Surface Water Quality Standards for PFOS and PFOA

Rule Package Technical Support Document

Rule package WY-23-19, related to
Chapters NR 102, 105, 106, and 219, Wis. Adm. Code

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Executive Summary

Poly- and perfluoroalkyl substances (PFAS) are synthetic, organic compounds that have been manufactured for use in non-stick coatings, waterproof fabrics, firefighting foams, food packaging, and many other applications since the 1940s. PFAS are highly resistant to degradation and have been detected globally in water, sediment, and wildlife. This global distribution is of concern as PFAS have been demonstrated to have toxic effects on animals and because epidemiological studies have suggested probable links to several human health effects. In Wisconsin, PFAS have been detected in drinking and surface water near sources of industrial use or manufacture and near spill locations. One PFAS compound, perfluorooctane sulfonate (PFOS), has frequently been detected in fish tissue, resulting in the issuance of special fish consumption advisories for some surface waters in the state.

The proposed rules include a water quality standard for two types of PFAS: PFOS and perfluorooctanoic acid (PFOA). Under the Clean Water Act, surface water quality standards can include criteria that are either numeric or narrative. Wisconsin's existing Administrative Codes contain both numeric and narrative criteria for toxic substances:

- Chapter NR 105, Wis. Adm. Code, contains specific numeric criteria for numerous toxic pollutants as well as formulas for calculating numeric criteria for toxics that do not yet have promulgated criteria.
- Section NR 102.04(d) contains Wisconsin's narrative criteria for toxics. This existing rule states that substances in concentrations or combinations which are toxic or harmful to humans *shall not be present in amounts found to be of public health significance* [emphasis added], nor shall substances be present in amounts which are acutely harmful to animal, plant or aquatic life.

The proposed PFOS and PFOA standard interprets Wisconsin's existing narrative criterion with numeric thresholds, created under s. NR 105.04(4m) and s. NR 102.04. As shown above existing rule language specifies that substances shall not be present in amounts found to be of public health significance. The proposed rule defines levels of public health significance for the two types of PFAS based on preventing adverse effects from contact with or ingestion of surface waters of the state, or from ingestion of fish taken from waters of the state.

- For PFOS, the proposed level of public health significance is 8 ng/L for all waters except those that cannot naturally support fish and do not have downstream waters that support fish.
- For PFOA, the proposed level of public health significance is 20 ng/L in waters classified as public water supplies under ch. NR 104, and 95 ng/L for other surface waters.

Related to the proposed PFOS and PFOA standard, the proposed rule package also includes assessment protocols that clarify when a surface water that contains levels of PFOS or PFOA above the public health significance threshold levels in the narrative standard should be listed on the state's impaired waters list.

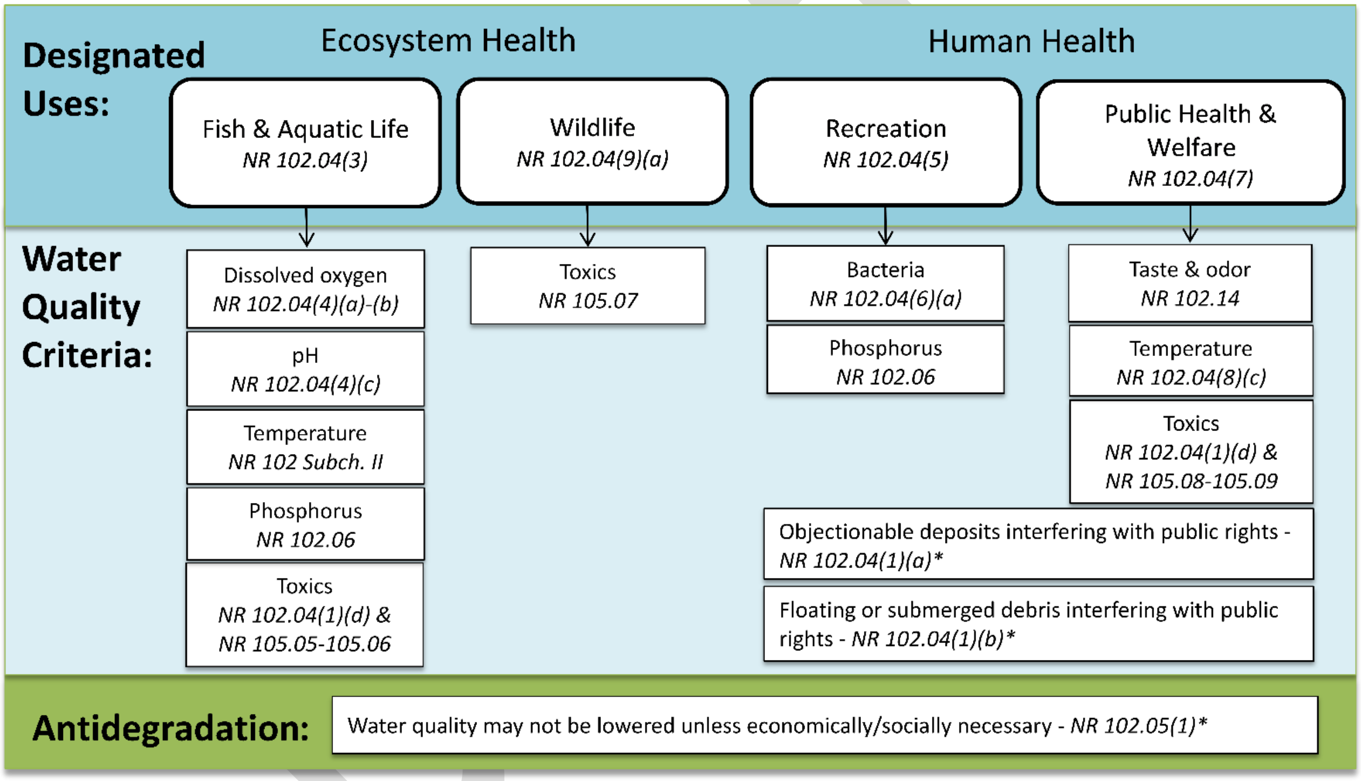
Additionally, the proposed rules establish WPDES permit requirements for wastewater discharges of PFOS and PFOA to surface waters of the state in ch. NR 106 – Subchapter VIII, including: the determination of the need for a PFAS Minimization Plan based on data generation in a reissued permit, a general schedule for PFAS Minimization Plan permit implementation procedures, PFAS Minimization Plan requirements, and determination of need for and calculation procedures for water quality based effluent limits for PFOA and PFOS.

Finally, this rule adds specifications for the preservation and holding times of aqueous, biosolids (sludge), and tissue samples that will be analyzed for PFAS in ch. NR 219.

Introduction

OVERVIEW OF WATER QUALITY STANDARDS

The Clean Water Act (CWA) established the objective of restoring and maintaining the chemical, physical, and biological integrity of the Nation's waters. To meet this objective, the act established a national goal that "water quality shall provide for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water." The CWA requires states to adopt water quality standards to protect these functions. Water quality standards consist of three components: designated uses, water quality criteria, and antidegradation. These three components are described in more detail in Fig. 1 and in the following sections.



** paraphrased; see code to cite actual language*

Figure 1. Components of Wisconsin's Water Quality Standards and relevant code citations.

Designated Uses

Designated uses establish the appropriate water quality goals for a given waterbody. The CWA requires each state/tribe to set designated uses that protect aquatic organisms (e.g., fish, shellfish), wildlife, and recreation and allows states/tribes to consider other uses. Wisconsin has four general designated use categories, which are defined in s. NR 102.04: fish and aquatic life, recreation, public health and welfare, and wildlife (Fig. 1). The public health and welfare use is being addressed in this rule.

Water Quality Criteria

Water quality criteria represent the quality of water that supports a particular use. Water quality criteria can be numeric values or narrative descriptions and are used to derive permit limits, make waterbody assessment decisions, and develop total maximum daily load (TMDL) analyses for impaired waters. As criteria are designed to protect a particular use for a given waterbody, each designated use class has its own set of criteria (Fig. 1). Narrative criteria that describe undesirable amounts of toxic substances in support of the public health and welfare use are being proposed in the rule.

Antidegradation

The antidegradation policy is designed to maintain and protect high quality waters. The policy establishes how proposed new or increased discharges to high quality waters are addressed to ensure that water quality is protected. While the antidegradation policy is a crucial component to water quality standards, it is not applicable to this rule package.

Water Quality Criteria for Human Health Protection

The CWA was adopted in 1972 and states as one of its goals that “it is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited”[1]. In order to accomplish this goal, the CWA requires states to adopt water quality standards to protect public health and welfare. Since adoption of the CWA, the United States Environmental Protection Agency (EPA) has published recommended human health water quality criteria for toxic substances to protect people from illness caused by incidental consumption of surface waters or consumption of fish taken from surface waters. States are permitted to adopt EPA’s recommended criteria or develop their own, which may be expressed as numeric values or narrative descriptions of a waterbody’s condition. Wisconsin’s narrative criteria can be found in s. NR102.04. Specifically, NR102.04(1)(d) states that “Substances in concentrations or combinations which are toxic or harmful to humans shall not be present in amounts found to be of public health significance, nor shall substances be present in amounts which are acutely harmful to animal, plant or aquatic life.”

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[1] 33 USC § 1251 (a)(3)

OVERVIEW OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of over 5,000 synthetic chemicals that do not occur naturally in the environment. PFAS were invented in the 1930s and were introduced into industrial manufacturing and commercial use in the 1940's, with peak production occurring between 1970 and 2000.

PFAS can be broadly described as chemicals that have carbon atoms linked to one another and to fluorine atoms. This structure is also referred to as a "fluorinated carbon chain" (highlighted by the red box in Fig. 2). When all carbon atoms in the chain are bonded to fluorine atoms, the resulting chemical is called a **per**fluoroalkyl substance. When one or more carbon atoms is not bonded to a fluorine atom, the resulting chemical is called a **poly**fluoroalkyl substance (green text in Fig. 2). PFAS also contain a functional group that is attached to one end of the carbon-fluorine chain. Functional groups are most often carboxylates/carboxylic acids or sulfonates/sulfonic acids (highlighted by the blue box in Fig. 2). The functional group is reflected in the name of the substance – for example, perfluorooctane sulfonate (PFOS) has a sulfonic functional group, whereas perfluorooctanoic acid (PFOA) has a carboxylic acid functional group.

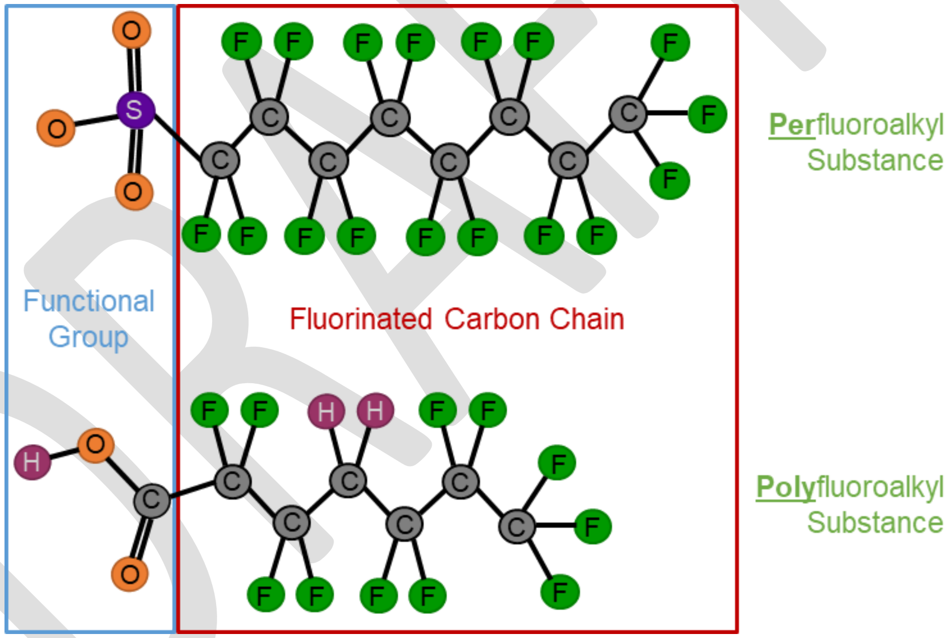

Figure 2. General structure of per- and polyfluoroalkyl substances.

In manufacturing, PFAS are particularly useful due to their carbon-fluorine bonds, which make them temperature resistant and water and oil repellent. As a result, these chemicals have been widely used in many products, including nonstick cookware, waterproof clothing, stain-resistant textiles, Aqueous Film Forming (AFFF) firefighting foam, and food packaging. However, carbon-fluorine bonds are also exceptionally resistant to degradation. Thus, when PFAS are discharged into the environment, they linger for prolonged periods of time and compounds that contain 8 or more carbon atoms are particularly likely to build up in humans, fish, and wildlife. This means that PFAS have been discovered in groundwater, soil, air, sediment, surface water and drinking water, as well as in humans, wildlife and fish across the globe.

Ingestion of contaminated water or food are the primary pathways through which PFAS enter the human body. In recent years, studies have found that most Americans have measurable levels of PFAS in their blood[2]. According to the EPA, certain PFAS substances including PFOA and PFOS have been linked to human health risks, including developmental problems in fetuses and infants, certain types of cancer, reduced antibody response, decreased immune response to vaccinations, and kidney disease[3].

Due to their widespread distribution and negative human health effects, the main PFAS-producing companies began to phase out production and use of long-chain PFAS (those with 8 or more carbon atoms) in the early 2000s. However, these chemicals may still enter the environment for several reasons: due to production of PFAS or their importation to the United States by companies not participating in the phase out program; because precursor PFAS compounds can be degraded into PFOS and PFOA; and via household dust, surface water runoff, or in landfill leachate. Figure 3 from the Interstate Technology Regulatory Council[4], below, demonstrates a how PFAS may move through the environment.

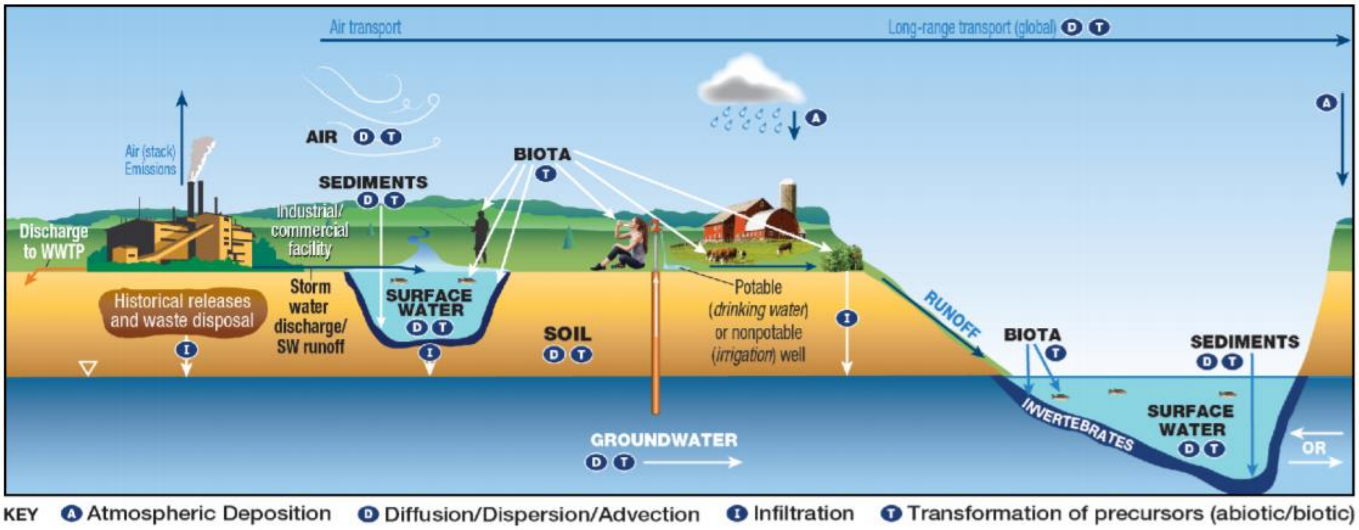

Figure 3. Depiction of how PFAS may move through different environmental media, including the processes that may facilitate movement between media types. Image credit: ITRC.

