LEVELS OF PFOS RECOVERED FROM LES CHENEAUX WATERS AND FROM LES CHENEAUX FISH

LES CHENEAUX WATERSHED COUNCIL

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ABSTRACT: Waters and selected fish species were examined for perfluorooctane sulfonate (PFOS) content to develop baseline data. PFOS concentrations recovered from LC waters were at, or below, the instrumentation detection limit of 1.25 part per trillion. Levels of PFOS found in fish muscle was consistently lower than in fatty tissue. Concentrations of PFOS in Yellow Perch (Perca flavescens) averaged 12.8 parts per billion, a similar range reported by the MI Department of Environment, Great Lakes and Energy (EGLE). As of 2023, PFOS levels in LC fish are considered the standard to which fish from other MI waters bodies are compared by MDNR and EGLE.

BACKGROUND: Per- and polyfluoroalkyl substances (PFAS) comprise a class of synthetic compounds that have been detected in all environments surveyed. (1). These compounds have been produced for over 80 years, and are found ubiquitously in all environments, plants and animals, to include in the human body. Perfluorooctane sulfonate, or perfluorooctane sulfonic acid (PFOS), is the terminal metabolite of a family of thousands of fluorinated hydrocarbons. As the terminal metabolite, PFOS can be expected to be most commonly recovered from environmental sources.

Filtration systems that can remove PFOS from residential drinking water are available but methods to remove the compounds to “safe” levels in food are of concern. PFOS concentrations in fish is especially important to Michigan residents due to the popularity of anglers catching their own meals from MI streams, lakes and from Lakes Michigan and Huron. Fish consumption guidelines have been published by the DNR which indicates, by county, the safety of eating a wide variety of native fish (2). Fish consumption data for PFOS have not yet been established.

Data were presented by DNR and EGLE during a 2023 MDNR Fisheries meeting in Cedarville (Les Cheneaux Islands) that reported findings for PFOS recovered from multiple fish species from the Straits of Mackinac area over a six-year period (3). The EGLE report included data for Yellow Perch but did not include information for other fish commonly caught by Les Cheneaux (LC) anglers such as Northern Pike, Small & Largemouth Bass.

Both summer and winter angling are popular in LC. Due to the angling popularity, this study was initiated to determine PFOS levels recovered from commonly caught fish in LC. Fish were made available from the annual 2024 fall DNR netting.

Literature indicates that the total PFOS concentrations recovered from fish is the result of PFOS in the water body from which the fish was taken (bioaccumulation) as well as the concentrations found in the fish itself (4). In addition to PFOS levels in the water body from which the fish was taken, concentrations found in the fish food web contribute as well as. The more food from the lower web organisms consumed, the more PFOS will be "biomagnified" in the fish examined.

METHOD:

