White Paper

Development of Surface Water Screening Levels for PFOA and PFOS Based on the Protection of Human Health

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This white paper develops surface water screening levels for perfluorooctanoic acid (PFOA; CAS# 335-67-1) and perfluorooctane sulfonate (PFOS; CAS# 1763-23-1) protective of human health. These screening levels are based on fish and shellfish ingestion pathways. PFOA and PFOS are manmade chemicals that belong to a group of thousands of chemicals known as perfluoroalkyl substances (PFAS). PFASs are water- and lipid-resistant. They are used as waterproofing and stain-resistant coatings for carpets, leather, textiles, furniture, and packaging materials. They are also used in fire-fighting foam and are added to aviation fluids to decrease flammability. PFOA and PFOS degrade slowly and are very persistent in the environment and the human body (USEPA, 2016a; USEPA, 2016b). The PFOA and PFOS present in surface water bioconcentrates and bioaccumulates into fish and shellfish that are consumed by local populations.

The following sections describe the technical basis for the proposed surface water screening levels.

<u>Equation and assumptions</u>

We calculated surface water screening levels protective of fish and shellfish consumption using a modified equation from the U.S. Environmental Protection Agency (USEPA) for the calculation of fish consumption limits based on concentrations of contaminants in fish tissue (USEPA, 2000a). Because the critical effects of PFOA and PFOS are non-cancer effects, the equation for non-carcinogens was used. Parameters used in the equation are listed in Table 1.

$$SWSL\ (\mu g/L) = RfD \times RSC \times \left(\frac{BW}{FI \times BAF}\right) \times CF$$

Where:
SWSL = surface water screening level (μg/L)
RfD = oral reference dose (mg/kg-d)
RSC = relative source contribution
BW = body weight (kg)
CF = correction factor, 1000 μg/mg
FI = freshwater and estuarine finfish and shellfish consumption rate (kg/d)
BAF = bioaccumulation factor (L/kg)

Table 1 – Parameters used in the derivation of surface water screening levels for PFOA and PFOS

Parameter	PFOA	PFOS	Source
Reference dose (mg/kg-d)	2E-05	2E-05	USEPA, 2016a USEPA, 2016b
Body weight (kg)	75	75	USEPA, 2011
Relative source contribution	0.2	0.2	USEPA, 2016a USEPA, 2016b
Freshwater and estuarine finfish and shellfish consumption rate (kg/d)	0.029	0.029	See section on consumption rate
Bioaccumulation factor (L/kg)	68	2358	See section on bioaccumulation factor

Reference Dose

The USEPA has developed reference doses for PFOA and PFOS in order to create drinking water Health Advisory Levels for these compounds. FDEP has used these reference doses for the calculation of alternative groundwater cleanup target levels (GCTLs) and soil cleanup target levels (SCTLs) for PFOA and PFOS (See letters to the FDEP dated April 16, 2018 and August 16, 2018 for details regarding the derivation of those screening levels). For consistency, the same RfD values are used in the surface water calculation, i.e., an oral reference dose (RfD) of 2E-05 mg/kg-d for both PFOA and PFOS.

We are aware that there is a lack of consistency among federal and state agencies in the derivation of safe limits for oral exposure to these substances. The Agency for Toxic Substances and Disease Registry (ATSDR) has recently released a draft toxicity profile for PFAS, including PFOA and PFOS. The proposed Minimal Risk Levels (MRLs; analogous to RfDs) are an order of magnitude lower than the USEPA RfDs. This draft document received extensive public comment and has not yet been finalized. Additionally, North Carolina, Texas, Maine, Minnesota, and New Jersey have developed toxicity values for PFOA and PFOS based on differing endpoints and/or uncertainty factors. This results in different toxicity values than were proposed by the USEPA and ATSDR. Further, the potential toxicity of PFOA and PFOS is a subject of active research, and the data available is rapidly evolving. Thus, while the USEPA RfD values are used for the surface water screening levels proposed here, we recommend re-visiting these screening levels as new information develops. Use of the USEPA RfDs instead of toxicity values developed based upon other endpoints may underestimate the toxicity of PFAS.