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[2] Centers for Disease Control and Prevention. 2021. Fourth National Report on Human Exposure to Environmental Chemicals Updated Tables, March 2021, Volume One. https://www.cdc.gov/exposurereport/index.html. [last accessed September 2021]

[3] United States Environmental Protection Agency. Drinking Water Health Advisories for PFOA and PFOS. https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

[4] Image from ITRC's Site Characterization Considerations and Media-Specific Occurrence for Per- and Polyfluoroalkyl Substances (PFAS) Fact Sheet. Available: https://pfas-1.itrcweb.org/wp-content/uploads/2020/10/site_char_508_2020Aug.pdf [last accessed July 2021]

Proposed Changes

The department is proposing new narrative water quality standards for PFOS and PFOA and related implementation procedures for the WPDES program for wastewater discharges.

- Chapter NR 102, Wis. Adm. Code, contains the water quality standards for Wisconsin's surface waters. In this rule package, the department created new narrative water quality criteria for PFOS and PFOA.
- Chapter NR 105, Wis. Adm. Code, contains numeric surface water quality criteria and secondary values for toxic substances. In this rule package, the department added a subsection adding PFOS and PFOA narrative criteria to the list of compounds considered when determining adverse effects on public health and welfare.
- Chapter NR 106, Wis. Adm. Code, contains procedures for calculating Water Quality Based Effluent Limitations for point source discharges to surface waters. A new subsection was added to this chapter to address WPDES permit implementation procedures for the new PFOS and PFOA criteria.
- Chapter NR 219, Wis. Adm. Code, contains tables of EPA's approved analytical laboratory methods. Select tables in this chapter were updated to include specifications for the preservation and holding times of aqueous, biosolids (sludge), and tissue samples that will be analyzed for PFAS.

The following sections of this document provide more details on each of the proposed changes.

CRITERIA FOR PFOS AND PFOA

This rule package proposes to add narrative criteria for PFOS and PFOA to chs. NR 102 and NR 105. As part of this rulemaking effort, the department conducted preliminary calculations of numeric criteria using the procedures outlined ch. NR 105. At this time, however, the department selected the approach outlined in the following sections to develop public health significance thresholds under ch. NR 102. This approach was selected because PFOS public health significance levels are more closely correlated with the issuance of fish consumption advisories than the ch. NR 105 numeric criteria would have been.

Further, the department believes that public health significance thresholds combined with PFAS minimization plans will result in more timely reductions in levels of PFOS, PFOA and all other parameters regulated in WPDES permits, as permittees exceeding the proposed public significance thresholds will begin PFAS minimization plans immediately upon permit reissuance rather than after a prolonged variance application and review process. The department expects that the selected approach will be effective at reducing sources of PFOS and PFOA in areas of the state where PFOS or PFOA concentrations in wastewater are elevated.

Defining a level of public health significance for PFOS in surface waters

Summary

Fish ingestion is the exposure pathway of most concern for PFOS (i.e., PFOS can build up to high levels in fish even when there is a small amount in the water column). There is a strong positive relationship between surface water PFOS and fish tissue PFOS, based on available data from samples taken in waterbodies in Wisconsin and Minnesota. Additionally, there are established PFOS thresholds corresponding to recommended fish consumption frequencies which are designed to reduce risks from exposure to PFOS while still receiving the benefits of fish consumption[5].

Thus, for the purposes of narrative criteria under NR102.04, it is reasonable to define public health significance as a PFOS water concentration that will not result in the issuance of a 1 meal per month PFOS-based fish consumption advisory for any species taken from that surface water. In other words, the proposed definition of public health significance aims to ensure that levels of PFOS in fish will be such that people can consume fish at a frequency of up to one meal per week (32 grams/day)[6] without exceeding EPA's non-cancer toxicity RfD of 2×10^{-5} mg/kg-day.

This approach resulted in a definition of public health significance which is not dependent on whether a waterbody is used as a public water supply. Consequently, for all surface waters that naturally support fish or have downstream waters that support fish, the department proposes that public health significance is defined as 8 ng/L PFOS.

Additional information on the basis for this proposed definition is provided in subsequent sections of this document.

Waterbody Use	Exposure Pathway	1 meal/week Maximum Fish Tissue Concentration	Level of Public Health Significance
All surface waters	Fish ingestion	50 ng/g	8 ng/L

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[5] Great Lakes Consortium for Fish Consumption Advisories. 2019. Best Practice for Perfluorooctane Sulfonate (PFOS) Guidelines. Available at: https://www.health.state.mn.us/communities/environment/fish/docs/consortium/bestpracticepfos.pdf [last accessed May 2021]

[6] The department recognizes that due to concentrations of other contaminants, such as mercury and polychlorinated biphenyls (PCBs), the recommended meal frequency for some species from some waterways may be less than 1 meal per week regardless of the PFOS level.

Determining PFOS Exposure Pathways

To determine which pathway or pathways by which people might be exposed to PFOS, the department reviewed several datasets of samples analyzed for PFAS, including: 1) paired surface water and fish tissue samples collected from waterways throughout Wisconsin and Minnesota, 2) fish tissue samples collected as part of Wisconsin's fish contaminant monitoring program, and 3) surface water samples collected from major rivers as part of long term trends (LTT) monitoring in Wisconsin. Summary details about each dataset are displayed in in the table below.

Dataset	Number of Waterways	Number of Fish samples	Number of Species	Number of Water samples	Year(s)
Paired fish and water	95	2005	19	124	2006-2020
Fish contaminants	35	722	35	n/a	2006-2020
Rivers LTT	42	n/a	n/a	42	2020

In the paired fish and water dataset, PFOS was detected in over 90% of fish tissue samples, even when PFOS was not detected in the water column (Fig. 4).

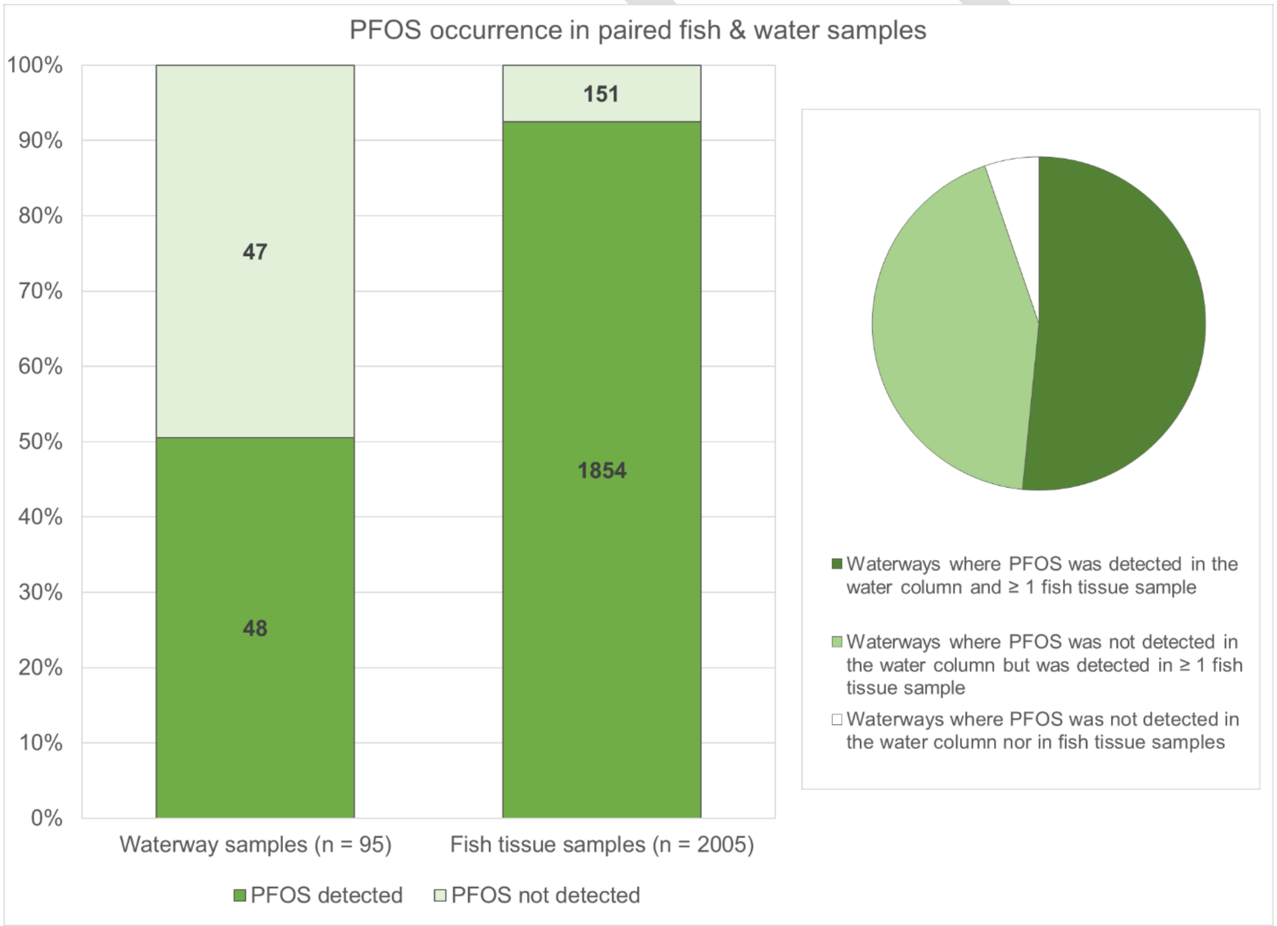

Figure 4. PFOS occurrence patterns in samples from the paired fish and water dataset. Most fish tissue samples contained detectable levels of PFOS, and surface water samples from approximately 50% of waterways contained detectable levels of PFOS. Fish that contained PFOS were found even in waterways where PFOS was not detected in water samples (pie chart).

The pattern that was observed in the paired fish and water dataset of PFOS being detected in most fish tissue samples was mirrored in the fish contaminants data, where more than 85% of fish samples contained detectable levels of PFOS. In the LTT dataset, PFOS was detected in over 62% of waterways.

The data described above demonstrates that PFOS is a highly bioaccumulative compound (in contrast with PFOA, which is rarely detected in fish tissue samples but widely detected in the water; Fig. 7) and suggests that exposure to PFOS via fish consumption is likely to provide a substantive contribution to overall body burdens of PFOS. This conclusion is further supported by work done by the Great Lakes Consortium for Fish Consumption Advisories. Their 2019 Best Practice for PFOS Guidelines[5] document explored sources of PFOS to determine whether it was necessary to include a measure of Relative Source Contribution (RSC) when calculating fish consumption advisories for PFOS. They used serum data from the 2013-2014 National Health and Nutrition Examination Survey (NHANES) to calculate an average background exposure of 0.423 ng/kg-day. This background exposure value was then compared to exposure from consuming one meal per month of fish containing 50 ng/g PFOS, which was estimated to be 5.4 ng/kg-day. Their analysis indicates that fish consumption is overwhelmingly the dominant PFOS exposure pathway, and they conclude that an RSC is not needed. The department agrees with these conclusions and therefore chose to define a public health significance threshold for PFOS using water concentrations that are associated with certain fish tissue concentrations (described below) in order to protect Wisconsin's public health and welfare designated use (Fig. 1).

Modeling the Relationship between PFOS in Water and in Fish Tissue

PFOS was detected in both fish tissue and water samples from 49 waterways in the paired fish tissue and water dataset described above and there is a clear log-linear relationship between levels of PFOS in the water and those in fish tissue ($R^2 = 0.69$, $p<0.001$; Fig. 5). In other words, the level of PFOS in the water is a good predictor of the level of PFOS that will be in fish taken from that water.

Once the department had identified that fish consumption is humans' primary PFOS exposure route and that water PFOS concentrations can be used to predict fish PFOS concentrations, we needed to determine a threshold where the PFOS concentration in the water will pose a risk to human health via fish consumption. Fortunately, we already have a relevant number for fish tissue concentrations we can use as a target. As shown in Fig. 5, fish PFOS concentrations are associated with different consumption advisory meal categories. These categories were developed using a reference dose (RfD) of 2×10^{-5} mg/kg-day[7] as the non-cancer toxicity value, a body weight of 70kg, a meal size of 227g, and an RSC of 100% as described above. Detailed information on how fish PFOS concentrations correspond to each fish consumption meal category can be found in Appendix B.

When the average concentration of PFOS in a species from a waterbody exceeds 50 ng/g, the department issues a special fish consumption advisory of 1 meal/month, depending on sample sizes and variability[5]. While there are some fish species that sensitive populations (i.e., women under 50 and children under 15) are always advised to consume no more than 1 meal/month, a special advisory is

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[7] United States Environmental Protection Agency. 2016. Health Effects Support Document for PFOS. EPA-822-R-16-002. Washington, DC. https://www.epa.gov/sites/production/files/2016-05/documents/pfos_hesd_final_508.pdf [last accessed September 2021]

more stringent than the general statewide Safe Eating Guidelines and applies to everyone[8]. More information on the Fish Contaminant Monitoring and Advisory Program can be found at https://dnr.wisconsin.gov/topic/Fishing/consumption.