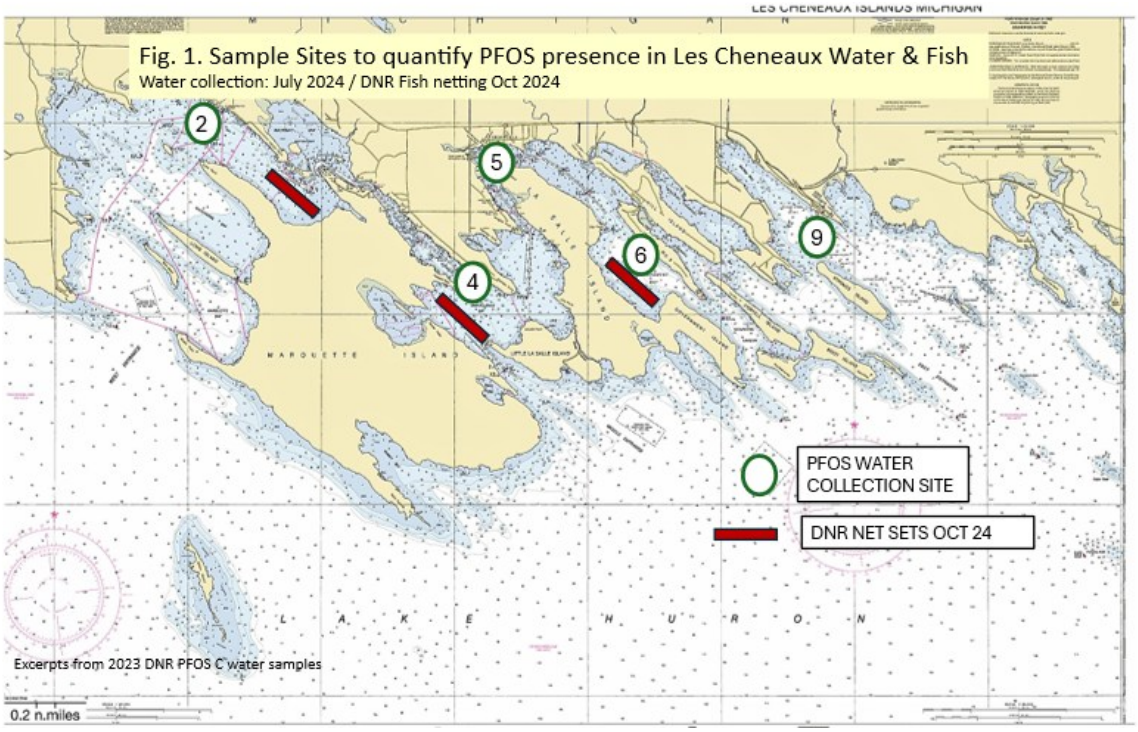
PFOS in LC waters. Water samples were collected and delivered to the Superior Analytical Laboratory (SAL) at Lake Superior State University (LSSU) for PFOS analysis by members of the Les Cheneaux Watershed Council (LCWC) and the Les Cheneaux Islands Association (LCIA) in July 2024. Triplicate water samples were taken at each of five sites historically monitored for recreational water quality by LCWC and LCIA (Fig.1). PFOS analytes (classes of PFAS compounds) were quantified by SAL to a lower instrument sensitivity of 1.25 parts per trillion using an Agilent 1290 liquid chromatograph with a 6470 tandem mass spectrometer (App A).

PFOS in LC fish. LCWC obtained multiple fish per species from the 2024 DNR net survey from which the organs had been removed for DNR research purposes. Specimens were then frozen until examined for the presence of nine different analytes (classes of PFOS) in the fatty tissues (lipid) and flesh (muscle) samples by the Superior Analytical Laboratory (SAL) at Lake Superior State University (LSSU). PFOS analytes were quantified to levels of parts per billion (ppb) using the same instrumentation used for water studies (App B). Species studied were Yellow Perch (*Perca flavescens*, YEP), Smallmouth Bass (*Micropterus dolomieu*, SMB), Brown Bullhead (*Ameriurus nebulosus*, BBH, BB) and Northern Pike (*Esox lucius*, NOP). The weight and sex of each specimen was recorded as shown in (App C). SMB sex could not be determined due to the organ removal process. Net sets were in three LC locations surveyed annually by MI DNR for over fifty years (Fig. 1).

RESULTS: Of nine PFAS analytes, only PFOS was present in detectable concentrations at the parts per trillion range (App 1). With an instrument detection limit of 1.25 parts per trillion (ppt), PFOS was undetectable in water samples from all sites except sites 4 and 5. The PFOS concentration at site 5 averaged 1.99 ppt and one PFOS sample from site 4 was recorded at the detection limit of 1.25 ppt and averaged 1.99 ppt at site 5. This low PFOS concentration is almost two orders of magnitude less than expected based upon literature reports of concentration factors for bioaccumulation and biotransformation (1,4).

Data from an EGLE study of PFOS concentrations from fish in the Les Cheneaux and northern Lake Huron area indicated an average of 39 ppb (App D). Literature suggests that a factor from

PFOS concentrations recovered from fish is greater than levels in the found in the waters in which fish are found by approximately one thousandfold due biomagnification and bioaccumulation (4).



RESULTS: PFOS concentrations of species examined were uniformly higher in lipid samples vs muscle tissue (Table 1.). Highest PFOS levels were recovered from Smallmouth Bass and Northern Pike vs. lowest concentrations recovered from Yellow Perch and Brown Bullhead. In a separate study YEP muscle values were reported by EGLE from three sampling events in the Les Cheneaux area from 2016 through 2021 (App D). See Table 1 EGLE inset. With these limited data, the PFOS levels in YEP were recorded in the same range for this LCWC study and for the EGLE study. PFOS is known to be better adsorbed into lipid regions than into muscle regions and that was the case for this study in that PFOS concentrations were uniformly higher for lipid-rich regions than for muscle regions of each species.