Body Weight

The receptor of concern, and therefore the body weight assumption used in the equation, is dependent upon the toxicity value chosen for the assessment. As stated above, the toxicity values selected are the USEPA RfDs of 2E-05 mg/kg-d for PFOA and PFOS. These are based on developmental effects. Specifically, the critical effect for PFOA is decreased ossification of pup phalanges and accelerated preputial separation (USEPA, 2016a). The critical effect for PFOS is decreased pup weight (USEPA, 2016b). Because these effects are based on the developing fetus and newborn pup, the receptor of concern for PFOA and PFOS is the pregnant/lactating woman. This is because fetal and newborn exposure to PFOA and PFOS from fish consumption will be dependent upon the mother's consumption of fish. Body weights used in risk equations are usually based on means. Therefore, we chose a mean body weight of 75 kg for pregnant women (USEPA, 2011, Table 8-29). This is based on a National Health and Nutrition Examination Survey (NHANES) 1999-2006 study of 1,222 American pregnant women in all trimesters of pregnancy. We could not locate any studies on the body weights of lactating women. The mean body weight of pregnant women (75 kg) is lower than the average body weight for all adults (80 kg) and is slightly higher than the average body weight for adult females (73 kg; USEPA, 2011, Table 8-5).

Relative Source Contribution

This assessment uses the USEPA recommended relative source contribution (RSC) of 20% (0.2) for PFOA and PFOS. These RSCs were developed for use in calculating drinking water health advisory levels and human health-based criteria for surface water (USEPA, 2000b; USEPA, 2016a; USEPA, 2016b). Chemical-specific RSCs for PFOA and PFOS were derived by the USEPA using their Exposure Decision Tree methodology (USEPA, 2000b). Using this methodology, the USEPA concluded there are significant potential sources of PFOA and PFOS other than drinking water ingestion. Other potential exposures to PFOA and PFOS include consumption of fresh and estuarine fish, consumption of marine fish, eating food packaged in material that contains PFAS, inhalation of contaminated dust, and from consumer products (e.g., non-stick cookware, stain resistant clothing). However, there is not enough information to characterize the exposure quantitatively. Therefore, the USEPA recommended default RSC of 20% was used for both chemicals. The decision to use an RSC of 20% to calculate screening levels for PFOA and PFOS in surface water is consistent with USEPA's recommendation to use the same RSC for the calculation of drinking water advisory levels for the two compounds (USEPA, 2016a; USEPA, 2016b).

Finfish and Shellfish Consumption Rate

There are studies of fish consumption rates for pregnant and lactating women; however, none are specific to Florida or the Southeast U.S. We could only locate three studies that surveyed fish consumption in pregnant and lactating women. Of these, only one was from the United States. There are several other studies that measured consumption rates based on ranges. These studies list the percent of women that consume the amount of fish in each range. It was not possible to elucidate fish consumption rates for upper percentiles from these studies.

The U.S. fish consumption study (Oken et al., 2008) included a cohort of 341 pregnant women from Massachusetts. The 88th percentile fish consumption rate during pregnancy was 48.5 g/d. This is similar to the NHANES fish consumption rate for the Northeastern U.S. of 45.0 g/d (USEPA, 2014). The fish consumption rate for pregnant women in Massachusetts appears to reflect the regional fish consumption rate. Two studies were identified on fish consumption for pregnant women in Europe. Miklavcic et al. (2011) surveyed fish consumption for 574 pregnant and lactating women in Slovenia. The 90th percentile fish consumption rate was 40.1 g/d. Another study in Sweden, (Bjornberg et al., 2003) surveyed fish and shellfish consumption for 689 women the year that the woman became pregnant. The 90th percentile fish and shellfish consumption rate was 56 g/d. Bjornberg et al. (2003) stated the average seafood consumption for pregnant women in Sweden (25 g/d) is similar to the average consumption of non-pregnant women in Sweden from the same age range (30 g/d). While the pregnant/lactating woman fish ingestion rate for Florida is unknown, it is likely to follow a similar trend as the other studies have shown. Specifically, pregnant/lactating women do not appear to eat an appreciably larger or smaller amount of fish than other adults in the region. Instead of using the pregnant woman fish consumption rate from Massachusetts, we recommend using an adult finfish region-specific consumption rate for the development of surface water screening levels in Florida.