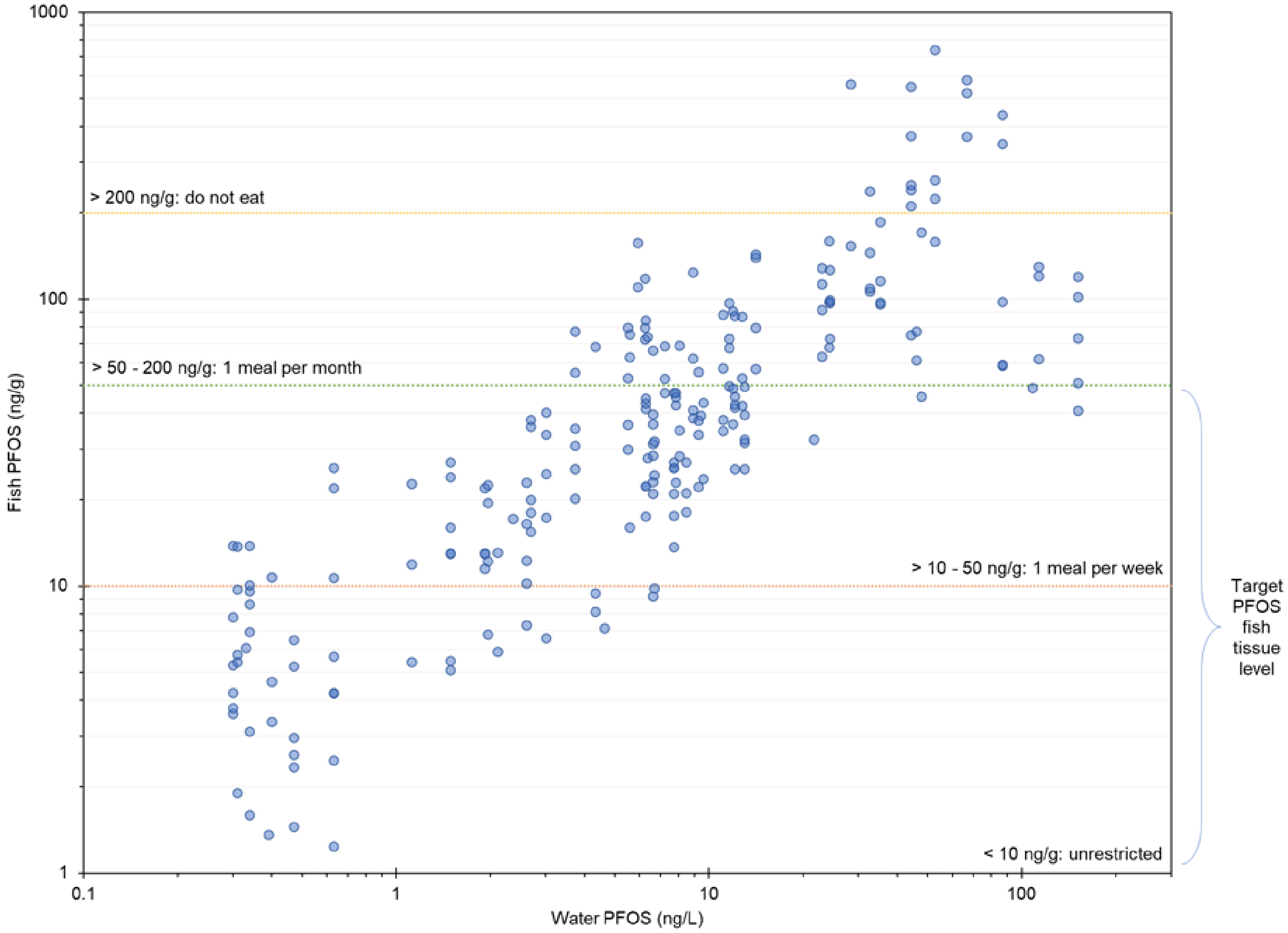

Figure 5. Relationship between concentrations of PFOS in water samples (x-axis) and fish tissue samples (y-axis) in Minnesota and Wisconsin waterbodies. Each circle represents the average PFOS concentration in fillets of a fish species from a waterbody. Horizontal dashed lines delineate fish PFOS concentrations that correspond to different meal frequency categories, and the brackets indicate fish PFOS concentration range that is targeted with this standard. The data that contributed to this figure can be found in Appendix A.

The department evaluated several models to determine the water PFOS concentration that best predicts, or best delineates, fish tissue that is over or under 50 ng/g. For most analysis, fish tissue concentrations were transformed into a binary response variable denoting whether the concentration was over or under the 50 ng/g target concentration. The department conducted several statistical analyses and compared the thresholds from binary response analysis. Additionally, the department assessed thresholds

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[8] Schrank CS. 2014. Wisconsin’s Fish Contaminant Monitoring and Advisory Program: 1970-2010. Fisheries Management Administrative Report No. 73. Wisconsin Department of Natural Resources, Madison, WI. https://p.widencdn.net/k0h6zw/Admin_FH073 [last accessed May 2021]

developed using the original continuous fish tissue data to ensure our analytical techniques did not artificially obscure the observed relationship. Based on these evaluations, the department ultimately selected a method called the Receiver Operating Characteristics (ROC) curve to determine a water concentration that represents a level of public health significance. Information on the models that were evaluated but not selected can be found in Appendix C.

The ROC Curve Tool

The department used the statistical program R to run a mathematical tool called the ROC curve using the package pROC[9] on the data to predict the water concentration where most fish tissue concentrations exceed 50 ng/g PFOS.

The ROC curve is an analytical tool used to evaluate the performance of a binary response variable using bootstrapping to test several measures of model performance. Here, the binary response was whether the average fish tissue concentration in a species from a waterbody was below or above 50 ng/g PFOS. The ROC curve evaluates overall model performance using area under the curve (AUC) method. Water column PFOS concentrations reliably predicted fish tissue classification with strong model performance (AUC = 88.5% CI = 84.1-93.8, package pROC).

The ROC curve additionally calculates two metrics, known as sensitivity and specificity, of the observed model. Sensitivity measures how often responses (fish tissue concentration) that are actually above the threshold (50 ng/g PFOS) are predicted correctly. This is known as the true positive rate. Specificity measures how often responses below that threshold are correctly predicted. This is known as the true negative rate. The point where the sensitivity and specificity converge is often considered the numeric value where the predictor variable (water concentration) best predicts the response variable (fish tissue concentration). The R code used to run the ROC model, as well as other models that were not selected, can be found in Appendix D. The paired fish and water dataset upon which the models were run can be found in Appendix A.

Figure 6 shows sensitivity and specificity for this dataset. The water concentration value where the two curves converge is 8 ng/L PFOS. This means that at a water concentration of 8 ng/L PFOS, we are ~78% sure that fish tissue concentrations below that point are actually lower than 50 ng/g, and fish tissue concentrations above that point are actually greater than 50 ng/g. This is somewhat analogous to balancing the Type I and Type II error rate.

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[9] Robin X, Turck N, Hainard A, Tiberti N, Lisacek F, Sanchez JC, Müller M. 2011. pROC: an open-source package for R and S+ to analyze and compare ROC curves. BMC Bioinformatics 12(77). https://doi.org/10.1186/1471-2105-12-77

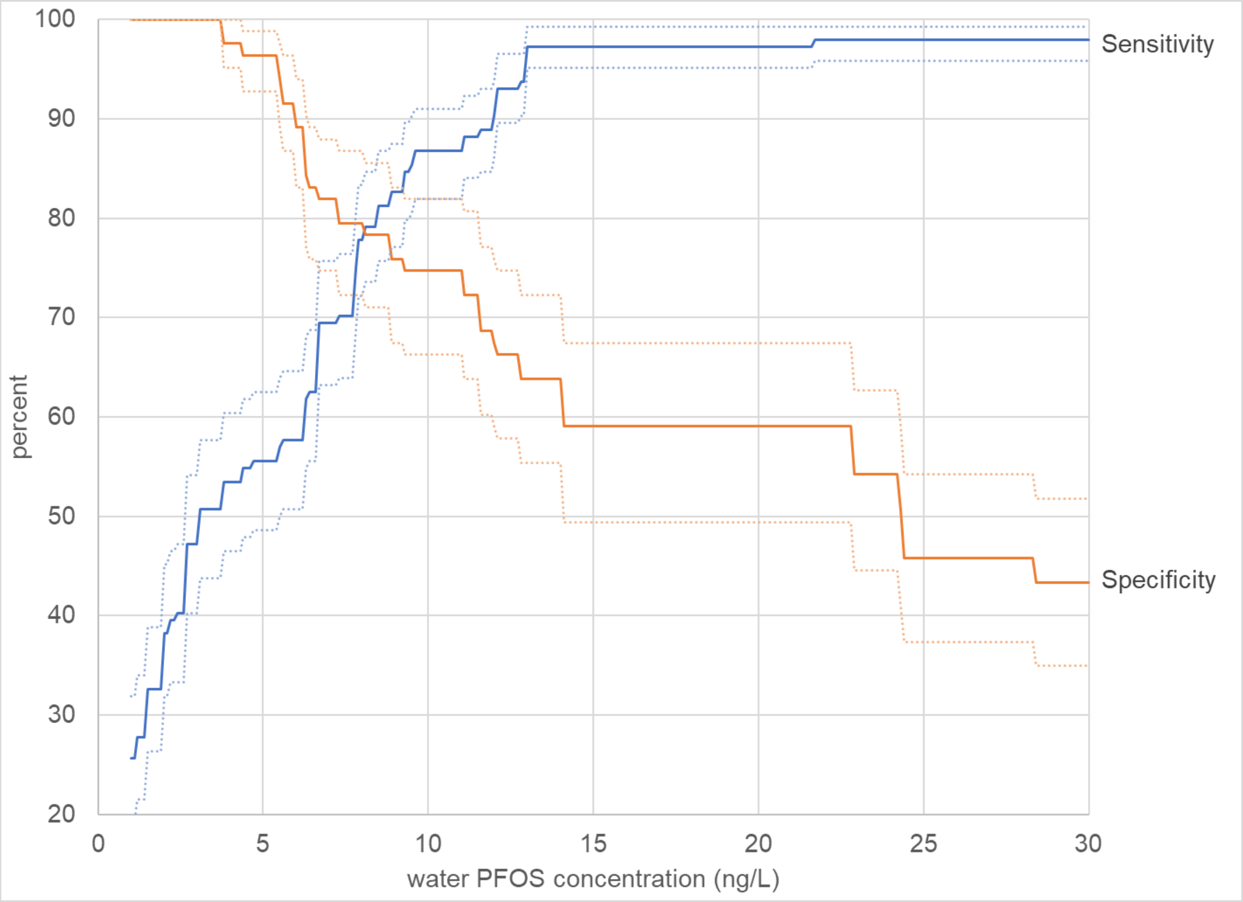

Figure 6. Specificity and sensitivity curves from the ROC analysis of the paired fish tissue and water PFOS dataset. Sensitivity measures how often the model correctly predicts fish tissue concentrations above 50 ng/g PFOS at a given water concentration. Specificity measures how often the model correctly predicts fish tissue concentrations below 50 ng/g at a given water concentration.

Thus, the department proposes that public health significance is defined as 8 ng/L PFOS in order to protect all people from adverse effects of PFOS in surface waters via consumption of fish taken from those surface waters.

Defining a level of public health significance for PFOA in surface waters

Summary

PFOA doesn't bioaccumulate to high concentrations in fish, and therefore water ingestion is the exposure pathway of most concern for PFOA. Thus, for the purposes of narrative criteria under NR102.04, it is reasonable to define public health significance based on the likelihood that, and degree to which, surface waters could be ingested.

This approach resulted in a proposed definition of public health significance which is dependent upon whether a waterbody is used as a public water supply. For public water supply waters, the department proposes that public health significance is defined as 20 ng/L PFOA. For non-public water supply waters, the department proposes that public health significance is defined as 95 ng/L PFOA.

Additional information on the basis for these proposed definitions is provided in subsequent sections of this document.

Waterbody Use	Exposure Pathway	Water Intake Rate	Level of Public Health Significance
Public Water Supply	Drinking water ingestion	1.0 L/day	20 ng/L
Non-Public Water Supply	Incidental ingestion during recreation	0.21 L/day	95 ng/L

Determining PFOA Exposure Pathways

To determine which pathway or pathways by which people might be exposed to PFOA, the department reviewed several datasets of samples analyzed for PFAS, including: 1) paired surface water and fish tissue samples collected from waterways throughout Wisconsin and Minnesota, 2) fish tissue samples collected as part of Wisconsin’s fish contaminant monitoring program, and 3) surface water samples collected from major rivers as part of long term trends (LTT) monitoring in Wisconsin. Summary details about each dataset are displayed in in the table below.

Dataset	Number of Waterways	Number of Fish samples	Number of Species	Number of Water samples	Year(s)
Paired fish and water	95	2005	19	124	2006-2020
Fish contaminants	35	722	35	n/a	2006-2020
Rivers LTT	42	n/a	n/a	42	2020

In the paired fish and water dataset, PFOA was detected in surface water samples from over 80% of the waterways, but was detected in only 2% of fish tissue samples. Those fish samples that contained PFOA came from 8 waterways (Fig. 7). There were no PFOA detects in samples of fish taken from waterways where PFOA was undetected in the water itself.

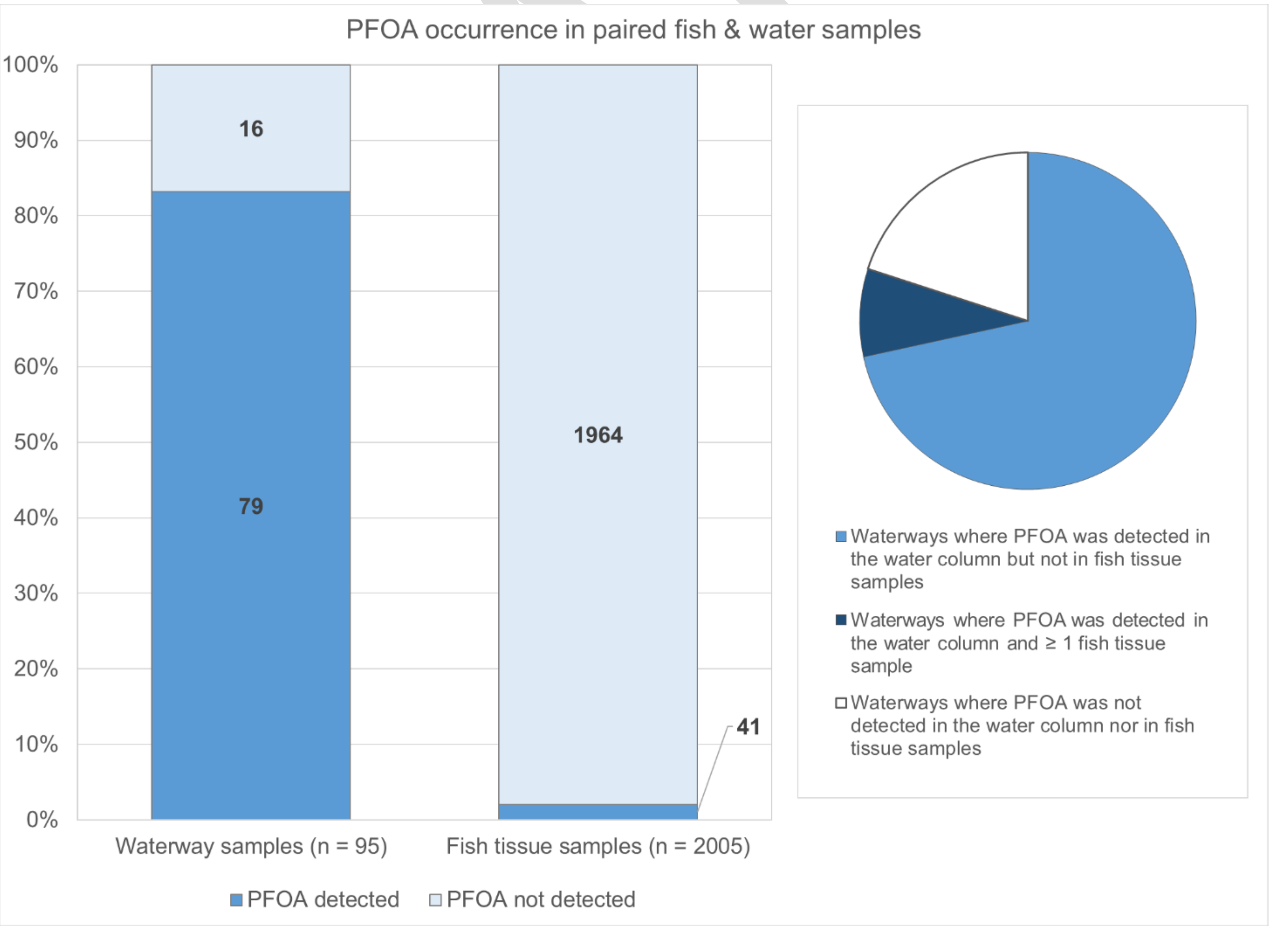

Figure 7. PFOA occurrence in samples from the paired fish and water dataset. Most water samples contained detectable levels of PFOA, while few fish tissue samples contained PFOA. Those fish that did contain PFOA were from a small proportion of waterways (pie chart).

