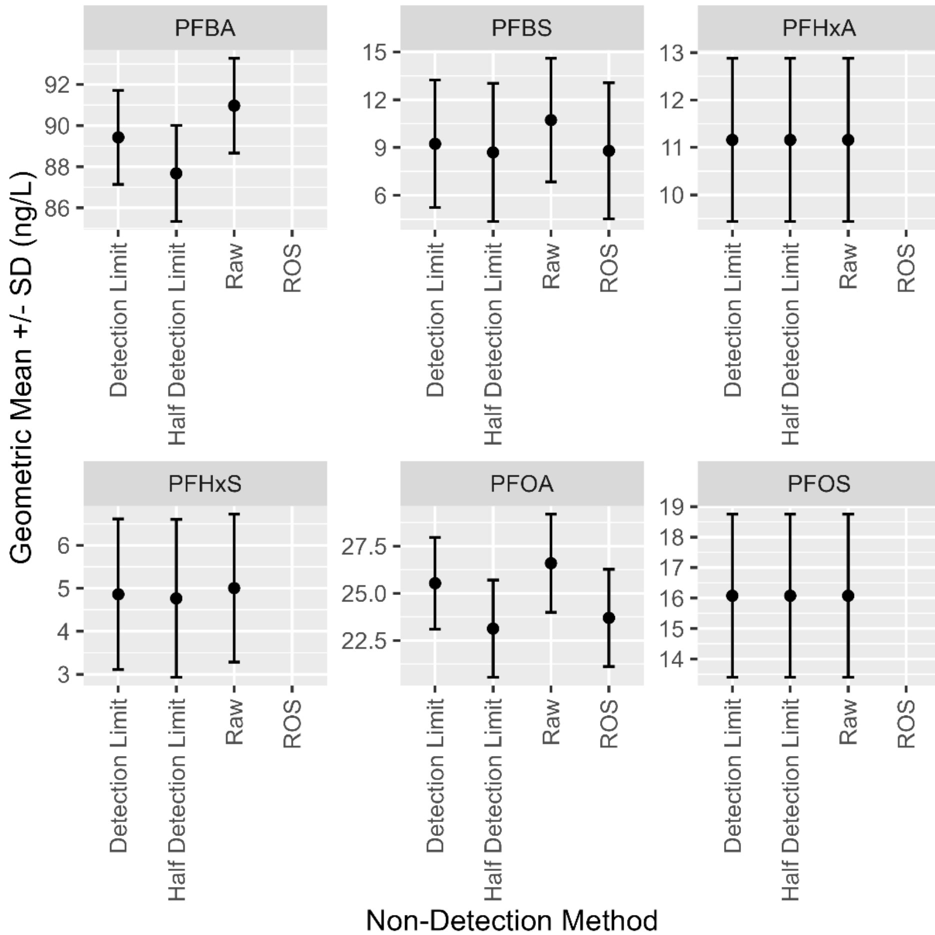

Figure A-1. Surface water geometric means ± standard deviation (SD) for PFAS.

Fish PFAS data

All combined fish data

Per- and polyfluoroalkyl substances geometric means were calculated for all combined fish samples, as well as per trophic level and taxa. For combined fish, calculated means are comparable between all non-detection methods as with surface water results (Table A-4 and Figure A-2). Perfluorooctane sulfonic acid means are equivalent among raw, detection limit, and half detection limit methods since this dataset contains only detected values (Table A-5). Kaplan-Meier and ROS methods were not used for PFOS since the dataset does not contain non-detection values (Table A-5). Additionally, geometric means were not calculated for the Kaplan-Meier non-detection methods for PFAS. Calculation of geometric means is not possible with a dataset that contains zeros. The Kaplan-Meier non-detection method requires positive values and by log-transforming this dataset, as done for geometric mean calculation, negative values are produced.

Table A-4. Fish geometric means (ng/g) per PFAS.