No current Florida-specific fish consumption studies are available. The Degner et al. (1994) fish consumption study in Florida was used previously to develop fish consumption rates for Chapter 62-302, F.A.C. However, it is dated and may not represent current fish consumption rates. Therefore, we used NHANES 2003-2010 fish consumption data. The NHANES data are presented based on age, gender, and geographic region. Intake rates in risk equations are usually based on upper-percentile values.

We could not locate any studies regarding shellfish consumption during pregnancy, excepting the study by Bjornberg et al. (2003) which combined fish and shellfish consumption. The Degner et al. (1994) fish consumption study includes Florida-specific data on shellfish consumption for the general population. As stated above, this study is dated and may not represent current shellfish consumption rates.

The USEPA document summarizing the NHANES fish and shellfish consumption data presents several consumer categories that may be relevant to fish consumption in Florida (USEPA, 2014). However, none are specific to Florida or pregnant women. It does not appear appropriate to use national data to represent fish consumption rates in Florida, especially when data are provided for different geographic regions. The female fish and shellfish consumption rates and woman of childbearing age fish and shellfish consumption rates are based on national data. Based on the differences in fish and shellfish consumption rates for each geographic region in the U.S., these national data may not be appropriate for Florida.

Regional data applicable to Florida include the South, Gulf of Mexico coastal counties, and Atlantic coastal counties. For a Florida-specific fish consumption rate, we calculated a weighted consumption based on the percentage of the Florida population within each region (FDEP, 2016) and the freshwater and estuarine finfish and shellfish consumption rate for these regions (USEPA 2014, Table 9b). The 90th percentile Florida-specific freshwater and estuarine finfish and shellfish weighted consumption rate is 29.0 g/d (0.029 kg/d) (Table 2).

Table 2 – Derivation of a Florida-specific freshwater and estuarine finfish and shellfish consumption rate

Region	90th Percentile freshwater and estuarine finfish and shellfish consumption (g/d)	Percentage of Florida population in each region	Weighted consumption (g/d)
South	26.3	23.6	6.2
Gulf of Mexico	28.6	31.6	9.0
Atlantic	30.8	44.8	13.8
		Total weighted consumption	29.0

Bioaccumulation Factor

Bioaccumulation factors (BAFs) for PFOA and PFOS from the literature are listed in Appendix Tables A1 and A2. The literature search was conducted on May 1, 2019. Studies that included data on bioaccumulation in the muscle tissue (e.g., fillet) were utilized to calculate the freshwater BAFs. These studies include fish not present in Florida (e.g., rainbow trout) and fish not usually consumed (e.g., minnows, whitebait). The BAFs for these fish were used to calculate a freshwater BAF for PFOA and PFOS because bioaccumulation data in fish and shellfish are limited. By including all of the data available, it provides a better estimate of the BAF. Based on the data listed in Appendix Tables A1 and A2, there is no general trend regarding the bioaccumulation of PFOA and PFOS in fresh versus marine environments.

Bioaccumulation factors for the derivation of human health surface water criteria were calculated based on a modified version of the USEPA framework for deriving BAFs (USEPA, 2016c). Based on the USEPA proposed framework, we utilized field BAFs to calculate baseline BAFs for PFOA and PFOS. Field BAFs are the preferred source for calculating BAFs for nonionic organic chemicals. Typically, in this methodology, a baseline BAF is calculated based on the field BAF, the concentration of particulate organic carbon (POC) in the water, the concentration of dissolved organic carbon (DOC) in the water, the chemical-specific n-octanol-water partition coefficient (Kow), and the fraction of finfish and shellfish tissue that is lipid. However, for the purposes of this assessment, the field BAFs were used as the baseline BAFs. The reasoning for this includes:

1. The POC and DOC were not known for the majority of the BAF studies. Calculation of the fraction of chemical in water that is freely dissolved would require assumptions regarding the amount of dissolved and particulate carbon. Although national averages may be used as defaults, the majority of studies took place outside the United States and default POC and DOC values for these countries are unknown.