TABLE 1. PFOS CONC REPORTED AS PART PER BILLION (ppb)
<PFOSDAT LCI DNR 2024 BD19>

SPECIES (a)	n = (b)	LIPID	AVG	MUSCLE	AVG
YEP	5	19 - 49	24.9	7.0 - 15.0	12.8
SMB	5	98 - 311	200.1	105 -340	169.0
BH	5	16-47	30.5	18-24	21.0
NOP	4	211-392	306.8	149-283	191.8

Key:

(a) YEP: Yellow Perch
SMB: Smallmouth Bass
BB: Brown Bullhead
NOP: Northern Pike

(b) n = number of fish sampled

EGLE YEP muscle data :
2016: < 0.25 ppb (below detection limit)
2021 a: 11 ppb
2021 b: 58 ppb

Mean PFOS lipid concentrations in LC fish were uniformly higher than for muscle values for Yellow Perch and for Brown Bullhead (Table 2). One would expect BB PFOS values to be higher than recorded since the BB is a bottom-dwelling species and could accumulate PFOS from the sediment. That BB lipid and muscle PFOS levels were so similar suggests that the LCI sediment PFOS concentrations can be expected to be relatively low. With minimal data from these four species, it was instructive to learn that the species lipid/muscle ratio was so similar. It is unknown currently if this is common with other species.

It is recommended that a repeat PFOS evaluation in LC fish netted from the upcoming 2025 DNR survey be conducted to learn year-to-year the range, if any, of differences in PFOS levels.

CONCLUSION: This LCWC study found that PFOS concentrations in YEP muscle from LC waters were in the same range reported by EGLE. Low PFOS levels in fish muscle reflected of the low PFOS concentrations found in LC waters which is consistent with reported biomagnification and bioaccumulation factors(4).

TABLE 2. MEAN PFOS VALUE RECORDED FOR EACH SPECIES (ppb)
<PFOSDAT LCI DNR 2024 BD48>

SPECIES	LIPID	MUSCLE	L/M RATIO
YEP	25	13	1.9
SMB	200	169	1.5
BH	30	21	1.4
NOP	307	192	1.6

Acknowledgments

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LITERATURE CITED

1. Barbo, N. et al., 2023. Locally caught freshwater fish across the United States are likely a significant source of exposure to PFOS and other perfluorinated compounds. Env. Res. 115165.
2. MI Dept of Health & Human Services. Eat Safe Food Guide. Michigan.gov/Eat Safe Fish.
3. EGLE. 2023. State of the fishery in the Les Cheneaux Islands. Mi Dept of Environment, Great Lakes and Energy (EGLE). Oral presentation.
4. WI Dept Natural Resources. 2021. Updated water and fish tissue sampling results from 2019 DNR PFAS Survey. June 2021.

APPENDIX.

A. PFOS recovered from Les Cheneaux Waters.

B. Raw data for PFOS recovered from Les Cheneaux fish.

C. Fish length and sex for specimens examined in this study.

D. EGLE data for PFOS concentrations recovered from fish in Les Cheneaux and in Northern Lake Huron over a six year period.

App A

PFOS recovered from Les Cheneaux Waters, Sep 2024
Analyte Concentration ng/L (ppt, parts per trillion)
<PFOS dat for LC waters SAL 25 Sep 2024>

Sample Name	Collection Date	N-EtFOSAA	N-MeFOSAA	PFBS	PFDA	PFHxS	PFHxA	PFNA	PFOS	PFOA
TS-2L	7/11/24	<1.25	<1.25	**1.86**	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-2R	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-2C	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-4L	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	**1.25**	<1.25
TS-4R	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-4C	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-5L	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	**1.75**	<1.25
TS-5R	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	**1.44**	<1.25
TS-5C	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	**2.79**	<1.25
TS-6L	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-6R	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-6C	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-9L	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-9R	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25
TS-9C	7/11/24	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25	<1.25

App B. Raw data from fish analysis by Superior Analytical Lab. 3 Jun 2025. Logged into Excel and formatted to Pub file format.