Method	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
Raw	0.513	0.157	0.294	0.119	0.229	11.7
Detection limit	0.328	0.137	0.136	0.071	0.306	11.7
Half detection limit	0.208	0.083	0.071	0.047	0.178	11.7
ROS	0.648	0.397	0.309	0.123	0.562	NA
Kaplan-Meier	NA	NA	NA	NA	NA	NA

Table A-5. Fish sample composition. *ND* abbreviates *non-detected*.

	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
Total count	139	139	140	140	140	140
ND count	91	100	132	84	107	0
Percent ND (%)	65.5	71.9	94.3	60.0	76.4	0

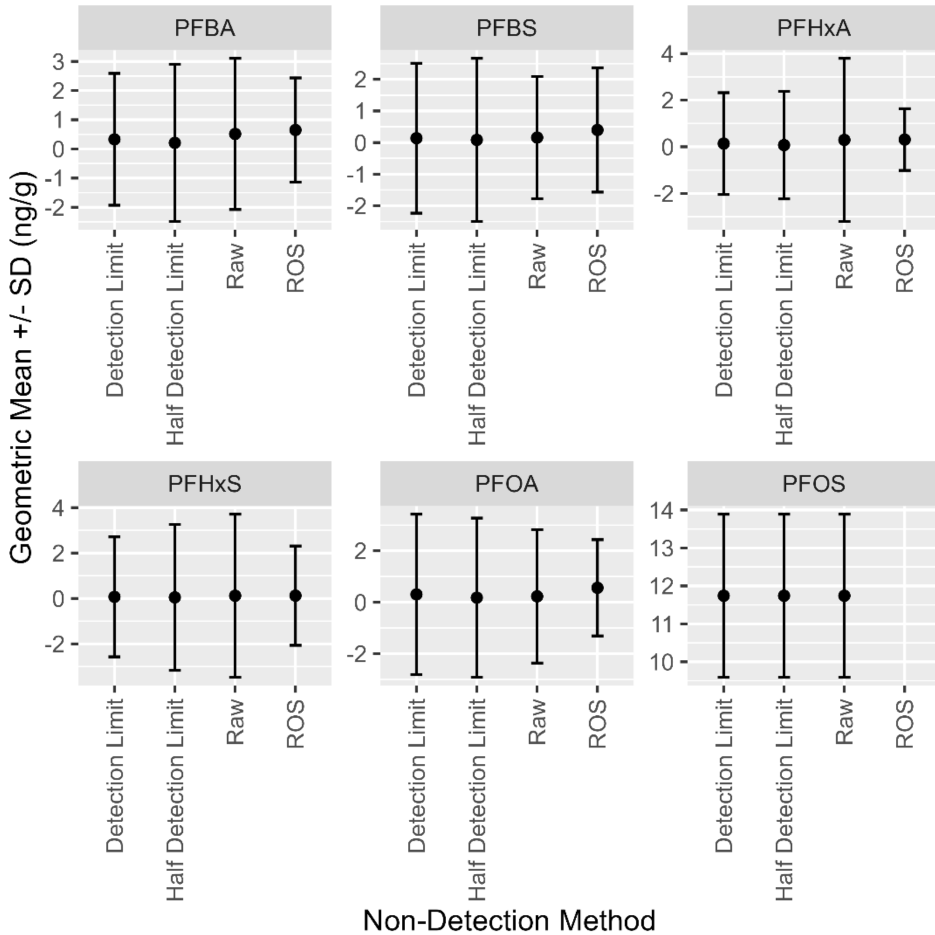

Figure A-2: PFAS means ± standard deviation (SD) for all fish samples with six non-detection methods.

Fish data by trophic level

As with surface water and fish PFAS data, calculated geometric means are comparable among non-detection methods per fish trophic level (Table A-6 and Figure A-3). Perfluorooctane sulfonic acid means are equivalent among raw, detection limit, and half detection limit methods since this dataset contains only detected values (Table A-7). Kaplan-Meier and ROS methods were not used for PFOS since the dataset does not contain non-detection values (Table A-7). Additionally, geometric means for the Kaplan-Meier non-detection methods were not calculated for any PFAS for reasons described above. Calculation of geometric means is not possible with a dataset that contains zeros. Means of PFAS are generally comparable among trophic levels (Figure A-3).

