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"AVOID FOAM" AND OTHER CONSEQUENCES OF LIVING IN A WORLD WITH PFAS

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6 September 2023



SIGNS FROM OSCODA





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MICHIGAN PFAS SITES



https://gis-egle:#rub.arcgis.com/datasets/egle::michigan-pfas-sites/



MICHIGAN PFAS SITES





https://gis-egle:#wb.arcgis.com/datasets/egle::michigan-pfas-sites/

Air Force Base





PFAS IN MARQUETTE





- Historic: <u>Perfluorinatedalkyl</u> <u>Substances</u>
- Recent: <u>Perfluorinated and Polyfluorinatedalkyl</u>
 <u>Substances</u>
- Shorthanded: <u>Per- and Polyfluorinated</u> <u>Substances</u>

EPA used a limited definition of PFAS: "Chemicals with at least two adjacent carbon atoms, where one carbon is fully fluorinated and the other is at least partially fluorinated."

For the purposes of Nov 2022 CCL 5, the structural definition of per- and polyfluoroalkyl substances (PFAS) includes chemicals that contain at least one of these three structures:

- (1) R-(CF2)-CF(R')R", where both the CF2 and CF moieties are saturated carbons, and none of the R groups can be hydrogen.
- (2) R-CF2OCF2-R', where both the CF2 moleties are saturated carbons, and none of the R groups can be hydrogen.
- (3) CF3C(CF3)RR', where all the carbons are saturated, and none of the R groups can be hydrogen.







In 2017, the International Agency for Research on Cancer (IARC) classified perfluorooctanoic acid (PFOA), the most well-studied perand polyfluoroalkyl substance (PFAS), as a possible human carcinogen based in part on limited epidemiologic evidence of associations with cancers of the kidney and testis in heavily exposed subjects.



Perfluorooctanoic Acid = PFOA



MOST WELL-STUDIED PFAS



Perfluorooctanesulfonic acid

On August 26, 2022, EPA proposed designating these as hazardous substances under CERCLA, or Superfund. This rulemaking would increase transparency around releases of these harmful chemicals and help to hold polluters accountable for cleaning up their contamination. March 3, 2021, EPA made final determinations to regulate perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in drinking water March Safe Drinking Water Act (SDWA).

PFOA and PFOS are:

- man-made chemicals
- have been widely used in industry and consumer products since the 1940s
- remain in the environment for a long time.



Fluorinated organic substances:

- overwhelmingly man-made chemicals
- have been widely used in industry and consumer products since the 1940s
- remain in the environment for a long time.

The most famous naturally existing organic fluorine containing compound is probably monofluoroacetic acid (FCH₂CO₂H). This compound is found in a South African plant called "Gifblaar," which is known to be so poisonous that ingesting only a half of its leaf is enough to kill a cow.



EPIDEMIOLOGY

epidemiologic study was published in 1775 by Percival Pott of Saint Bartholomew's Hospital in London, who described cancer of the scrotum in chimney sweeps, caused by constant exposure to soot



1890s that a German surgeon reported the first cases of bladder cancer in dye workers. Ludwig Wilhelm Carl Rehn (1849–1930), Presented results 1895.



EPIDEMIOLOGICAL STUDIES OF PFOA AND PFOS

Decreased vaccine response in children

Research involving humans suggests that high levels of certain PFAS **may** lead to the following:



Increased cholesterol levels



Changes in liver enzymes



Increased risk of high blood pressure or pre-eclampsia in pregnant women



Small decreases in infant birth weights



Increased risk of kidney or testicular cancer



https://www.atsdr.cdc.gov/pfas/health-effects/index.html





PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)

With a few exceptions, any chemical with at least a perfluorinated methyl group (–CF3) or a perfluorinated methylene group (–CF2–) is a PFAS.



from Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance, July 2021



EVOLVING EPA DEFINITION

EPA used a limited definition of PFAS: "Chemicals with at least two adjacent carbon atoms, where one carbon is fully fluorinated and the other is at least partially fluorinated."