		Analyte Concentration (pg analyte / g sample)													
Sample Name	Sample Type	PFBA	PFPeA	PFHxA	L-PFBS	FBSA	PFOA	PFHxS	PFNA	PFDA	PFOS	L-PFNS	N-MeFOSAA	PFUdA
YEP 1	Lipid	47.94	5.44	9.10	2.04	<0.71	18.54	<0.71	9.75	6.60	48.78	<3.54	<17.69	21.02
YEP 2	Lipid	15.48	<4.57	12.48	2.21	<0.92	38.92	<0.92	7.52	<4.57	34.30	<4.57	<22.88	<22.88
YEP 3	Lipid	19.85	13.65	19.76	5.70	<1.21	12.42	<1.21	<6.04	<6.04	22.20	<6.04	<30.22	<30.22
YEP 4	Lipid	31.69	<5.88	26.13	2.49	<1.18	11.40	<1.18	5.87	<5.88	19.02	<5.88	<29.43	<29.43
YEP 5	Lipid	<4.03	<4.03	14.20	1.15	<0.81	8.26	<0.81	<4.03	8.37	39.02	<4.03	<20.16	<20.16
YEP 1	Muscle	<7.81	<7.81	<7.81	<1.56	<19.52	<7.81	<19.52	<7.81	<7.81	8.21	<7.81	<39.04	<39.04
YEP 2	Muscle	<8.97	<8.97	<8.97	<1.79	<22.43	11.74	<22.43	<8.97	<8.97	9.12	<8.97	<44.86	<44.86
YEP 3	Muscle	<5.34	<5.34	<5.34	<1.07	<13.36	6.45	<13.36	<5.34	<5.34	7.23	<5.34	<26.71	<26.71
YEP 4	Muscle	<16.37	<16.37	<16.37	<3.27	<40.93	<16.37	<40.93	<16.37	<16.37	17.11	<16.37	<81.85	<81.85
YEP 5	Muscle	<10.81	<10.81	<10.81	<2.16	<27.05	<10.81	<27.05	<10.81	<10.81	15.12	<10.81	<54.09	<54.09
SMB 1	Muscle	388.8	15.02	50.71	62.84	<2.63	32.42	<2.63	<13.12	<13.12	339.5	<13.12	<65.62	69.47
SMB 2	Muscle	391.4	<12.69	39.72	13.60	<2.54	14.69	<2.54	<12.69	14.42	129.2	<12.69	<63.46	<63.46
SMB 3	Muscle	219.6	15.94	22.82	4.02	<1.05	9.57	<1.05	<5.24	9.64	105.6	<5.24	<26.22	33.20
SMB 4	Muscle	195.5	<6.77	19.26	1.39	<1.35	11.66	<1.35	<6.77	16.22	125.7	<6.77	<33.84	43.58
SMB 5	Muscle	215.3	<7.93	20.97	3.34	<19.83	11.23	<19.83	<7.93	19.15	145.2	<7.93	<39.65	<39.65
SMB 1	Lipid	7.24	<6.15	9.78	1.45	<15.38	<6.15	<15.38	<6.15	12.24	257.1	<6.15	<30.77	45.12
SMB 2	Lipid	6.42	<3.85	11.23	0.80	<9.62	4.25	<9.62	<3.85	5.21	145.3	<3.85	<19.23	51.00
SMB 3	Lipid	4.57	<3.99	8.17	<0.80	<9.98	5.19	<9.98	<3.99	<3.99	189.1	<3.99	<19.96	36.21
SMB 4	Lipid	8.87	<2.98	9.12	<0.60	<7.44	5.97	<7.44	<2.98	11.87	98.11	<2.98	<14.88	19.45
SMB 5	Lipid	9.87	<3.24	10.55	1.07	<0.65	6.27	<0.65	<3.24	28.46	311.0	<3.24	<16.17	81.30
BULL 1	Lipid	18.96	<3.92	7.56	1.17	<0.78	5.61	<0.78	<3.92	<3.92	26.46	<3.92	<19.58	22.86
BULL 2	Lipid	43.46	<6.22	14.35	<1.24	<1.24	11.30	<1.24	<6.22	7.04	39.31	<6.22	<31.11	42.62
BULL 3	Lipid	36.81	<5.15	12.99	<1.03	<1.03	9.04	<1.03	<5.15	<5.15	47.92	<5.15	<25.77	28.01
BULL 4	Lipid	11.99	<4.55	12.23	<0.91	<0.91	5.89	<0.91	<4.55	<4.55	16.06	<4.55	<22.76	29.38
BULL 5	Lipid	12.33	<4.74	9.32	<0.98	<11.86	<4.74	<11.86	<4.74	5.12	22.84	<4.74	<23.71	24.91
BULL 1	Muscle	75.12	<9.59	24.33	6.12	<23.98	12.13	<23.98	<9.59	<9.59	17.19	<9.59	<47.96	<47.96
BULL 2	Muscle	88.22	<18.82	28.91	8.10	<39.54	<18.82	<39.54	<18.82	<18.82	21.33	<18.82	<79.08	<79.08
BULL 3	Muscle	67.19	<23.83	37.99	6.49	<59.57	<23.83	<59.57	<23.83	<23.83	<23.83	<23.83	<119.1	<119.1
BULL 4	Muscle	95.12	<11.74	31.21	8.12	<29.36	14.23	<29.36	<11.74	<11.74	18.12	<11.74	<58.72	<58.72
BULL 5	Muscle	110.6	<14.64	42.15	13.64	<2.93	17.29	<2.93	<14.64	<14.64	27.49	<14.64	<73.21	<73.21
PIKE 1	Lipid	19.88	<8.11	22.61	<1.62	<1.62	20.79	<1.62	17.45	31.50	392.1	<8.11	<40.55	61.99
PIKE 2	Lipid	10.54	<6.42	15.12	<1.28	<16.04	7.61	<16.04	<6.42	<6.42	211.3	<6.42	<32.09	45.30
PIKE 3	Lipid	5.14	<4.59	13.84	1.99	6.26	7.07	<0.92	15.63	40.79	400.6	<4.59	<22.96	73.94
PIKE 4	Lipid	15.93	<2.95	11.20	1.43	3.72	6.03	<0.59	14.41	22.67	223.2	<2.95	<14.77	30.53
PIKE 1	Muscle	22.45	<18.24	19.12	4.56	<45.61	<18.24	<18.24	<18.24	<18.24	184.1	<18.24	<91.22	<91.22
PIKE 2	Muscle	37.80	<9.92	23.53	6.00	17.17	15.72	<1.99	23.35	30.88	283.3	<9.92	<49.62	72.26
PIKE 3	Muscle	38.12	<4.60	10.27	5.12	2.13	10.18	<4.60	12.45	22.11	150.7	<4.60	<23.02	<23.02
PIKE 4	Muscle	24.12	<9.55	16.12	<9.55	3.12	9.82	<9.55	18.19	23.18	149.1	<9.55	<47.73	<47.73