Table A-6: Fish taxa geometric means (ng/g) per PFAS.

Trophic level	Method	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
	Raw	0.483	0.188	0.379	0.179	0.252	10.6
	Detection Limit	0.309	0.185	0.132	0.088	0.274	10.6
	Half Detection Limit	0.197	0.107	0.070	0.059	0.173	10.6
	ROS	0.553	0.457	0.307	0.143	0.495	NA
3	Kaplan-Meier	NA	NA	NA	NA	NA	NA
	Raw	0.559	0.139	0.137	0.064	1.36	13.4
	Detection Limit	0.356	0.090	0.141	0.054	0.355	13.4
	Half Detection Limit	0.222	0.059	0.072	0.034	0.186	13.4
	ROS	0.672	0.328	NA	0.063	0.666	NA
4	Kaplan-Meier	NA	NA	NA	NA	NA	NA

Table A-7: Fish trophic level sample composition. *ND* abbreviates *non-detected*.

Trophic level	Statistic	PFBA	PFBS	PFHxA	PFHxS	PFOA	PFOS
	Total Count	79	80	80	80	80	80
	ND Count	51	64	74	46	52	0
3	Percent ND (%)	64.6	80	92.5	57.5	65.0	0
	Total Count	60	59	60	60	60	60
	ND Count	40	36	58	38	55	0
4	Percent ND (%)	66.7	61.0	96.7	63.3	91.7	0