Per- and polyfluorinated substances that structurally contain the unit $R-(CF_2)-C(F)(R')R''$ where both the CF_2 and CF moieties are saturated carbons and none of the R groups (R, R', or R'') can be hydrogen. 2021 Multi-industry Report

As of November 2, 2022 Contaminant Candidate List (CCL) 5, the structural definition of PFAS includes chemicals that contain at least one of these three structures:

- 1. R-(CF2)-CF(R')R", where both the CF2 and CF moieties are saturated carbons, and none of the R groups can be hydrogen.
- 2. R-CF2OCF2-R', where both the CF2 moieties are saturated carbons, and none of the R groups can be hydrogen.

3. CF3C(CF3)RR', where all the carbons are saturated, and none of the R groups can be

The Contaminant Candidate List lists contaminants currently not subject to any proposed or promulgated national primary drinking water regulations but are known or anticipated to occur in public water systems. Contaminants listed may require future regulation under the Safe Drinking Water Act.























Tetrafluoroethylene





PTFE = Teflon





Hexafluoropropylene oxide (HFPO) dime asi the its animonium salt, FRD-902 (ammonium (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate)), are known as "GenX chemicals" because they are used in the GenX process. GenX is the Chemours trade name for technology used to make fluoropolymers without PFOA.











One of the most widely used fluorinated pesticides is bifenthrin. It targets insects' nervous system and is the prime ingredient in more than 600 pesticide formulations used on corn, soy, vegetables, berries and orchard crops. Bifenthrin is also a persistent pollutant with a half-life of 97 to 345 days in soil, depending on soil type.





Metofluthrin is a pyrethroid used as an insect repellent. The vapors of metofluthrin are highly effective and capable of repelling up to 97% of mosquitoes in field tests. Metofluthrin is used in a variety of consumer products, called emanators, for indoor and outdoor use.





Eli Lilly introduced Prozac (fluoxeine) in Jan 1988. It is the first marketed selective serotonin reuptake inhibitor. Over 25 million prescriptions per year in US alone - estimated over 100 million world wide. A top 25 drug. Listed by WHO as an essential medication. Best selling antidepresant of all time.

Fluoxetine = Prozac



Aprepitant, sold under the brand name Emend among others, is a medication used to prevent chemotherapy-induced nausea and vomiting and to prevent postoperative nausea and vomiting. HN-NH **Aprepitant** 2005 Green Chemistry Challenge winner



Nirmatrelvir is an antiviral medication developed by Pfizer which acts as an orally active 3C-like protease inhibitor. It is part of a nirmatrelvir/ritonavir combination used to treat COVID-19 and sold under the brand name Paxlovid.

NH

Nirmatrelvir = Paxlovid













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AFFF (AQUEOUS FILM-FORMING FOAM)



AFFF has a low viscosity and spreads rapidly across the surface of most hydrocarbon fuels. A water film forms beneath the foam, which cools the liquid fuel, stopping the formation of flammable vapors. This provides dramatic fire knockdown, an important factor in crash rescue firefighting.

polymeric membrane





Several studies found polytetrafluoroethylene (PTFE) cookware to contain residual PFOA in the low µg/kg range, concluding that fluoropolymer food contact materials were not likely to be a major source of PFASs. PFCAs, particularly PFOA, and fluorotelomer alcohols (FTOHs) have been shown to be released from coated cookware at normal cooking temperatures. Studies of migration into food during the cooking process are inconclusive. Only relatively small amounts are released into foods, when compared to concentrations that are found in the raw food.





Initial POSF-based product lines for surface treatment applications were developed in 1957 and marketed under the trade name of Scotchgard, and paper and packaging applications in the 1960s marketed under the trade name of Scotchban.

GREASE-RESISTANT FOOD PACKAGING





CR's Food Packaging Test Results

These results show levels of total organic fluorine, a measure of PFAS, in 118 food packaging products gathered from major fast-food and fast-casual restaurants, as well as supermarkets. PFAS in food packaging have been linked to potential harms to human health and the environment. Products with two red squares have 100 parts per million organic fluorine or more. Starting next year, California will ban food packaging that exceeds that level. Products with one red square have 20 ppm organic fluorine or more, a stricter standard for food packaging set by Denmark. CR supports that lower cutoff.