2. The K_{ow} has not been measured for PFOA and PFOS. Calculation of a baseline BAF would require a K_{ow} based on physical/chemical property estimation software (e.g., EPI Suite).

3. Unlike most non-ionic organics, PFAS are not distributed to the lipid. Therefore, use of a lipid adjustment to derive a baseline BAF is inappropriate for PFAS chemicals.

Individual field BAFs were combined as the geometric mean for each species. Species BAFs for PFOA and PFOS are presented in Appendix Tables A3 and A4, respectively. The baseline BAF is calculated as the geometric mean of all species geometric means (Table 3). Two of the studies (Naile et al., 2013; MPCA, 2007b) combined several species to calculate a study-specific BAF. The BAFs calculated by the State of Minnesota for bluegill and white bass are geometric means (MPCA, 2007b) and were retained in the assessment. However, geometric means were not provided in Naile et al. (2013). These BAFs were based on arithmetic means. Therefore, the Naile et al. (2013) BAFs were not included in the baseline BAF calculations.

Table 3 – Geometric mean bioaccumulation factor for freshwater and estuarine finfish and shellfish

Bioaccumulation Factor (L/kg)	PFOA	PFOS
Freshwater and estuarine finfish and shellfish	68	2358

The BAF for PFOA of 68 L/kg is the geometric mean concentration of 12 BAFs. These BAFs represent 12 different species in 3 different studies. The BAF for PFOS of 2358 L/kg is the geometric mean concentration of 16 BAFs. These BAFs represent 16 species in 4 different studies.

Screening levels

Surface water screening levels for PFOA and PFOS were calculated using the Equations and Assumptions section of this document and are presented in Table 4.

Table 4 – Surface water screening levels for freshwater and estuarine finfish and shellfish

Surface Water Screening Levels (μg/L)	PFOA	PFOS
Freshwater and estuarine finfish and shellfish	0.15	0.004

The USEPA drinking water Health Advisory Levels (HALs) for PFOA and PFOS are each 0.07 μg/L. The USEPA recommends that the combined concentrations of PFOA and PFOS in drinking water be compared with this limit, based upon an assumption that their effects are additive. The rationale for this assumption is that their RfDs are derived for the same toxic endpoint (developmental effects) and that, although the mode of action for these effects has not been established, it is likely to be the same for these closely related chemicals. The fact that their individual Health Advisory Levels are identical makes it relatively straightforward to implement this recommendation. While the same argument could be made that the surface water screening levels for PFOA and PFOS should also address combined effects, this is more difficult because of the large difference in their values, approximately two orders of magnitude. Picking the lower, higher, or average of these values for comparison with combined PFOA and PFOS concentrations could result in gross over- or underestimation of risk, depending on the individual PFOA and PFOS concentrations. As a practical matter, comparison of PFOA and PFOS concentrations in surface water with the screening levels should be made individually.

Surface water screening levels in other states

Table 5 – Surface water screening levels in other states

State	PFOA (μg/L)	PFOS (μg/L)
Minnesota (lakes)	1.6	0.006
Minnesota (rivers)	2.7	0.007
Michigan	0.42	0.011
Alaska	0.07*	0.07*

* - Concentrations of PFOA and PFOS are summed before being compared to the criterion.

Minnesota has also developed freshwater surface water criteria based on fish consumption for the protection of human health. These criteria are based on site-specific bioaccumulation factors. For PFOA, the Minnesota surface water criteria include 1.6 μg/L for lakes and 2.7 μg/L for rivers (MPCA, 2017; Table 5). These criteria are higher than our proposed screening level of 0.15 μg/L. The difference in values is due to the use of a higher oral reference dose (1.4E-04 mg/kg-d) and slightly lower bioaccumulation factor (40 L/kg for lakes and 24 L/kg for rivers). Recently, the Minnesota Department of Health (MDOH) updated their reference doses for PFOA and PFOS (MDOH, 2019a; MDOH, 2019b). The updated reference dose for PFOA is 1.8E-05 mg/kg-d (MDOH, 2019a). Using this reference dose in their surface water equation would decrease the Minnesota criterion by approximately one order of magnitude. These updated values would be similar to our proposed screening level of 0.15 μg/L.