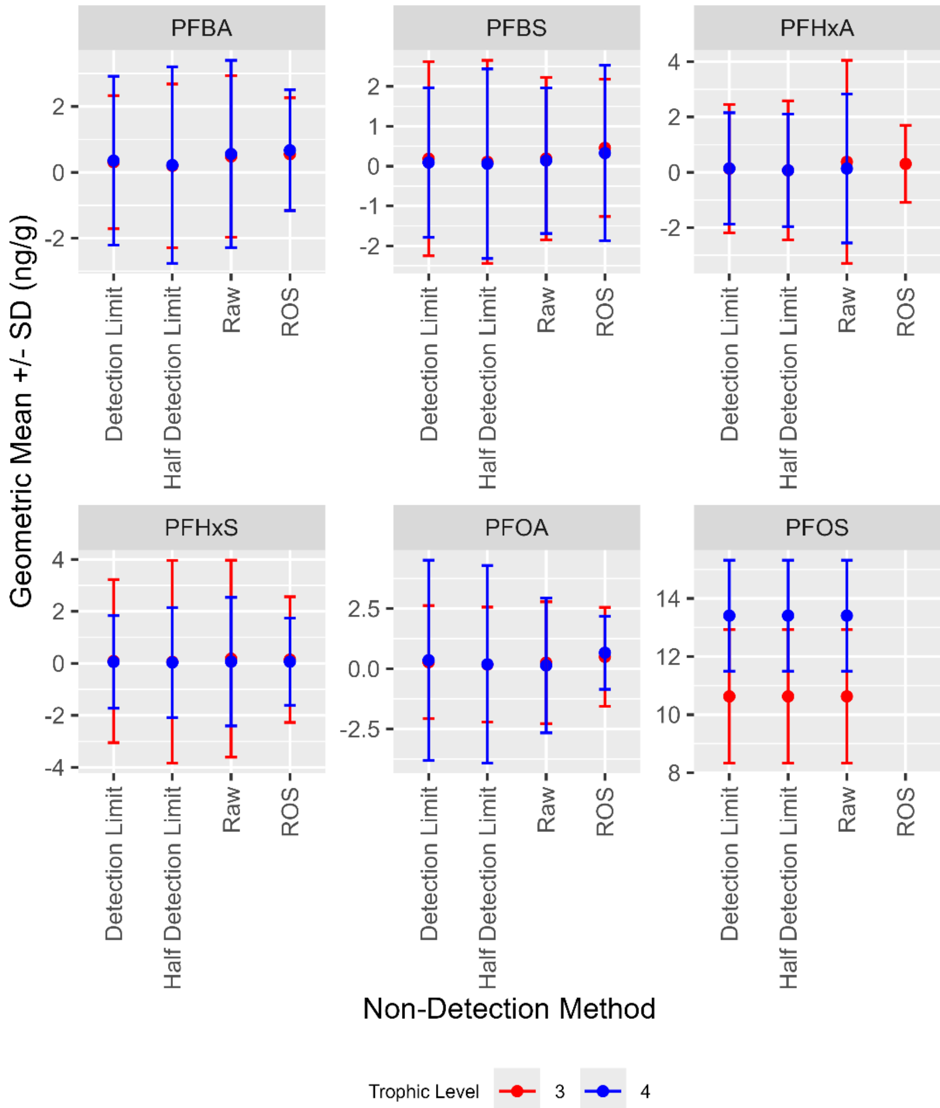

Figure A-3: PFAS geometric means ± SD by fish trophic level for six non-detection methods.

Fish data by taxa

Among the non-detection methods, geometric means per taxa and PFAS are comparable (Figures A-4 – A-7). Calculations for some methods were limited as described above. Figures A-4 –A-7 show box and whisker plots per PFAS among all taxa for raw, detection limit-substituted, and half detection limit substituted data.