The pattern that was observed in the paired fish and water dataset of PFOA being detected in most water samples, but few fish tissue samples, was mirrored in the fish contaminants and LTT datasets. Less than 4% of the fish samples contained detectable levels of PFOA (in contrast, over 85% of these fish samples contained detectable levels of PFOS). Similarly, in the LTT dataset, PFOA was detected in over 80% of waterways.

The data described above demonstrates that PFOA is unlikely to bioaccumulate in fish tissue. These accumulation patterns contrast with those of PFOS, which is widely detected in fish tissue samples even when it is not detected in the water (Fig. 4) and suggest that while there is widespread risk of exposure to PFOA via ingestion of surface waters, exposure via consumption of fish tissue is unlikely to provide a substantive contribution to overall body burdens of PFOA.

Public Health Significance for Public Water Supplies

Based on the analysis described above, the department believes that for those waters currently used as public water supplies (lakes Superior, Michigan, and Winnebago), setting the level of public health significance as the level already defined by the Departments of Health Services (WDHS) and Natural Resources for the purposes of drinking water protection will protect Wisconsin's public health and welfare designated use (Fig. 1).

As part of a concurrent rulemaking process, the department is proposing to promulgate a drinking water maximum contaminant level (MCL) for PFOA of 20 ng/L. This proposed MCL is based on a recommended groundwater standard for PFOA released by WDHS in 2019[10] and was developed according to s.160.13(2)(c), Wis. Stats. using Formula 1 below. This formula is designed to protect children by incorporating a body weight of 10 kg, a drinking water intake rate of 1 L/day, and an assumption that water is the only source of PFOA (represented by an RSC of 100%). The ADI was set at 2 ng/kg-d based on risk of PFOA exposure to developing fetuses and infants. More information on how the ADI was developed can be found in the WDHS Scientific Support Document[10].

Formula 1:

$$Drinking\ Water\ MCL = \frac{ADI\left(\frac{ng/_{kg}}{day}\right) \times Body\ weight\ (kg)\ \times RSC}{Water\ Consumption\ \left(\frac{L}{day}\right)} = \frac{2\,\frac{ng/_{kg}}{day} \times 10kg \times 100\%}{1\,\frac{L}{day}} = 20\,\frac{ng}{L}$$

Where:

ADI = Acceptable Daily Intake
RSC = Relative Source Contribution

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[10] Wisconsin Department of Health Services. 2019. Scientific support document for PFOA groundwater standard. Madison, WI. https://dnr.wi.gov/topic/Contaminants/documents/pfas/PFOAScientificSupport.pdf [last accessed May 2021]

Public Health Significance for Non-Public Water Supplies

For waters not used as public water supplies, the water consumption rate in Formula 1 (above) may be adjusted to reflect the incidental water consumption rate that occurs during recreation. To determine the incidental ingestion rate, the department followed an approach published by EPA in 2019[11].

Incidental Ingestion Rate

The incidental ingestion rate (L/day) is a product of the ingestion volume (L/hour) and the recreation duration (hours/day), shown in Formula 2.

Formula 2:

$$Ingestion\ Volume\ \left(\frac{L}{hour}\right) \times Recreation\ Duration\ \left(\frac{hours}{day}\right) = Daily\ Incidental\ Ingestion\ Rate\ \left(\frac{L}{day}\right)$$

To calculate recreational incidental ingestion rates for different age groups, EPA (2019) explored the distributions of incidental ingestion volumes and exposure durations. Then, consistent with EPA's Human Health Methodology[12], the 90th percentile of the combined distribution of ingestion rate and exposure duration was used to represent incidental ingestion per day.

The resulting probability density plots of the combined distributions display how likely it is that each age group will ingest a certain amount of water per day (Fig. 8, from EPA 2019). The data that contributed to these distributions are discussed in more detail in the following sections.

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[11] United States Environmental Protection Agency. 2019. Recommended Human Health Recreational Ambient Water Quality Criteria or Swimming Advisories for Microcystins and Cylindrospermopsin. EPA/822/R-19/001. Washington, DC. https://www.epa.gov/wqc/recommended-human-health-recreational-ambient-water-quality-criteria-or-swimming-advisories [last accessed May 2021]

[12] United States Environmental Protection Agency. 2000. Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health. EPA/822/B-00/004. Washington, DC. https://www.epa.gov/wqc/methodology-deriving-ambient-water-quality-criteria-protection-human-health-2000-documents [last accessed May 2021]

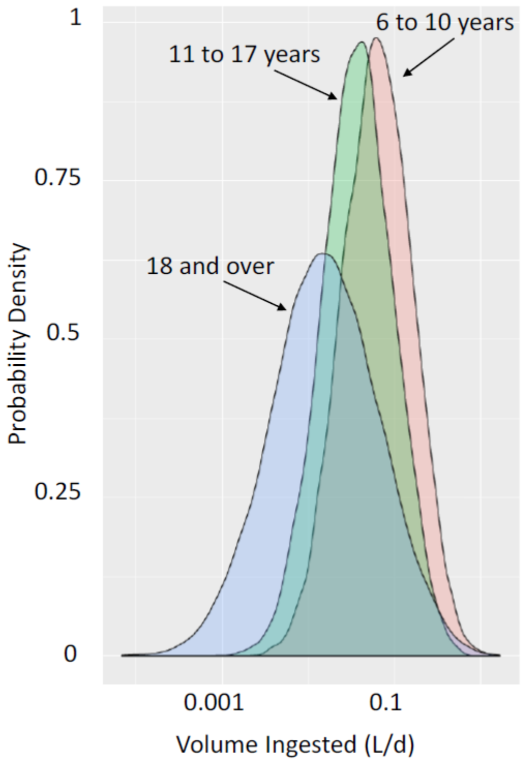

Figure 8. Probability density plots of ingestion rates for different age groups (from EPA 2019). The following sections describe how these plots were derived.

Determination of Ingestion Volume

EPA (2019) evaluated seven ingestion studies and ultimately selected the dataset collected and analyzed by Dufour et al. (2017)[13] which included age information for each participant (ages 6 to 81 years) and recorded each participant's time spent in the water. This study used the same methodology as an earlier study[14] but included 10 times more participants. Both studies used cyanuric acid as an indicator of the amount of pool water ingested while swimming in an outdoor pool. Researchers collected pool water samples before the start of swimming activities, and participants' urine was collected for 24 hours after the swimming event ended. Pool water and urine samples were then analyzed for cyanuric acid to determine ingestion rates.

EPA (2019) selected the Dufour et al. (2017) dataset to calculate incidental ingestion volume because the study included a larger number of participants and additional age groups, and recorded the duration of exposure of each participant. Appendix F of EPA (2019) describes in more detail the seven studies that were evaluated as part of this analysis and provides additional rationale for selecting Dufour et al. (2017).

The raw data collected and analyzed by Dufour et al. (2017) was provided by the study authors. EPA (2019) normalized the volume ingested by each participant to one hour based on the length of time that

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[13] Dufour AP, Behymer TD, Cantú R, Magnuson M, Wymer LJ. 2017. Ingestion of swimming pool water by recreational swimmers. Journal of Water and Health 15(3): 429-437. https://doi.org/10.2166/wh.2017.255

[14] Dufour AP, Evans O, Behymer TD, Cantú R. 2006. Water ingestion during swimming activities in a pool: A pilot study. Journal of Water Health 4(4): 425-430. https://doi.org/10.2166/wh.2006.0026

the participant reported being in the water, then calculated density plots for the ingestion volume per recreation event for different age groups (Fig. 9, from EPA 2019).

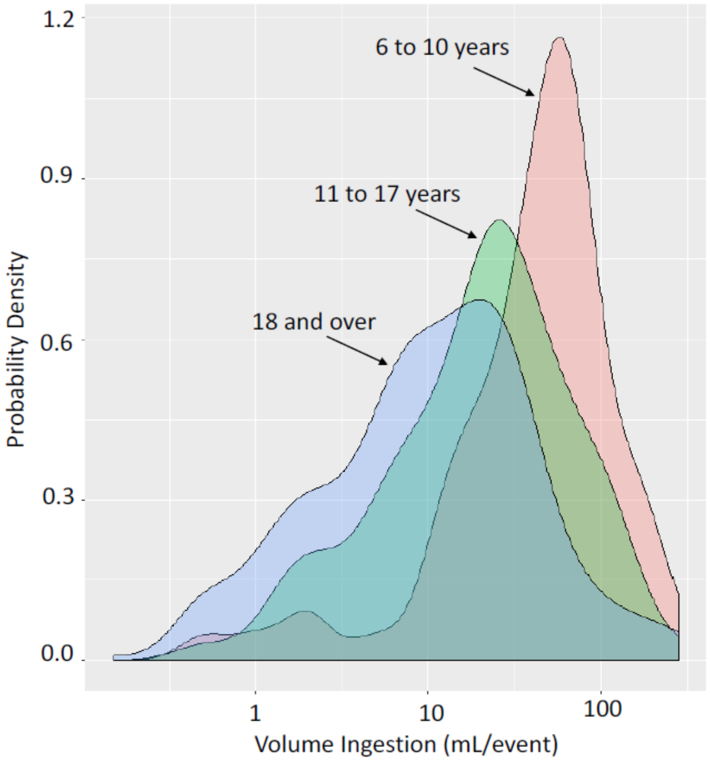

Figure 9. Probability density plots of ingestion volume per recreational event for different age groups (from EPA 2019). Plots were developed by normalizing each participant's volume ingested to one hour based on the length of time they reported being in the water. Data from this analysis, along with the data on the amount of time spent recreating each day shown in Figure 10, was combined to generate the daily ingestion rates shown in Figure 8.

Determination of Recreational Exposure Duration

For the purposes of developing surface water criteria, recreational exposure duration quantifies the length of time that people might be exposed to contaminants in surface waters during primary contact recreation. Defining the exposure duration allows for the recreational ingestion volumes calculated above to be converted to an amount incidentally ingested per day.

EPA (2019) selected recreational exposure data from Table 16-20 of the Exposure Factors Handbook[15] (EFH) for the development of incidental ingestion rates. Table 16-20 of the 2011 EFH lists time spent per 24 hours in an outdoor pool or spa for different age groups. These data are based on analysis of the 1996 National Human Activity Pattern Survey[16]. Although they do not directly measure time spent in

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[15] United States Environmental Protection Agency. 2011. Exposure Factors Handbook 2011 Edition (Final). EPA/600/R-09/052F. Washington, DC. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252 [last accessed May 2021]

[16] United States Environmental Protection Agency. 1996. Descriptive statistics from a detailed analysis of the National Human Activity Pattern Survey (NHAPS) responses. EPA/600/R-96/148. Washington, DC.

freshwaters, previous research[17] demonstrates that time spent in outdoor swimming pools is similar to time spent in freshwaters and thus EPA (2019) concluded that these data could reasonably be used to represent recreational exposure to freshwaters. Figure 10 displays the range of recreational duration data for different age groups.

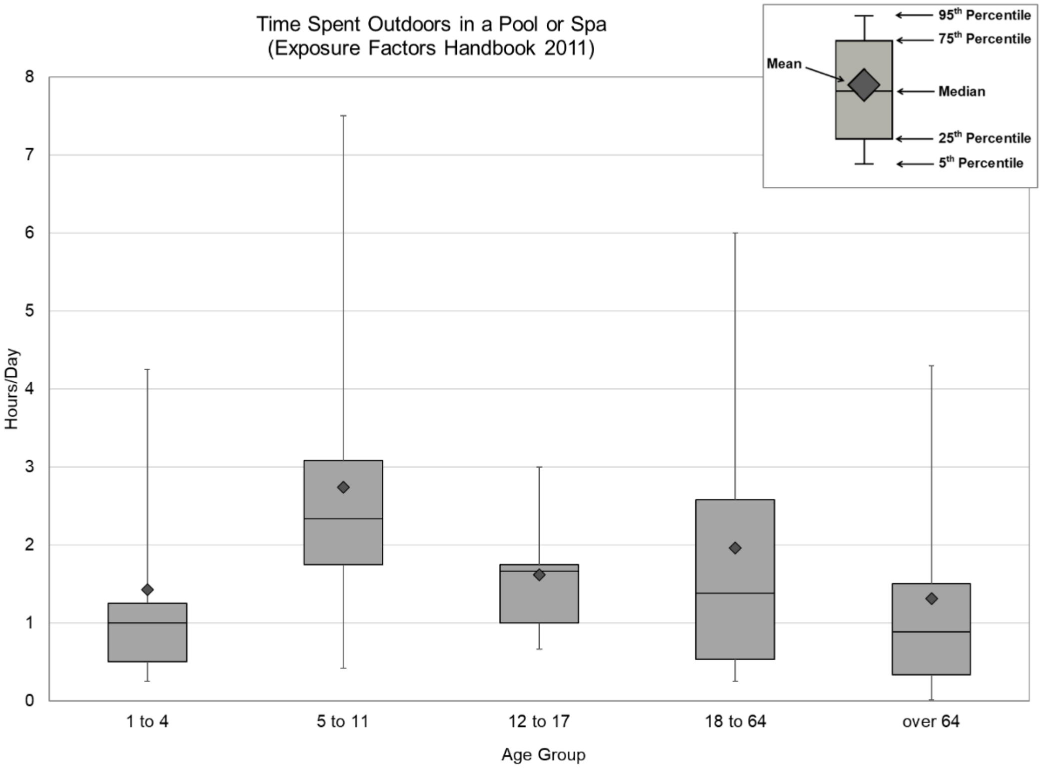

Figure 10. Summary statistics for the amount of time that was spent outdoors in a pool or spa each day by people of different age groups.

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[17] Schets FM, Schijven JF, de Roda Husman AM. 2011. Exposure assessment for swimmers in bathing waters and swimming pools. Water Research 45(7): 2392-2400. https://doi.org/10.1016/j.watres.2011.01.025

Determination of Daily Incidental Ingestion

As mentioned above, the incidental ingestion rate (L/day) is the product of the distribution of incidental ingestion volumes from Dufour et al. (2017) and the distribution of exposure durations from the EFH.