The screening level for PFOS is lower than PFOA due to the large bioaccumulation factor for PFOS. For PFOS, the Minnesota surface water criteria include 0.006 μg/L for lakes 0.007 μg/L for rivers (MPCA, 2017). Our proposed PFOS screening level of 0.004 μg/L is similar to these two criteria. This is due to the use of a similar reference dose (8E-05 mg/kg-d), bioaccumulation factors (6,087 L/kg for lakes and 3,877 for rivers), and fish ingestion rate (0.030 kg/d) (MPCA, 2010a; MPCA, 2010b). The MDOH updated reference dose for PFOS is 3.1E-06 mg/kg-d (MDOH, 2019b). Use of this reference dose would lower the PFOS criteria to less than 0.001 μg/L, which is below our proposed screening level of 0.004 μg/L.

The Michigan Department of Environmental Quality (MDEQ) criteria for PFOA and PFOS are human health-based non-cancer values for surface drinking water sources. They were derived based on Michigan Rule 57 for toxic substances (MDEQ, 2015; Table 5). The Alaska Department of Environmental Conservation uses a criterion of 0.07 μg/L for PFAS in surface water used as drinking water (ADEC, 2019; Table 5). The criterion includes the sum of PFOA and PFOS concentrations. It is based on the USEPA drinking water HAL.

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Appendix

Table A1 – Bioaccumulation factors for PFOA in fish fillets and shellfish tissue

Species	Place	Fresh or Marine	Exposure	Tissue	BAF	Study
Common carp	laboratory	Fresh	static 28d, 28d flow through depuration	muscle	3.85	Fang et al, 2016
Minnow	Taihu Lake, China	Fresh	wild caught	muscle	112.5	Fang et al., 2014
Silver carp	Taihu Lake, China	Fresh	wild caught	muscle	11.8	Fang et al., 2014
Whitebait	Taihu Lake, China	Fresh	wild caught	muscle	147	Fang et al., 2014
Crucian carp	Taihu Lake, China	Fresh	wild caught	muscle	81	Fang et al., 2014
Lake saury	Taihu Lake, China	Fresh	wild caught	muscle	284	Fang et al., 2014
Common carp	Taihu Lake, China	Fresh	wild caught	muscle	177	Fang et al., 2014
Mongolian culter	Taihu Lake, China	Fresh	wild caught	muscle	161	Fang et al., 2014
Mud fish	Taihu Lake, China	Fresh	wild caught	muscle	163	Fang et al., 2014
Chinese bitterling	Taihu Lake, China	Fresh	wild caught	muscle	87.9	Fang et al., 2014
Goby	Taihu Lake, China	Fresh	wild caught	muscle	37.7	Fang et al., 2014
Common carp	China	Fresh	wild caught	muscle	182	Zhou et al., 2012
Finfish	Korea	Marine	wild caught	fillet	16.2	Naile et al., 2013
White shrimp	Taihu Lake, China	Fresh	wild caught	soft part	12.5	Fang et al., 2014
Pearl mussel	Taihu Lake, China	Fresh	wild caught	soft part	39.7	Fang et al., 2014
Crab	Korea	Marine	wild caught	soft tissue	77.6	Naile et al., 2013