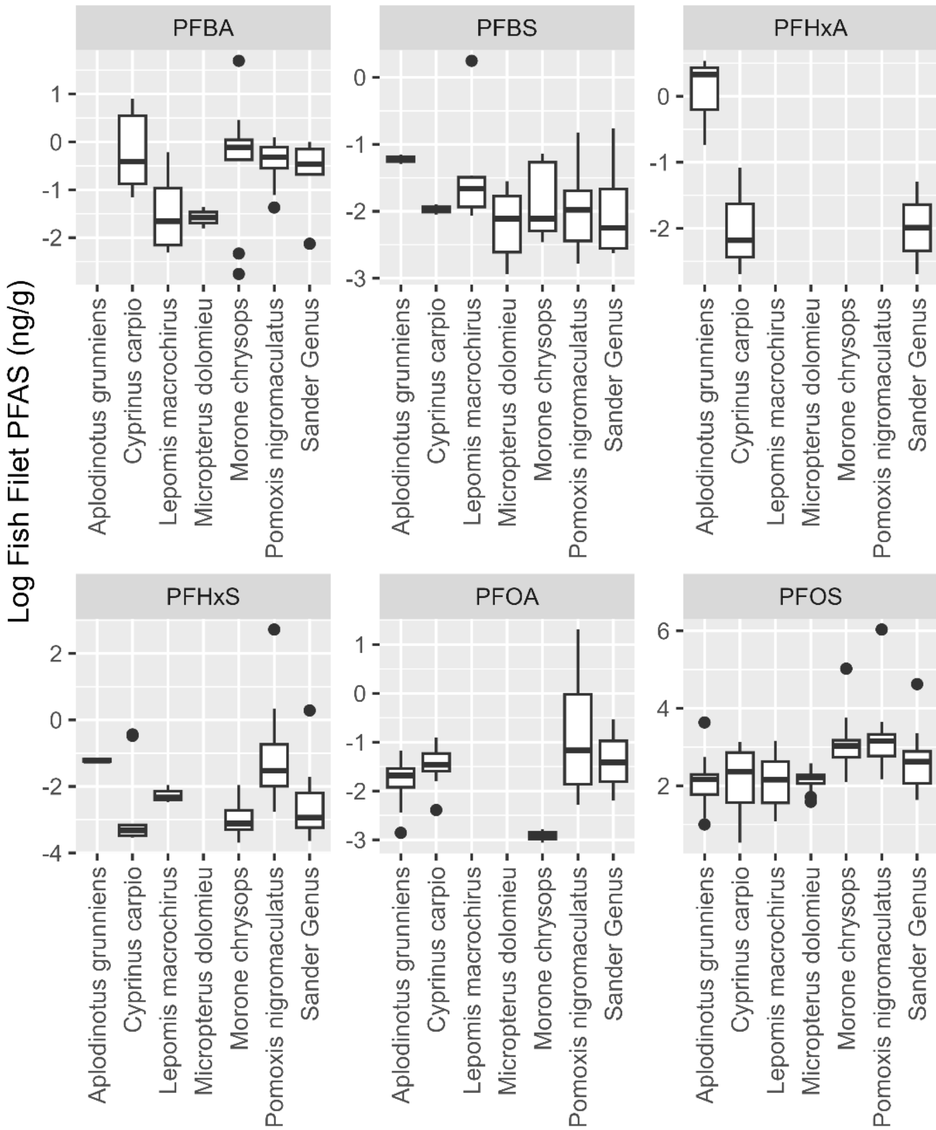

Figure A-4: Box and whisker plots for natural log transformed raw PFAS data (ng/g) by taxa.

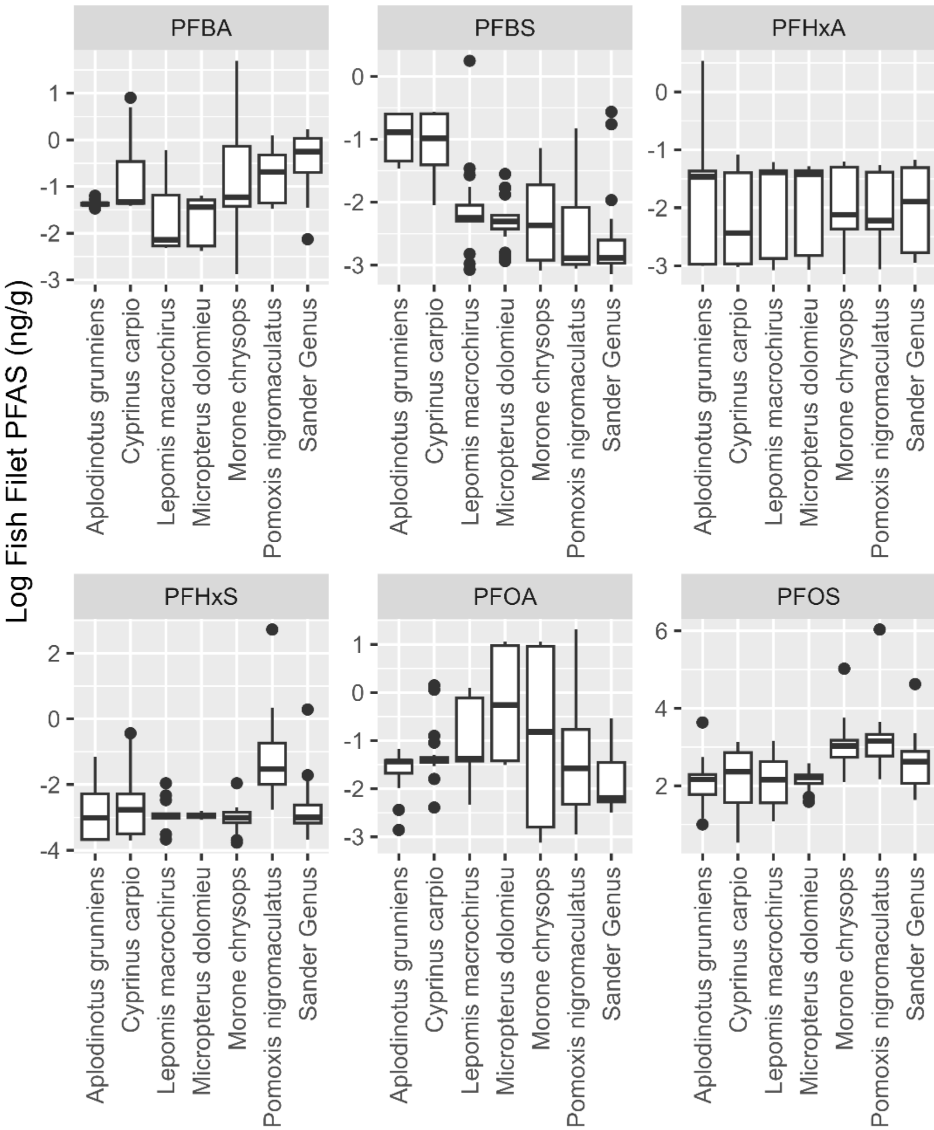

Figure A-5: Box and whisker plots for detection limit substituted PFAS data with natural log transformation (ng/g) by taxa.