Understanding that there are many different daily ingestion rates that could be calculated from the combination of ingestion volumes and recreation durations reported in the literature, EPA (2019) used the statistical program R to run a mathematical model called a Monte Carlo simulation. This model calculates the distribution of possible ingestion rates for each age group using the following steps:

1) Using the descriptive statistics that were reported in the literature, estimate distributions for ingestion volume and recreation duration for each age group.
2) Randomly select one value from each distribution calculated in step 1.
3) Multiply the two sampled values together to produce an ingestion rate.
4) Repeat steps 2 and 3 over and over (1,000,000 times) to create the distribution of possible daily ingestion rates for each age group.

The distributions and summary statistics resulting from the Monte Carlo simulations are shown on the following pages in Figure 11 and Table 1, respectively. The annotated R code for this analysis is shown in Appendix E.

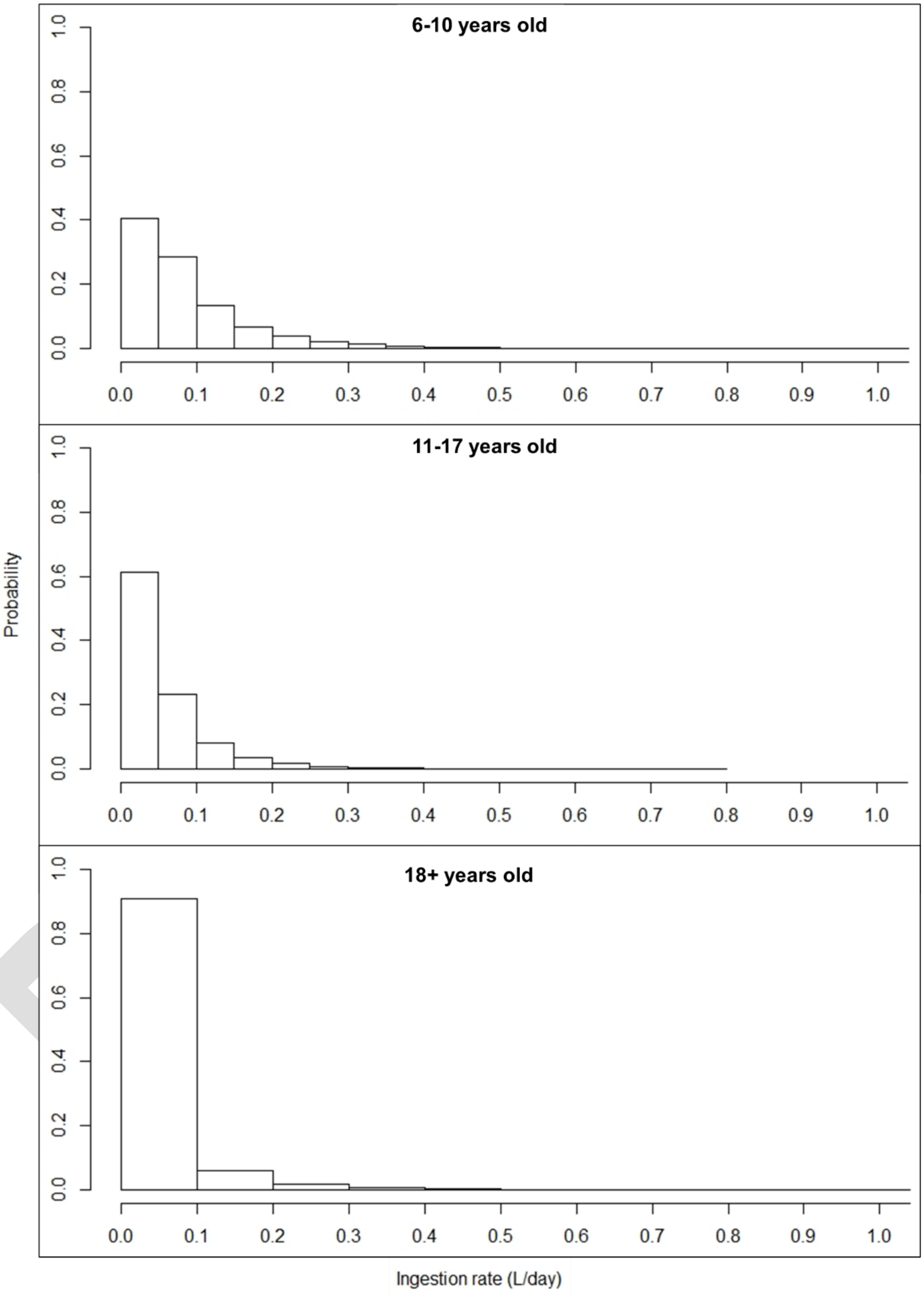

Figure 11. Probability distributions demonstrating the range of ingestion rates that could be calculated by combining ingestion volume and recreation duration data for each age group.

Table 1. Summary statistics for the different age groups based on the distributions produced by the Monte Carlo simulation.

Age Group	**Summary Statistics for Ingestion Rate (L/day)**		
	Median	**Mean**	**90th Percentile**
6 to 10 years	0.063	0.094	0.21
11 to 17 years	0.038	0.058	0.13
18+ years	0.015	0.04	0.10

In order to assess the risk of PFOA exposure to children during recreation in surface waters and as per EPA's 2000 Human Health Methodology, the department selected the 90th percentile of exposure for the 6 to 10 years old age group (0.21 L/day) as a point estimate for deriving the level of public health significance for PFOA in non-public water supply waters.

As mentioned on page 19 of this document, Formula 1 was used to develop the drinking water MCL and the public health significance threshold for surface waters used as public water supplies. Substituting the incidental ingestion rate of 0.21 L/day for the drinking water intake rate of 1 L/day into Formula 1 produces a value of 95.24 ng/L, which represents the PFOA public health significance threshold for non-public water supply waters.

$$\frac{ADI\ \left(\frac{ng/kg}{day}\right) \times Body\ weight\ (kg)\ \times RSC}{Water\ Consumption\ \left(\frac{L}{day}\right)} = \frac{2\,\frac{{}^{ng}/_{kg}}{day} \times 10kg\ \times 100\%}{0.21\,\frac{L}{day}} = 95.24\ ng/L$$

Thus, the department proposes a threshold for public health significance of 95 ng/L for non-public supply waters in order to protect children from adverse effects of PFOA in surface waters via incidental ingestion while recreating.

Criteria magnitude, duration, and frequency

Water quality criteria consist of three components: magnitude, duration, and frequency. These three components are used when assessing a waterbody's impairment status and determining the need for pollutant minimization plans or setting water quality based effluent limits (WQBELs) in permits.

For waterbody assessments, magnitude is the numeric threshold for determining if the waterbody is meeting the criterion (i.e. the levels of public health significance described above), duration is used to select the period over which data are analyzed, and frequency of exceedance is used in determining whether the criterion is attained based on how frequently the threshold is exceeded.

IMPLEMENTATION

Waterbody Assessments

The CWA requires states to prepare a report every 2 years that documents the results of waterbody assessments. This report is titled Wisconsin's Water Quality Report to Congress[18] and describes which waterbodies are attaining their designated uses (healthy waters) and which are not meeting water quality standards (impaired waters).

Assessments are conducted by comparing available water quality data[19] to established criteria and then determining whether the waterbody supports its designated uses (Fig. 1). Thus, every criteria value or description should ideally contain the duration and frequency components described in the previous section, so that waterbody assessments are not based on a rare, limited-time event that does not represent the typical conditions of the waterbody.

This rule package proposes to add language in NR 102.04(8)(d) specifying that "a surface water shall be considered an impaired water if the PFOS or PFOA level of public health significance is exceeded more than once every 3 years". An exceedance frequency of no more than once every 3 years is consistent with what is currently recommended in Wisconsin's Consolidated Assessment and Listing Methodology (WisCALM) to protect the public health and welfare designated use[20]. Samples taken within 30 days of an exceedance event may be considered part of the same event (i.e., duration of exceedance), while samples taken 30 or more days apart will be considered separate events. The department plans to add assessment protocols specific to PFAS in the next revision of WisCALM.

Attainment Sampling

To reliably assess a waterbody for PFOS and PFOA using the exceedance frequency metric described above, the department must have a dataset with at least 2 sample events, which are at least 30 days

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[18] The most recent version of this report as well as previous years' reports can be found at https://dnr.wisconsin.gov/topic/SurfaceWater/Congress.html

[19] Waterbodies may also be listed as impaired if PFOS in fish tissue taken from that waterbody are high enough to warrant a special fish consumption advisory.

[20] WDNR. 2021. Wisconsin 2022 Consolidated Assessment and Listing Methodology for CWA Section 303(d) and 305(b) Integrated Reporting. Guidance # 3200-2021-01.

apart to identify separate exceedance events, within a 3-year period. Surface water PFAS samples may be collected at the same time and same location within a waterbody as other water quality parameters (water chemistry, secchi depth, etc.) as long as collectors follow practices for sample collection, handling, and storage that minimize the potential for contamination[21].

Spills Sampling

Samples collected during and after a spill event are not necessarily representative of a waterbody's overall condition but are important for assessing public health and welfare. This is particularly true of spills of PFAS-containing products; due to their persistent nature, PFAS spills may pose an increased risk to public health and welfare because the spill impact may be longer in duration.

When conducting a waterbody assessment initial spill samples may or may not be used as representative samples for assessment purposes depending on the duration of contamination. Department staff may use best professional judgment to determine the duration of the spill event's impact, up to 3 months. If, after 3 months, PFOS or PFOA levels have returned to pre-spill levels, spill event samples will likely be excluded from the assessment because they represent a short-term impact. However, if PFOS or PFOA levels remain elevated after 3 months, spill event samples may be used for waterbody assessment.

ANALYTICAL METHODS

Chapter NR 219 contains Table F, "Required Containers, Preservation Techniques, and Holding Times for wastewater". This table is revised as part of this rule package to include requirements for sample collection and storage for the analysis of PFAS compounds in multiple media. Footnote numbering in department tables differs from EPA methods because EPA rows pertinent only to marine environments are not included in Wisconsin code.

Information about adjacent states' approaches to regulating PFAS can be found in Appendix F.

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[21] A useful resource for sampling PFAS in surface waters can be found at: https://www.michigan.gov/documents/pfasresponse/Surface_Water_PFAS_Sampling_Guidance_639408_7.pdf

Appendix A: Samples where PFOS was detected in both fish and water

Waterway	State	Year	Species	N	Fish PFOS (ng/g)	Water PFOS (ng/L)
Bde Maka Ska (Calhoun)	MN	2006	Bluegill	5	318.80	108.00
Bde Maka Ska (Calhoun)	MN	2006	White sucker	5	49.10	108.00
Bde Maka Ska (Calhoun)	MN	2008	Black crappie	6	267.17	36.73
Bde Maka Ska (Calhoun)	MN	2008	Bluegill	9	214.33	36.73
Bde Maka Ska (Calhoun)	MN	2008	Largemouth bass	5	454.43	36.73
Bde Maka Ska (Calhoun)	MN	2013	Black crappie	6	96.20	35.30
Bde Maka Ska (Calhoun)	MN	2013	Bluegill	9	97.60	35.30
Bde Maka Ska (Calhoun)	MN	2013	Largemouth bass	11	186.22	35.30
Bde Maka Ska (Calhoun)	MN	2013	Northern pike	11	115.83	35.30
Bde Maka Ska (Calhoun)	MN	2016	Black crappie	3	99.27	24.30
Bde Maka Ska (Calhoun)	MN	2016	Bluegill	5	72.76	24.30
Bde Maka Ska (Calhoun)	MN	2016	Largemouth bass	5	126.40	24.30
Bde Maka Ska (Calhoun)	MN	2016	Northern pike	2	96.85	24.30
Bde Maka Ska (Calhoun)	MN	2018	Northern pike	5	48.94	11.93
Bde Maka Ska (Calhoun)	MN	2018	Walleye	2	91.00	11.93
Bde Maka Ska (Calhoun)	MN	2018	Yellow perch	6	36.60	11.93
Bearskull	WI	2020	Walleye	4	6.11	0.33
Black Earth Creek	WI	2020	Brown trout	6	21.93	0.63
Clear	MN	2018	Bluegill	5	47.20	7.21
Clear	MN	2018	Northern pike	5	68.52	7.21
Clear	MN	2018	Walleye	5	52.76	7.21
Crystal	MN	2018	Black crappie	3	77.30	46.05
Crystal	MN	2018	Bluegill	4	61.40	46.05
Duroy	WI	2020	Black crappie	5	5.25	0.47
Duroy	WI	2020	Bluegill	4	2.34	0.47
Duroy	WI	2020	Walleye	4	2.59	0.47
Elmo	MN	2008	Bluegill	10	153.17	28.40
Elmo	MN	2008	Largemouth bass	2	559.67	28.40
Elmo	MN	2016	Black crappie	4	524.50	66.70
Elmo	MN	2016	Bluegill	6	368.00	66.70
Elmo	MN	2016	Largemouth bass	5	581.20	66.70
Elmo	MN	2018	Black crappie	4	550.00	44.25
Elmo	MN	2018	Bluegill	5	211.00	44.25
Elmo	MN	2018	Northern pike	5	239.60	44.25
Elmo	MN	2018	Cisco	5	74.98	44.25
Elmo	MN	2018	Walleye	1	370.00	44.25
Elmo	MN	2018	Yellow perch	3	250.00	44.25
Fish (Dakota)	MN	2018	Black crappie	5	24.40	6.69
Fish (Dakota)	MN	2018	Bluegill	5	9.81	6.69
Fish (Dakota)	MN	2018	Northern pike	1	31.90	6.69
Fish Lake Flowage	MN	2008	Black crappie	5	86.76	12.77
Fish Lake Flowage	MN	2008	Bluegill	5	42.62	12.77
Fish Lake Flowage	MN	2008	Largemouth bass	5	88.24	12.77
Fish Lake Flowage	MN	2008	Northern pike	5	53.02	12.77
Fish Lake Flowage	MN	2008	Walleye	5	87.14	12.77
Fish Lake Flowage	MN	2007	Black crappie	5	157.20	5.92
Fish Lake Flowage	MN	2007	Bluegill	10	110.07	5.92
Fish Lake Flowage	MN	2007	Largemouth bass	5	183.60	5.92
Gervais	MN	2018	Black crappie	1	79.50	5.50
Gervais	MN	2018	Bluegill	10	29.90	5.50
Gervais	MN	2018	Largemouth bass	8	52.98	5.50