BAF – bioaccumulation factor

Table A2 – Bioaccumulation factors for PFOS in fish fillets and shellfish tissue

Species	Place	Fresh or Marine	Exposure	Tissue	BAF (L/kg)	Study
Bluegill	Lake Calhoun, MN	Fresh	wild caught	fillet	2802	MPCA, 2007b
Bluegill and white bass	Mississippi River, MN	Fresh	wild caught	fillet	5737	MPCA, 2007b
Common carp	laboratory	Fresh	static 28d, 28d flow through depuration	muscle	9500	Fang et al, 2016
Minnow	Taihu Lake, China	Fresh	wild caught	muscle	3212	Fang et al., 2014
Silver carp	Taihu Lake, China	Fresh	wild caught	muscle	832	Fang et al., 2014
Whitebait	Taihu Lake, China	Fresh	wild caught	muscle	1350	Fang et al., 2014
Crucian carp	Taihu Lake, China	Fresh	wild caught	muscle	6898	Fang et al., 2014
Lake saury	Taihu Lake, China	Fresh	wild caught	muscle	4401	Fang et al., 2014
Common carp	Taihu Lake, China	Fresh	wild caught	muscle	3679	Fang et al., 2014
Mongolian culter	Taihu Lake, China	Fresh	wild caught	muscle	6927	Fang et al., 2014
Mud fish	Taihu Lake, China	Fresh	wild caught	muscle	4854	Fang et al., 2014
Chinese bitterling	Taihu Lake, China	Fresh	wild caught	muscle	2861	Fang et al., 2014
Goby	Taihu Lake, China	Fresh	wild caught	muscle	2876	Fang et al., 2014
Common carp	China	Fresh	wild caught	muscle	11749	Zhou et al., 2012
Finfish	Korea	Marine	wild caught	fillet	1660	Naile et al., 2013
Taihu Lake shrimp	Taihu Lake, China	Fresh	wild caught	soft part	2161	Fang et al., 2014
White shrimp	Taihu Lake, China	Fresh	wild caught	soft part	978	Fang et al., 2014
Freshwater mussel	Taihu Lake, China	Fresh	wild caught	soft part	256	Fang et al., 2014
Pearl mussel	Taihu Lake, China	Fresh	wild caught	soft part	466	Fang et al., 2014
Crab	Korea	Marine	wild caught	soft tissue	141	Naile et al., 2013

BAF – bioaccumulation factor

Table A3 – Species-specific BAFs and geometric mean BAF for PFOA

Species	Scientific name	BAF
Crucian carp	*Carassius cuvieri*	81
Lake saury	*Coilia mystus*	284
Goby	*Ctenogobius giurinus*	37.7
Mongolian culter	*Culter mongolicus*	161
Silver carp	*Hypophthalmichthys molitrix*	11.8
Whitebait	*Reganisalanx brachyrostralis*	147
Chinese bitterling	*Rhodeus sinensis*	87.9
Common carp	*Cyprinus carpio*	50
White shrimp	*Exopalaemon sp.*	12.5
Minnow	*Hemiculter leucisculus*	112.5
Pearl mussel	*Lamellibranchia sp.*	39.7
Mud fish	*Misgurnus anguillicaudatus*	163
	Geometric mean BAF	62

Table A4 – Species-specific BAFs and geometric mean BAF for PFOS

Species	Scientific name	BAF (L/kg)
Crucian carp	*Carassius cuvieri*	6898
Lake saury	*Coilia mystus*	4401
Goby	*Ctenogobius giurinus*	2876
Mongolian culter	*Culter mongolicus*	6927
Silver carp	*Hypophthalmichthys molitrix*	832
Whitebait	*Reganisalanx brachyrostralis*	1350
Chinese bitterling	*Rhodeus sinensis*	2861
Common carp	*Cyprinus carpio*	7433
White shrimp	*Exopalaemon sp.*	978
Minnow	*Hemiculter leucisculus*	3212
Freshwater mussel	*Lamellibranchia sp.*	256
Pearl mussel	*Lamellibranchia sp.*	466
Bluegill	*Lepomis macrochirus*	2802
Taihu Lake shrimp	*Macrobrachium nipponense*	2161
Mud fish	*Misgurnus anguillicaudatus*	4854
Bluegill and white bass[c]	various sp.	5737
	Geometric mean BAF	2358

[c]Geometric mean concentrations including *Lepomis macrochirus* and *Morone chrysops*