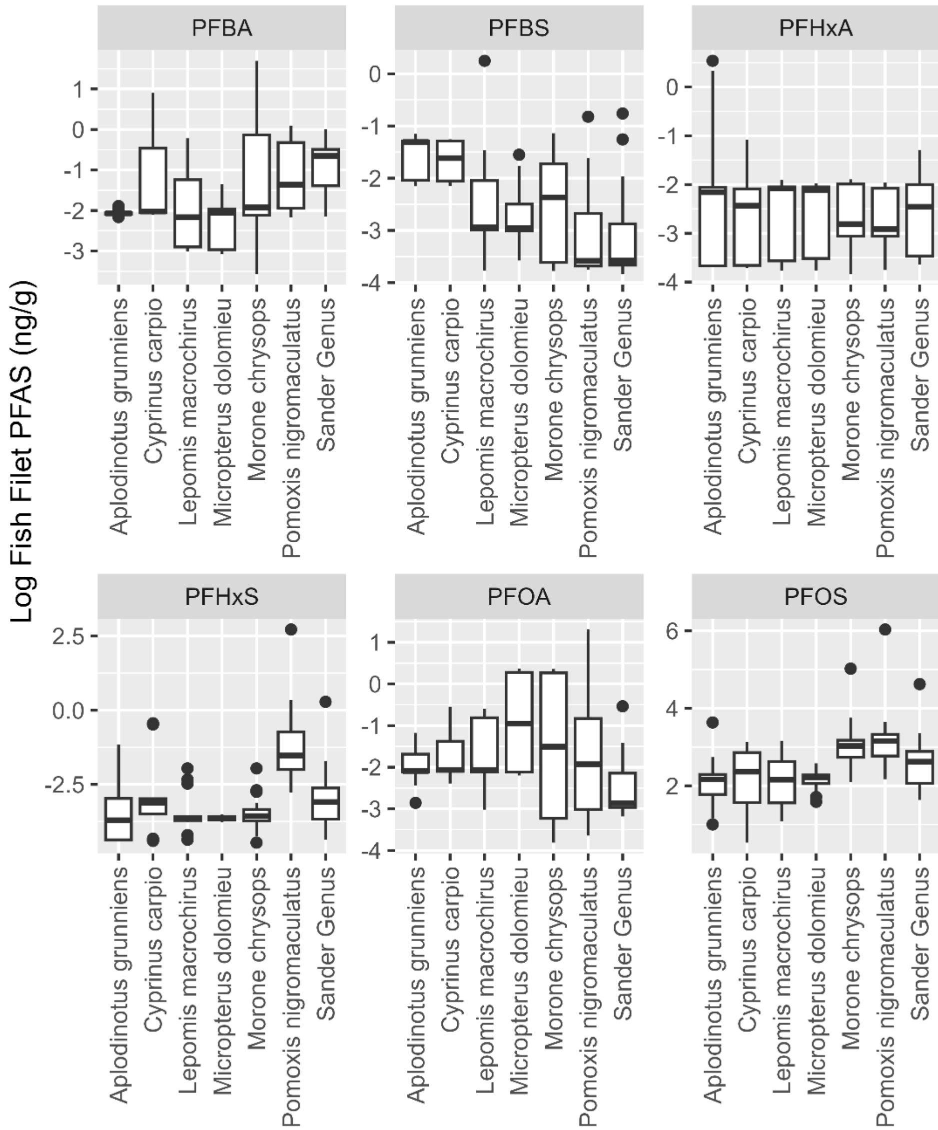

Figure A-6: Box and whisker plots for half detection limit substituted PFAS data with natural log transformation (ng/g) by taxa.