Waterway	State	Year	Species	N	Fish PFOS (ng/g)	Water PFOS (ng/L)
Gervais	MN	2018	Northern pike	2	36.55	5.50
Gervais	MN	2008	Black crappie	5	138.40	29.50
Gervais	MN	2008	Bluegill	5	137.00	29.50
Harriet	MN	2008	Largemouth bass	5	261.50	29.50
Harriet	MN	2013	Black crappie	10	106.39	32.63
Harriet	MN	2013	Bluegill	15	107.81	32.63
Harriet	MN	2013	Largemouth bass	10	237.60	32.63
Harriet	MN	2013	Northern pike	7	145.29	32.63
Harriet	MN	2013	Walleye	7	108.93	32.63
Harriet	MN	2016	Black crappie	5	97.98	24.27
Harriet	MN	2016	Bluegill	5	67.88	24.27
Harriet	MN	2016	Largemouth bass	5	159.40	24.27
Harriet	MN	2018	Black crappie	2	72.75	11.57
Harriet	MN	2018	Bluegill	5	67.68	11.57
Isles	MN	2018	Largemouth bass	5	97.06	11.57
Isles	MN	2018	Yellow perch	5	49.90	11.57
Isles	MN	2008	Black crappie	6	166.97	13.50
Isles	MN	2008	Bluegill	3	68.40	13.50
Isles	MN	2008	Largemouth bass	5	228.83	13.50
Isles	MN	2013	Black crappie	10	38.01	11.09
Isles	MN	2013	Bluegill	10	34.69	11.09
Isles	MN	2013	Largemouth bass	10	88.12	11.09
Isles	MN	2013	Northern pike	7	57.41	11.09
Isles	MN	2016	Black crappie	5	31.32	6.63
Isles	MN	2016	Bluegill	3	39.63	6.63
Isles	MN	2016	Largemouth bass	4	66.25	6.63
Johanna	MN	2016	Bluegill	5	57.28	14.10
Johanna	MN	2016	Largemouth bass	3	139.33	14.10
Johanna	MN	2016	Northern pike	2	79.40	14.10
Johanna	MN	2016	Walleye	4	143.00	14.10
Josephine	MN	2018	Bluegill	5	17.20	2.36
Kegonsa	WI	2020	Common carp	3	17.49	6.28
Kegonsa	WI	2020	Freshwater drum	5	41.50	6.28
Kegonsa	WI	2020	Largemouth bass	4	45.23	6.28
Kegonsa	WI	2020	Pumpkinseed	4	22.28	6.28
Kegonsa	WI	2020	Walleye	5	43.37	6.28
Kegonsa	WI	2020	White bass	3	84.30	6.28
Kegonsa	WI	2020	Yellow perch	3	22.34	6.28
Keller	MN	2007	Bluegill	10	69.00	8.04
Mccarron	MN	2018	Bluegill	1	28.00	6.35
Mccarron	MN	2018	Largemouth bass	5	73.88	6.35
Mead	WI	2020	Black crappie	2	1.36	0.39
Mendota	WI	2020	Rock bass	5	4.65	0.40
Mendota	WI	2020	Walleye	4	3.38	0.40
Mendota	WI	2020	Yellow perch	7	10.72	0.40
Menominee, center Scott Flowage	WI	2019	Black crappie	2	3.75	0.30
Menominee, center Scott Flowage	WI	2019	Largemouth bass	2	5.30	0.30
Menominee, center Scott Flowage	WI	2019	Pumpkinseed	1	7.80	0.30
Menominee, center Scott Flowage	WI	2019	Rock bass	2	13.85	0.30
Menominee, center Scott Flowage	WI	2019	Smallmouth bass	1	3.60	0.30
Menominee, center Scott Flowage	WI	2019	Yellow perch	4	4.25	0.30
Menominee, lower Scott Flowage	WI	2019	Northern pike	3	5.45	0.31
Menominee, lower Scott Flowage	WI	2019	Pumpkinseed	3	13.73	0.31
Menominee, lower Scott Flowage	WI	2019	Rock bass	1	5.78	0.31
Menominee, lower Scott Flowage	WI	2019	Smallmouth bass	2	1.90	0.31
Menominee, lower Scott Flowage	WI	2019	Yellow perch	6	9.76	0.31
Menominee, mouth to Green Bay	WI	2019	Bluegill	5	8.63	0.34
Menominee, mouth to Green Bay	WI	2019	Pumpkinseed	2	9.58	0.34

Waterway	State	Year	Species	N	Fish PFOS (ng/g)	Water PFOS (ng/L)
Menominee, mouth to Green Bay	WI	2019	Smallmouth bass	2	6.94	0.34
Menominee, mouth to Green Bay	WI	2019	Walleye	3	10.08	0.34
Menominee, mouth to Green Bay	WI	2019	Yellow perch	3	13.84	0.34
Mississippi River, Pool 2 Reach 2 (RM 836-843)	MN	2009	Bluegill	15	40.51	7.71
Mississippi River, Pool 2 Reach 2 (RM 836-843)	MN	2009	Common carp	15	17.56	7.71
Mississippi River, Pool 2 Reach 2 (RM 836-843)	MN	2009	Freshwater drum	15	55.89	7.71
Mississippi River, Pool 2 Reach 2 (RM 836-843)	MN	2009	Smallmouth bass	15	25.87	7.71
Mississippi River, Pool 2 Reach 2 (RM 836-843)	MN	2009	White bass	15	71.69	9.41
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2009	Bluegill	15	99.13	9.41
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2009	Common carp	16	39.31	9.41
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2009	Freshwater drum	15	71.54	9.41
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2009	Smallmouth bass	15	49.05	9.41
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2009	White bass	15	82.64	9.41
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2012	Bluegill	15	32.37	12.95
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2012	Common carp	15	49.57	12.95
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2012	Freshwater drum	15	31.61	12.95
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2012	Smallmouth bass	15	25.55	12.95
Mississippi River, Pool 2 Reach 3 (RM 821-834)	MN	2012	White bass	15	39.42	12.95
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2009	Bluegill	15	260.11	52.62
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2009	Common carp	15	223.72	52.62
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2009	Freshwater drum	15	739.08	52.62
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2009	Smallmouth bass	15	259.98	52.62
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2009	White bass	15	158.51	52.62
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2012	Bluegill	15	97.87	86.70
Mississippi River, Pool 2 Reach 4 (RM 815-820)	MN	2012	Common carp	15	438.48	86.70
Mississippi River, Pool 3	WI	2019	Bluegill	10	18.00	2.69
Mississippi River, Pool 3	WI	2019	Freshwater drum	1	36.00	2.69
Mississippi River, Pool 3	WI	2019	Largemouth bass	1	20.00	2.69
Mississippi River, Pool 3	WI	2019	Sauger	2	15.50	2.69
Mississippi River, Pool 3	WI	2019	White bass	1	38.00	2.69
Mississippi River, Pool 4	WI	2019	Bluegill	11	5.11	1.49
Mississippi River, Pool 4	WI	2019	Freshwater drum	1	16.00	1.49
Mississippi River, Pool 4	WI	2019	Largemouth bass	1	27.00	1.49
Mississippi River, Pool 4	WI	2019	Rock bass	2	12.95	1.49
Mississippi River, Pool 4	WI	2019	Sauger	1	24.00	1.49
Mississippi River, Pool 4	WI	2019	Smallmouth bass	1	13.00	1.49
Mississippi River, Pool 4	WI	2019	Yellow perch	1	5.50	1.49

Waterway	State	Year	Species	N	Fish PFOS (ng/g)	Water PFOS (ng/L)
Mississippi River, Pool 6	WI	2019	Bluegill	10	12.21	1.96
Mississippi River, Pool 6	WI	2019	Largemouth bass	2	22.50	1.96
Mississippi River, Pool 6	WI	2019	Northern pike	1	6.80	1.96
Mississippi River, Pool 6	WI	2019	Yellow perch	2	19.50	1.96
Mississippi River, Pool 8	WI	2019	Bluegill	10	12.94	1.92
Mississippi River, Pool 8	WI	2019	Rock bass	1	22.00	1.92
Mississippi River, Pool 8	WI	2019	Smallmouth bass	1	13.00	1.92
Mississippi River, Pool 8	WI	2019	Yellow perch	3	11.53	1.92
Monona @ center	WI	2020	Black crappie	2	37.85	9.23
Monona @ center	WI	2020	Bluegill	5	33.76	9.23
Monona @ center	WI	2020	Walleye	8	55.71	9.23
Monona @ center	WI	2020	Yellow perch	5	22.22	9.23
Monona @ Starkweather	WI	2019	Bluegill	6	40.83	151.19
Monona @ Starkweather	WI	2019	Largemouth bass	8	101.63	151.19
Monona @ Starkweather	WI	2019	Northern pike	4	51.00	151.19
Monona @ Starkweather	WI	2019	Walleye	2	73.00	151.19
Monona @ Starkweather	WI	2019	Yellow perch	2	120.00	151.19
Monona Bay	WI	2020	Black crappie	5	62.82	5.57
Monona Bay	WI	2020	Common carp	6	16.01	5.57
Monona Bay	WI	2020	Walleye	1	75.30	5.57
Northstar (Unnamed)	MN	2018	Common carp	5	7.15	4.62
Owasso	MN	2018	Bluegill	5	5.93	2.11
Owasso	MN	2018	Largemouth bass	5	13.12	2.11
Rebecca	MN	2018	Bluegill	5	45.80	47.80
Rebecca	MN	2018	Largemouth bass	5	170.50	47.80
Round	WI	2020	Black crappie	1	3.11	0.34
Round	WI	2020	Largemouth bass	1	1.59	0.34
Snelling	MN	2018	Northern pike	3	32.40	21.60
St. Louis River, Mouth	WI	2019	Black crappie	7	5.68	0.63
St. Louis River, Mouth	WI	2019	Channel catfish	1	1.24	0.63
St. Louis River, Mouth	WI	2019	Common carp	3	4.25	0.63
St. Louis River, Mouth	WI	2019	Musky	1	25.90	0.63
St. Louis River, Mouth	WI	2019	Northern pike	8	2.47	0.63
St. Louis River, Mouth	WI	2019	Walleye	2	4.23	0.63
St. Louis River, Mouth	WI	2019	Yellow perch	10	10.70	0.63
Tanners	MN	2007	Black crappie	5	118.14	6.23
Tanners	MN	2007	Bluegill	10	72.52	6.23
Tanners	MN	2007	Largemouth bass	5	79.56	6.23
Tanners	MN	2018	Black crappie	5	41.10	8.88
Tanners	MN	2018	Bluegill	5	62.10	8.88
Tanners	MN	2018	Largemouth bass	5	123.85	8.88
Tanners	MN	2018	Northern pike	1	38.50	8.88
Twin	MN	2016	Black crappie	5	18.08	8.46
Twin	MN	2016	Bluegill	5	21.10	8.46
Twin	MN	2016	Largemouth bass	5	26.96	8.46
Twin	MN	2018	Bluegill	5	28.40	8.03
Twin	MN	2018	Largemouth bass	3	34.95	8.03
Upper Petenwell	WI	2019	Black crappie	1	55.40	3.73
Upper Petenwell	WI	2019	Bluegill	7	25.56	3.73
Upper Petenwell	WI	2019	Rock bass	1	77.30	3.73
Upper Petenwell	WI	2019	Smallmouth bass	3	20.17	3.73
Upper Petenwell	WI	2019	Walleye	2	30.90	3.73
Upper Petenwell	WI	2019	Yellow perch	1	35.50	3.73
Van Zile	WI	2020	Bluegill	1	1.45	0.47
Van Zile	WI	2020	Largemouth bass	5	2.96	0.47
Van Zile	WI	2020	Walleye	4	6.51	0.47
Waubesa	WI	2020	Bluegill	5	23.02	7.83
Waubesa	WI	2020	Freshwater drum	5	42.73	7.83

Waterway	State	Year	Species	N	Fish PFOS (ng/g)	Water PFOS (ng/L)
Waubesa	WI	2020	Largemouth bass	4	47.26	7.83
Waubesa	WI	2020	Walleye	5	45.50	7.83
WI River, Above Hat Rapids dam	WI	2019	Bluegill	4	16.48	2.61
WI River, Above Hat Rapids dam	WI	2019	Northern pike	1	7.33	2.61
WI River, Above Hat Rapids dam	WI	2019	Pumpkinseed	3	22.97	2.61
WI River, Above Hat Rapids dam	WI	2019	Rock bass	1	12.30	2.61
WI River, Above Hat Rapids dam	WI	2019	Smallmouth bass	6	10.25	2.61
WI River, Below Merrill	WI	2019	Largemouth bass	1	6.61	3.01
WI River, Below Merrill	WI	2019	Northern pike	2	17.30	3.01
WI River, Below Merrill	WI	2019	Rock bass	1	40.20	3.01
WI River, Below Merrill	WI	2019	Smallmouth bass	4	24.60	3.01
WI River, Below Merrill	WI	2019	Walleye	3	33.67	3.01
WI River, Biron Flowage	WI	2020	Channel catfish	6	8.15	4.33
WI River, Biron Flowage	WI	2020	Redhorses	8	9.46	4.33
WI River, Biron Flowage	WI	2020	White bass	6	68.30	4.33
Wild Rice	MN	2008	Black crappie	5	164.00	113.33
Wild Rice	MN	2008	Bluegill	5	61.82	113.33
Wild Rice	MN	2008	Northern pike	5	120.25	113.33
Wild Rice	MN	2008	Walleye	5	129.73	113.33
Wild Rice	MN	2018	Black crappie	1	63.10	22.90
Wild Rice	MN	2018	Bluegill	5	91.92	22.90
Wild Rice	MN	2018	Northern pike	5	113.18	22.90
Wild Rice	MN	2018	Walleye	5	128.08	22.90
Wingra	WI	2020	Bluegill	5	22.79	1.12
Wingra	WI	2020	Largemouth bass	4	11.92	1.12
Wingra	WI	2020	Yellow perch	5	5.44	1.12
Winona	MN	2018	Bluegill	5	23.64	9.60
Winona	MN	2018	Largemouth bass	5	43.66	9.60

Appendix B: Calculating Fish Consumption Advisory Meal Categories

Fish consumption meal categories are calculated by inputting the reference dose, body weight, and fish consumption rate into Equation 1 to get the maximum concentration of a pollutant (here, PFOS) that is safe to consume at a given consumption rate.

Equation 1:

$$Maximum\ concentration_{\ meal\ frequency}\left(\frac{\mu g}{g}\ or\ ppm\right) = \frac{RfD\left(\frac{\mu g/_{kg}}{day}\right) \times BW(kg)}{FCR\left(\frac{g}{day}\right)}$$

Where:

$$PFOS\ Reference\ Dose\ = 2\ x\ 10^{-2}\ \frac{\mu g/_{kg}}{day}$$

$$Body\ weight\ = 70kg$$

$$Fish\ consumption\ rate\ \left(\frac{g}{day}\right) = meal\ size\ (g) \times \frac{Meals}{Year} \times \frac{Year}{365\ days}$$

$$Meal\ size = 227g\ or\ 8oz$$

These maximum concentrations then become the thresholds between different meal categories, as demonstrated in the Table 1 below from the Consortium 2019 PFOS Best Practice Guidelines document. Equations 2 through 4 demonstrate how these meal frequency thresholds were derived.