*primary content of the sample

App. C. Fish length and sex data for specimens examined in this study. <download file>

Fish Species	Fish #	Length mm	Sex
Bullhead	1	355.6	Female
Bullhead	2	279.4	Female
Bullhead	3	381	Male
Bullhead	4	304.8	Female
Bullhead	5	330.2	Male
Yellow Perch	1	254	Female
Yellow Perch	2	228.6	Female
Yellow Perch	3	254	Female
Yellow Perch	4	203.2	Male
Yellow Perch	5	203.2	Male
Pike	1	673.1	Female
Pike	2	812.8	Male
Pike	3	635	Male
Pike	4	558.8	Female
Small Mouth Bass	1	431.8	N/A
Small Mouth Bass	2	406.4	N/A
Small Mouth Bass	3	330.2	N/A
Small Mouth Bass	4	406.4	N/A
Small Mouth Bass	5	457.2	N/A

App D

PFOS concentrations in fish collected from Les Cheneaux and Northern Lake Huron waters reported by DNR and EGLE from 2016 - 2021.

Location	Year	Species	Avg PFOS
			ppb (a)
Carp River	2018	Rainbow Smelt	15.7
Bois Blanc	2019	Lake Herring	6
Les Cheneaux	2016	Lake Whitefish	4.7
Les Cheneaux	2016	Bluegill	ND (b)
Les Cheneaux	2016	Bluntnose Minnow	5.5
Les Cheneaux	2016	Yellow Perch	ND
Les Cheneaux	2021	Yellow Perch	11
Les Cheneaux	2021	Rock Bass	79.8
Swan River (c)	2021	Chinook	4.8
Les Cheneaux	2021	Yellow Perch	57.6
Les Cheneaux	2021	Golden Shiner	16.8
Les Cheneaux	2021	Bluegill	155
De Tour	2021	Rainbow Smelt	142.3

Legend:
(a) Parts per billion
(b) Non-detected (< 0.25 ppb)
(c) Rogers City milking station

Data reported by Dave Fielder (DNR) and Brandon Armstrong (EGLE) May 2023