PFOS in Fish (µg/kg)	Meal Frequency
≤ 10	Unrestricted
> 10 – 50	1 meal/week
> 50 – 200	1 meal/month
> 200	DO NOT EAT

Equation 2:

$$Maximum\ concentration_{Unrestricted} = \frac{(2 \times 10^{-2}) \times 70}{140\,\frac{g}{day}} = 0.01\ ppm = 10\ ppb$$

Equation 3:

$$Maximum\ concentration_{1\ meal/\ week} = \frac{(2 \times 10^{-2}) \times 70}{32\,\frac{g}{day}} = 0.044\ ppm \approx 50\ ppb$$

Equation 4:

$$Maximum\ concentration_{1\ meal/month} = \frac{(2 \times 10^{-2}) \times 70}{7.4\frac{g}{day}} = 0.189\ ppm \approx 200\ ppb$$

Appendix C: Models that were evaluated, but not selected, during PFOS criteria derivation

Classification and Regression Trees

Classification and Regression Trees (CART) is an analytical technique that attempts to split a response variable into two (or more) homogenous groups based on a predictor variable (R package rpart). CART uses recursive partitioning to find the numeric value of the predictor variable that best splits the response variable into two groups that minimizes with group variability while maximizing between group mean differences. We used CART to find only the single strongest split value (i.e. single node), although multiple splits can be computed. CART excels at finding thresholds, although it does not typically generalize the data as well as other methods, meaning that it is sensitive to the exact input data and confidence intervals (90% for this and all subsequent analyses) calculated through bootstrapping tend to be large (see Table 1, Figure 1 for all results). The final model predicted classification well; the group with water concentrations of PFOS >13.52 ng/l contained 93.0% of fish samples above 50.0 ng/g, and the group with PFOS water concentrations <13.52 ng/l only 17.6 % above 50.0 ng/g (post hoc t-test p <0.001). The department did not select CART for the final analysis because of the large variability in confidence intervals and known statistical issues with being less generalizable (i.e. very sensitive to exact input data) than other measures of model performance.

Logistic Regression

Logistic regression (LR) is a type of regression analysis that is especially suited to predicting a binary response variable. LR is more generalizable that CART (i.e. should be more resilient to adding new data) but determining specific thresholds of the predictor variable is not as clear cut. Using LR in conjunction with CART will provide a range of possible thresholds of PFOS water that best predict the fish tissue response variable. We used the glm function in R to create a LR model and used the model inflection point (where chances Positive fish tissue is ~50%) and the maximum rate of change-point (numeric value where % of Positive responses increases most rapidly) as two possible thresholds. Using LR water column PFOS predicted fish tissue binary variable well (p<0.001, log odds = 1.67). LR was not selected for the final model as the inflection point necessarily means 50% error on each side of the threshold. The maximum rate of change is more protective and ecologically significant, however not as easily interpreted as the ROC analysis.

Quantile Regression

Quantile regression (QR) is an extension of linear regression but instead of estimating the mean trend between two variables the user defines a particular percentile (20th, 50th [median], 80th, etc.) of the relationship. We used QR to examine the relationship between PFOS in water and numeric PFOS in fish tissue. In all previous analyses we examined fish tissue as a binary response variable. By adding QR we can examine the same type of threshold analyses (where fish tissue equals 50 ng/g) but using a continuous response variable. If the QR analyses are relatively similar to the binary analyses, then we are more certain that transforming the fish tissue to a binary response variable did not ultimately obscure the relationship between water and fish tissue PFOS. QR at the 50th percentile provides the water concentration where 50% of the fish are predicted to be above 50 ng/l (e.g. Positive). The 80th percentile QR estimates the point where 20% of the fish are Positive. In other words, a more protective water concentrations where fish are just starting to be consistently above the fish tissue threshold. Because the response variable is continuous extreme percentiles in QR are sensitive to outliers (high fish tissue concentration per water PFOS concentration) so we choose a moderately large percentile (80th) to balance human health protection and resilience to outliers. The department ultimately did not select QR because the more protective percentiles (e.g. high ends of the distribution) are potentially sensitive to outliers that over-influence the point the regression line meets 50 ng/l fish tissue.

Appendix D: R code for all PFOS models

```
require(rpart)
require(boot)
require(epitools)
require(pROC)
require(growthrates)
options(max.print=99999)

PFOS = data.table(read.csv("PFOS.csv")) #reads PFOS data into R

#Create rating variable for fish that are > or <50
PFOS$FishRating = NA

for(i in 1:nrow(PFOS)){
if(PFOS$Fish_PFOS[i] >= 50) PFOS$FishRating[i] = 1
if(PFOS$Fish_PFOS[i] <  50) PFOS$FishRating[i] = 0
}

####################################################################
#Classification and regression tree (cart)
control <- rpart.control(cp=0.0010,maxdepth=1, minbucket=10)
cart = rpart(FishRating~Water_PFOS, PFOS, control = control)
summary(cart)
print(cart)
plot(cart, uniform=TRUE, margin=0.1)
text(cart) # Best water PFOS value to split fish

######################################################################################
PFOS$WaterRating = NA
for(i in 1:nrow(PFOS)){
  if(PFOS$Water_PFOS[i] >= 13.52) PFOS$WaterRating[i] = "high"
  if(PFOS$Water_PFOS[i] <  13.52) PFOS$WaterRating[i] = "low"
}
t.test(PFOS$FishRating~PFOS$WaterRating)

############################################################
#Manually bootstrap cart to get 90% CI on estimate
NDR1 <- function(formula, data, indices){
  d<-data[indices,]
  control <- control
  fit<- rpart(formula, data=d, method="anova", control=control)
  fit$splits[4]
}

#Do the bootstrap
  df1 <- boot(data=PFOS, statistic=NDR1, R=5000, formula=FishRating~Water_PFOS)
  plot(df1)
  cartci = boot.ci(df1, conf= 0.9, type="norm")
  T_a = cartci[2]
  L_a = cartci[4]$normal[2]
  H_a = cartci[4]$normal[3]
##################################################################################

##############################################################################################
#Reciever Operating Characteristc
Predictor <- PFOS$Water_PFOS
Response <- PFOS$FishRating

test1 <- roc(response=Response, predictor=Predictor, ci=TRUE, of="auc",ci.type="shape", plot=TRUE,
smooth=FALSE, auc=TRUE, percent=TRUE, boot.n=20000)
test1

#Examins sensitivity and specificity
thresh = seq(1,30,0.1)
r1<-ci.thresholds(test1, conf.level=0.9, boot.n=10000,thresholds=thresh, smooth.roc=TRUE)
r1

plot(r1$specificity[,2]  ~ thresh, type="l")
lines(r1$specificity[,1] ~ thresh, lty=2) # lower CI
lines(r1$specificity[,3] ~ thresh, lty=2) # Upper CI
```

```
lines(r1$sensitivity[,2] ~ thresh, col="blue")
lines(r1$sensitivity[,1] ~ thresh, lty=2) # lower CI
lines(r1$sensitivity[,3] ~ thresh, lty=2) # Upper CI

#Find thresholds and CIs
T_c = names(which.min(abs(r1$specificity[,2]-90)))
H_c = names(which.min(abs(r1$specificity[,1]-90)))
L_c = names(which.min(abs(r1$specificity[,3]-90)))

T_b = names(which.min(abs(r1$sensitivity[,2]-90)))
H_b = names(which.min(abs(r1$sensitivity[,3]-90)))
L_b = names(which.min(abs(r1$sensitivity[,1]-90)))

T_d = names(which.min(abs(r1$sensitivity[,2]-78)))#78%, point where sensitivity and specificity meet
H_d = names(which.min(abs(r1$sensitivity[,3]-78)))
L_d = names(which.min(abs(r1$sensitivity[,1]-78)))

##################################################################################

#################################################################
#FancyPlot
plot(r1$specificity[,2]  ~ thresh, type="l")
polygon(c(thresh, rev(thresh)),
        c(r1$specificity[,1], rev(r1$specificity[,3])),
        col = "grey90", border = NA)

polygon(c(thresh, rev(thresh)),
        c(r1$sensitivity[,1], rev(r1$sensitivity[,3])),
        col = "lightsteelblue1", border = NA)
lines(r1$specificity[,2]  ~ thresh, type="l")
lines(r1$sensitivity[,2] ~ thresh, col="blue")

##################################################################################

##################################################################################
#Logistic regression
for(i in 1:nrow(PFOS)){
  if(PFOS$Fish_PFOS[i] >= 50) PFOS$FishRating[i] = 1
  if(PFOS$Fish_PFOS[i] <  50) PFOS$FishRating[i] = 0
}
PFOS$FishRating = as.numeric(PFOS$FishRating)

PFOS$logPFOS = log(PFOS$Water_PFOS)
lr = glm(FishRating~logPFOS, data=PFOS, family = binomial())
summary(lr)
exp(coef(lr))
exp(confint(lr))

#Create a plot
start = 0.9*range(PFOS$logPFOS)[1]
end   = range(PFOS$logPFOS)[2]*1.1
xweight = seq(start,end, (end-start)/200)
yweight = predict(lr, list(logPFOS=xweight), type="response")
plot(FishRating~logPFOS, data=PFOS)
lines(xweight, yweight)

#Find the inflection point
inflect = which(round(yweight, 2) == 0.5)[1]
T_e = exp(xweight[inflect]) # inflection point

L_e = exp(xweight[inflect]-(1.64*summary(lr)$coefficients[2,2]))#Lower CI
H_e = exp(xweight[inflect]+(1.64*summary(lr)$coefficients[2,2]))#upper CI

#Find maximum rate of change of logistic regression
res <- fit_spline(xweight , yweight)
T_f = exp(coef(res))[2] # maximum rate of change 5.50
L_f = exp(coef(res)[2]-(1.64*summary(lr)$coefficients[2,2]))#Lower CI
H_f = exp(coef(res)[2]+(1.64*summary(lr)$coefficients[2,2]))#upper CI
####################################################################

####################################################################
# Linear and quantile regression
```

```
PFOS$log10_fish = log10(PFOS$Fish_PFOS)
PFOS$log10_water = log10(PFOS$Water_PFOS)

rq_fit = function(formula, data, indices, tau){
  fit = rq(formula, data=data[indices,], tau=tau)
  below_90 = 10^((log10(50) - coef(fit)[1]) / coef(fit)[2])
  return(below_90)
}
rq_i_80 = boot(
  data=PFOS,
  statistic=rq_fit,
  R=5000,
  formula=log10_fish ~ log10_water,
  tau=0.8
)

plot(rq_i_80)
rq_ci = boot.ci(rq_i_80, conf=0.9, type="norm")
T_g = rq_ci[2]
L_g = rq_ci[4]$normal[2]
H_g = rq_ci[4]$normal[3]

rq_i_50 = boot(
  data=PFOS,
  statistic=rq_fit,
  R=5000,
  formula=log10_fish ~ log10_water,
  tau=0.5
)

plot(rq_i_50)
rq_ci = boot.ci(rq_i_50, conf=0.9, type="norm")
T_h = rq_ci[2]
L_h = rq_ci[4]$normal[2]
H_h = rq_ci[4]$normal[3]

#####################
#Plot quatile regression
plot(log10(Fish_PFOS)~log10(Water_PFOS), data = PFOS, pch=21, bg="grey80", cex=1.75)
top    = rq(log10(Fish_PFOS)~log10(Water_PFOS), data=PFOS, tau=0.8)
center = rq(log10(Fish_PFOS)~log10(Water_PFOS), data=PFOS, tau=0.5)
abline(top, col="red", lwd=2)
abline(center, col="blue", lwd=2)
abline(h=log10(50), lty=2)
#############################################################

####################################################################
#Build a plot to bring it all together
type = c("CART",  "Sens90", "Spec90", "ROC", "LRinflec", "LRmaxRate", "QuantReg80", "QuantReg50")
threshold = c(T_a, T_b, T_c, T_d, T_e, T_f, T_g, T_h)
threshUp  = c(H_a, H_b, H_c, H_d, H_e, H_f, H_g, H_h)
threshLow = c(L_a, L_b, L_c, L_d, L_e, L_f, L_g, L_h)

allFig = data.table(cbind(type,threshold, threshUp, threshLow))
allFig$threshold = as.numeric(allFig$threshold)
allFig$threshUp = as.numeric(allFig$threshUp)
allFig$threshLow = as.numeric(allFig$threshLow)

allFig = setorderv(allFig, cols = "threshold", order=1)
allFig$order = seq(1,8,1)

par(mar=c(5,6,4,2))
plot(order~threshold,allFig, pch=19, cex=2.5, xlim = c(0,20), yaxt="n", ylab ="", xlab = "PFOS Water
Threshold")
axis(2, at=allFig$order, labels=allFig$type, las = 2)
segments(allFig$threshLow,allFig$order, allFig$threshUp, allFig$order, lwd=2)
####################################################################

####################################################################
#Relative Risk at different thresholds of PFOS water
#plus all of the thresholds and CIs from the above plot
#at x concentration of water we are X.X times more likely to have fish >50
PFOS$FishRating = NA
```

```
PFOS$WaterRating = NA

tmp  = c(threshold, 10)
tmp2 = c(threshLow, 10)
tmp3 = c(threshUp, 10)

tmp  = as.numeric(tmp)
tmp2 = as.numeric(tmp2)
tmp3 = as.numeric(tmp3)

outTable = data.frame(matrix(ncol = 7, nrow = length(tmp)))
colnames(outTable) = c("Threshold","LowCI", "UpCI", "RR", "LowCI_RR", "UpCI_RR", "P_RR")

#Loop through different thresholds for RR
for(j in 1:length(tmp)){

for(i in 1:nrow(PFOS)){
  if(PFOS$Water_PFOS[i] >= tmp[j]) PFOS$WaterRating[i] = "b_W_high"
  if(PFOS$Water_PFOS[i] <  tmp[j]) PFOS$WaterRating[i] = "a_W_low"
  if(PFOS$Fish_PFOS[i]  >= 50)     PFOS$FishRating[i]  = "b_F_high"
  if(PFOS$Fish_PFOS[i]  <  50)     PFOS$FishRating[i]  = "a_F_low"
}

x = table(PFOS$WaterRating, PFOS$FishRating)
RR = epitab(x, method = "riskratio", verbose=TRUE, conf.level = 0.9)

outTable[j,1] = round(tmp[j],3)
outTable[j,2] = round(tmp2[j],3)
outTable[j,3] = round(tmp3[j],3)
outTable[j,4] = round(RR$tab[2,5],3)
outTable[j,5] = round(RR$tab[2,6],3)
outTable[j,6] = round(RR$tab[2,7],3)
outTable[j,7] = round(RR$tab[2,8],4)
}

#Thresholds and RR table
rownames(outTable) = c(type, "10")
outTable = setorderv(outTable, cols = "Threshold", order=1)
outTable

######################################################
```

Appendix E: R code for PFOA Monte Carlo simulation (from EPA 2019)

```
# This script is to combine distributions for water ingestion rate (L/hr) and recreational exposure
duration (hr/day) to develop a distribution for ingestion/day (L/day) and to generate a histogram of this
combined distribution

# The first distribution is the incidental ingestion rate per hour from the Dufour dataset

# The second distribution is the recreational exposure duration (hr/day) from the EPA 2011 Exposure
Factors Handbook Table 16-20. Time Spent (minutes/day) in Selected Outdoor Locations, Doers Only, At Home
in the Outdoor Pool or Spa

# Both distributions are assumed to be log-normal

#####Read required libraries and set simulation sample size #################

rm(list=ls()) # Remove all current R objects from memory
library(truncnorm) #import library for truncated normal distribution
nsamp = 1000000 # specify number of samples in monte-carlo analysis
set.seed(1984756) # set seed for analysis replicability

####################################################
# The combined distribution function (cdist) assumes a log-normal distribution for ingestion rate (L/hour)
and a log-normal distribution for exposure duration (hr/d) using the mean and sd as parameter inputs. This
function is called in later sections of the code for each age group analysis.

cdist<-function(nsamp,mean_dur,sd_dur,min_dur,max_dur,mean_ing,sd_ing,min_ing,max_ing){

n<-nsamp # number of samples to be drawn

# transform mean and sd of duration
sd_dur_ln<-sqrt(log((sd_dur/mean_dur)^2+1)) # standard deviation of duration in log space
mean_dur_ln<-log(mean_dur)-((sd_dur_ln^2)/2) # mean of duration in log space
min_dur_ln<-log(min_dur) # minimum duration in log space
max_dur_ln<-log(max_dur)

# transform mean and sd of ingestion rate
sd_ing_ln<-sqrt(log((sd_ing/mean_ing)^2+1))
mean_ing_ln<-log(mean_ing)-((sd_ing_ln^2)/2)
min_ing_ln<- -10^10
max_ing_ln<-log(max_ing)

# draw n samples from the truncated ingestion rate distribution in L/hr
ingperhr_ln_trunc<-exp(rtruncnorm(n=n, a=min_ing_ln, b=max_ing_ln, mean=mean_ing_ln, sd=sd_ing_ln))
#truncated log normal distribution

# draw n samples from the truncated duration distribution (hr/d)
duration_hr_ln_trunc<-exp(rtruncnorm(n=n, a=min_dur_ln, b=max_dur_ln, mean=mean_dur_ln, sd=sd_dur_ln))

# compute n samples for the combined ingestion rate per day distribution (L/d)
ingperday<-ingperhr_ln_trunc*duration_hr_ln_trunc #combine distributions
print(summary(ingperday)) # print summary statistics of the combined distribution
print(quantile(ingperday, probs=0.90)) # print 90th percentile of the combined distribution

# Generate histogram
hist(ingperday,xlab="Ingestion rate (L/day)",ylab="Probability", main ="Truncated hybrid distribution
fit", xlim=c(0, 2.0), ylim=c(0, 1))
h=hist(ingperday)
h$density=h$counts/sum(h$counts)
plot(h,xlab="Ingestion rate (L/day)",ylab="Probability", main ="Log-normal distribution fit", xlim=c(0,
1), ylim=c(0, 0.99), xaxp=c(0,1.5,15), freq=FALSE)
}

####################################################
#I. Analysis for 6 to 10 age group
# These values are from 2011 EFH table 16-20 for ages 5 to 11.
mean_dur_min=164.2
```

```
sd_dur_min=103.97
min_dur_min=25
max_dur_min=450

# Convert exposure data from the EPA’s EFH from min/day to hr/day
mean_dur<-mean_dur_min/60 #mean exposure duration hr/day
sd_dur<-sd_dur_min/60 #sd exposure duration hr/day
min_dur<-min_dur_min/60 #minimum exposure duration hr/day
max_dur<-max_dur_min/60 #maximum exposure duration hr/day

# These ingestion rate values are computed from the Dufour dataset
mean_ing<- 0.03745 # mean ingestion rate in L/hr
sd_ing<-0.03355 # sd ingestion rate in L/hr
min_ing<-0.00033 # minimum ingestion rate in L/hr
max_ing<-0.20000 # maximum ingestion rate in L/hr
cdist(nsamp,mean_dur,sd_dur,min_dur,max_dur,mean_ing,sd_ing,min_ing,max_ing) # call combined distribution
function

####################################################
#II. Analysis for 11 to 17 age group
# These values are from 2011 EFH table 16-20 for age 12 to 17
mean_dur_min=97
sd_dur_min=53.81
med_dur_min=100
min_dur_min=40
max_dur_min=180

# Convert exposure data from the EPA’s EFH from min/day to hr/day
mean_dur<-mean_dur_min/60 #mean exposure duration hr/day
sd_dur<-sd_dur_min/60 #sd exposure duration hr/day
med_dur<-med_dur_min/60 #median exposure duration hr/day
min_dur<-min_dur_min/60 #minimum exposure duration hr/day
max_dur<-max_dur_min/60 #maximum exposure duration hr/day

# These ingestion rate values are computed from the Dufour dataset
mean_ing<-0.03996 # mean ingestion rate in L/hr
sd_ing<-0.04377 # sd ingestion rate in L/hr
min_ing<-0.00067 # minimum ingestion rate in L/hr
max_ing<-0.26800 # maximum ingestion rate in L/hr
cdist(nsamp,mean_dur,sd_dur,min_dur,max_dur,mean_ing,sd_ing,min_ing,max_ing) # call combined distribution
function

####################################################
#III. Analysis for 18+ age group
# Combine exposure duration data for 18 to 64 and for >64 age groups from 2011 EFH table 16-20.
mean_dur_min=(117.61+78.9)/2
sd_dur_min=sqrt((112.72^2+85.32^2)/2)
min_dur_min=1
max_dur_min=450

# Convert exposure data from the EPA’s EFH from min/day to hr/day
mean_dur<-mean_dur_min/60 #mean exposure duration hr/day
sd_dur<-sd_dur_min/60 #sd exposure duration hr/day
min_dur<-min_dur_min/60 #minimum exposure duration hr/day
max_dur<-max_dur_min/60 #maximum exposure duration hr/day

# These ingestion rate values are computed from the Dufour dataset
mean_ing<-0.02811 # mean ingestion rate in L/hr
sd_ing<-0.04960 # sd ingestion rate in L/hr
min_ing<-0.00012 # minimum ingestion rate in L/hr
max_ing<-0.36800 # maximum ingestion rate in L/hr
cdist(nsamp,mean_dur,sd_dur,min_dur,max_dur,mean_ing,sd_ing,min_ing,max_ing) # call combined distribution
function

####################################################
# IV. Analysis for all age groups (including 1-4 yo)
# Combine exposure duration data for all age groups (1 to 4, 5 to 11, 12 to 17, 18 to 64, >64) from 2011
EFH table 16-20.
mean_dur_min=(85.56+164.2+97+117.61+78.9)/5
sd_dur_min=103.71 # SD reported in EFH for all ages
min_dur_min=1
max_dur_min=450
```

```
# Convert exposure duration data from min/day to hr/day
mean_dur<-mean_dur_min/60 #mean exposure duration hr/day
sd_dur<-sd_dur_min/60 #sd exposure duration hr/day
min_dur<-min_dur_min/60 #minimum exposure duration hr/day
max_dur<-max_dur_min/60 #maximum exposure duration hr/day

# These ingestion rate values are computed from the Dufour dataset
mean_ing<- 0.03290 # mean ingestion rate in L/hr
sd_ing<- 0.04643 # sd ingestion rate in L/hr
min_ing<-0.00012 # minimum ingestion rate in L/hr
max_ing<-0.36800 # maximum ingestion rate in L/hr

cdist(nsamp,mean_dur,sd_dur,min_dur,max_dur,mean_ing,sd_ing,min_ing,max_ing) # call combined distribution function
```

Appendix F: Adjacent States Comparison

This appendix summarizes general narrative water quality criteria and PFOS and PFOA criteria and implementation procedure policies from Minnesota, Michigan, Illinois, and Iowa.

Narrative Water Quality Criteria

The administrative codes of adjacent states contain narrative criteria for the protection of surface waters, although none of the adjacent states' narrative criteria are specific to PFOS or PFOA. The narrative criteria of Illinois, Iowa, and Michigan specifically prohibit concentrations of toxic substances in surface waters in amounts that will adversely affect human health or public health. Minnesota's narrative criteria prohibits discharge of wastes in such quantities that will cause pollution as defined by law. Code citations for these narrative criteria are as follows:

Minnesota *Minn. Stat. 7050.0210-13*

"Pollution prohibited. No sewage, industrial waste, or other wastes shall be discharged from either a point or a nonpoint source into the waters of the state in such quantity or in such manner alone or in combination with other substances as to cause pollution as defined by law. In any case where the waters of the state into which sewage, industrial waste, or other waste effluents discharge are assigned different standards than the waters of the state into which the receiving waters flow, the standards applicable to the waters into which the sewage, industrial waste, or other wastes discharged shall be supplemented by the following: The quality of any waters of the state receiving sewage, industrial waste, or other waste effluents shall be such that no violation of the standards of any waters of the state in any other class shall occur by reason of the discharge of the sewage, industrial waste, or other waste effluents."

Michigan *R 323.1057, Mich. Admin. Code*

"Rule 51. (1) Toxic substances shall not be present in the surface waters of the state at levels that are or may become injurious to the public health, safety, or welfare, plant and animal life, or the designated uses of the waters. As a minimum level of protection, toxic substances shall not exceed the water quality values specified in, or developed pursuant to, the provisions of subrules (2) to (4) of this rule or conditions set forth by the provisions of subrule (6) of this rule. A variance to these values may be granted consistent with the provisions of R 323.1103."

Illinois *Ill. Admin. Code tit. 35, § 302.210*

"Other Toxic Substances. Waters of the State shall be free from any substances or combination of substances in concentrations toxic or harmful to human health, or to animal, plant or aquatic life. Individual chemical substances or parameters for which numeric standards are specified in the Subpart are not subject to this Section."

Iowa *IAC § 567.61.3(2)(d)*

"General water quality criteria. The following criteria are applicable to all surface waters including general use and designated use waters, at all places and at all times for the uses described in 61.3(1) 'a.' … 'd.' Such waters shall be free from substances attributable to wastewater discharges or agricultural practices in concentrations or combinations which are acutely toxic to human, animal, or plant life."

PFOS and PFOA Water Quality Criteria

Two adjacent states – Michigan and Minnesota – have released numeric water quality values for PFOS, or PFOS and PFOA. Both states developed their values according to the procedures outlined in 40 CFR 132, but each state used different inputs, which resulted in different numeric values. Similarly, Wisconsin selected a different methodology and different inputs, as described below, and thus the proposed thresholds are different. Further, Minnesota released site-specific criteria (SSC) for PFOS rather than implementing the criteria statewide. Michigan has calculated statewide values as Wisconsin is proposing to do. Wisconsin chose not to pursue the development of SSC for this rulemaking effort. Over the past several years, the department has endeavored to collect data on the occurrence of PFAS across the state, and this data indicates the possibility of human exposure to PFOA and PFOS via surface waters or fish taken from surface waters in areas throughout the state. With statewide criteria the department seeks to provide protection for citizens' use of all waters. Additionally, Minnesota's code includes provisions for developing SSCs without rulemaking, but Wisconsin's does not. Thus, there would be no administrative time saved or expedited human health protections gained by developing SSCs compared to statewide criteria.

Wisconsin's proposed threshold of 8 ng/L for PFOS is more stringent than Michigan's value of 11 ng/L and, compared to Minnesota's PFOS criterion in waters where it applies, less stringent than Minnesota's criterion of 0.05 ng/L. Wisconsin's proposed thresholds of 20 ng/L and 95 ng/L for PFOA in public drinking water supply waters and non-public drinking supply waters, respectively, are more stringent than Michigan's values of 420 and 12,000 ng/L for PFOA in drinking and non-drinking waters, respectively.

Minnesota

In 2020, the Minnesota Pollution Control Agency (MPCA) released SSC for PFOS in surface waters and fish tissue for Lake Elmo and two connected waterbodies, Bde Maka Ska and Mississippi River Pool 2. These SSC are not promulgated standards but were developed according to the procedures outlined in 40 CFR 132 pursuant to Minnesota's state statutory provisions. Minnesota's administrative code provides the flexibility to implement SSCs without going through rulemaking. The value for fish tissue is 0.37 ng PFOS/g and the value for water that supports the fish tissue criterion is 0.05 ng PFOS/L. MPCA's SSC incorporated the Minnesota Department of Health's toxicity value, which was derived using a model that focuses on the protection of infants and women of childbearing age (WCBA). Accordingly, MPCA's SSC derivation also included WCBA-specific body weights and fish consumption and drinking water intake rates.

Michigan

Michigan Department of Environmental Quality (now called the Department of Environment, Great Lakes, and Energy; EGLE) released statewide water quality values for PFOS in 2014 and PFOA in

2011. The process for calculating surface water quality values, outlined in 40 CFR 132, is promulgated in Michigan's administrative code R. 323.1057. However, values resulting from this process are not promulgated and appear in "Rule 57 Water Quality Values Spreadsheets" available at https://www.michigan.gov/egle/0,9429,7-135-3313_3681_3686_3728-11383--,00.html. Michigan's PFOS and PFOA values apply to surface waters statewide. Concentrations of PFOS may not exceed 11 and 12 ng/L in drinking and non-drinking waters, respectively. Concentrations of PFOA may not exceed 420 and 12,000 ng/L in drinking and non-drinking waters, respectively. Michigan EGLE's surface water quality values incorporate toxicity values based on data from studies where cynomolgus monkeys were exposed to PFOS or PFOA for 182 days[22,23]. Derivation of both values also included adult body weights and fish consumption and drinking water rates.

Illinois

None

Iowa

None

Implementation of PFOS and PFOA Criteria

Minnesota

Minnesota implements SSC for PFOS in a handful of waterbodies in the Minneapolis-St. Paul metro area – both in the East Metro cleanup area and in other parts. For the most part, PFOS criteria was developed in order to provide appropriate cleanup values for the East Metro and for an area of Minneapolis that has been impacted by a chrome plater. Limitations based on the numeric PFOS SSC described above have not yet been applied in NPDES permits. In 2007, MPCA and STS Consultants, LTD., developed SSCs for PFOA and PFOS for Bde Maka Ska and Mississippi River Pool 2. Minnesota has had limited permit implementation of the 2007 criteria; to date, there is only one wastewater plant that has PFAS limits based on these criteria. See: https://www.pca.state.mn.us/waste/water-quality-criteria-development-pfas for more information.

Michigan

Michigan implements surface water PFOS and PFOA values through various water quality programs. Michigan is carrying out an Industrial Pretreatment Program PFAS Initiative, a Municipal NPDES Permitting Strategy, and an Industrial Direct and Industrial Storm Water Discharge Compliance Strategy for monitoring and addressing PFOS and PFOA in regulated discharges. Under the Municipal NPDES Permitting Strategy, municipal permits issued/re-issued after October 1, 2021 will include effluent limits for PFOS/PFOA if applicable. In addition, after July 1, 2021, Michigan will require sampling of biosolids prior to land application as part of a biosolids Interim Strategy. Michigan supports these programs through ambient surface water and fish tissue monitoring.

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[22] Butenhoff JL, Costa G, Elcombe C, Farrar D, Hansen K, Iwai H, Jung R, Kennedy Jr G, Lieder P, Olsen G, Thomford P. 2002. Toxicity of ammonium perfluorooctanoate in male cynomolgus monkeys after oral dosing for 6 months. Toxicological Sciences 69(1): 244–257.

[23] Seacat AM, Thomford PJ, Hansen KJ, Olsen GW, Case MT, Butenhoff JL. 2002. Subchronic toxicity studies on perfluorooctane sulfonate potassium salt in cynomolgus monkeys. Toxicological Sciences 68(1): 249–264.

These programs have been funded through general funds, federal PPG grant, permit fee programs, and special appropriations at the state level as well as by local governments operating wastewater treatment plants and private industries found to be discharging PFAS to WWTPs and/or surface waters.

Illinois

Not applicable

Iowa

Not applicable