Burger King







Susmann, Herbert P., Laurel A. Schaider, Kathryn M. Rodgers, and Ruthann A. Rudel. "Dietary habits related to food packaging and population exposure to PFASs." Environmental health perspectives 127, no. 10 (2019): 107003. https://doi.org/10.1289/EHP4092













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https://www.sciencenewsdigital.org/sciencenews/library/item/november_19_2022/4055387/



Touching lake, river, or stream water that has PFAS is not an immediate health concern. You should avoid drinking or accidentally swallowing water. You should also avoid touching foam on the water that might be contaminated with PFAS. After being in water or touching feam, was hands and rinse pets to prevent swallowing PFAS that may be on skin or Avoid Foam.



Is off-white and/or brown Often accumulates in bays, where there is circular movement of water, or river blockages May smell earthy or fishy



Foam may have high amounts of PFAS. Rinse off foam after contact. Rinsing

> Be lightweight · Be sticky

in the lake or river is okay. Bathe or shower after the day's outdoor activities.

PFAS contaminated foam can:

shaving cream

· Be bright white · Pile up like

· Blow inland

Touching the water is not a health concern. Enjoy swimming, boating, and fishing.

Do not allow pets to drink foamy water. Rinse pets with water after contact with foam to avoid swallowing PFAS that may be on their fur.

For more information, call MDHHS at 800-648-6942 or visit www.michigan.gov/PFASresponse.



PFAS foam....



Can have bright white coloring Tends to pile up like shaving cream Can be sticky May blow inland and collect on lake shores and river banks Is usually lightweight





non-detectable in Marquette municipal water: https://www.marquettetownship.org/sites/g/files/vyhlif66666/f/uploads/2 021_marquette_township_ccr.pdf

City report does not list PFAS. https://www.marquettemi.gov/wp-content/uploads/2023/04/CCR_2022_4120.pdf



WASTEWATER TREATMENT

- Multiple biosolids samples were collected with the highest PFOS concentration of 3,600 µg/Kg.
- The PFOS concentrations of more recent biosolids concentrations sampled in 2020 ranged between 85 to 160 µg/Kg.
- Leaking AFFF tank at Sawyer





WWT DOESN'T REMOVE PFAS



Figure 25. PFOS Influent and Effluent Concentrations for the 42 WWTPs Assessment

Figure 33. Final Treated Solids (Sludge and Biosolids) PFOS Concentrations for 42 WWTPs

https://www.michigan.gov/-/media/Project/Websites/egle/Documents/Programs/WRD/IPP/pfas-initiatives-statewide-full-report.pdf?rev=946d5956f41b45a2a00d752149f57dc0



EGLE REPORTING FOR WASTEWATER TREATMENT

PFAS Family	PFAS Name	Acronym	CAS #	PFAS Family	PFAS Name	Acronym	CAS #	
	Perfluorobutanoic Acid	PFBA	ronymCAS #PFAS FamilyPFAS NamePFBA375-22-4Perfluoroalkane Sulfonamides (FASA)Perfluorooctane SulfonamidePFPA2706-90-3(FASA)Perfluoroalkane Sulfonamides (FASA)PFPA307-24-4(r.2) Fluorotelomer Sulfonic Acids6:2 Fluorotelomer Sulfonic Acid 8:2 Fluorotelomer Sulfonic AcidPFDA335-67-1N-Ethyl Perfluoroalkane Sulfonamidoacetic Acids (N- EtFASAA)N-Ethyl Perfluoroalkane Sulfonamidoacetic Acids (N- EtFASAA)PFDA307-55-1N-Methyl Perfluoroalkane Sulfonamidoacetic Acids (MeFASAA)N-Methyl Perfluorooctane Sulfonamidoacetic AcidPFDA307-55-1N-Methyl Perfluoroalkane Sulfonamidoacetic Acids (MeFASAA)N-Methyl Perfluorooctane Sulfonamidoacetic AcidPFDA307-55-1N-Methyl Perfluoroalkane Sulfonamidoacetic Acids (MeFASAA)N-Methyl Perfluorooctane Sulfonamidoacetic AcidPFDA375-92-8PFPes2706-91-4PFNS1763-23-1PFNS474511-07-4	FOSA	754-91-6			
	Perfluoropentanoic Acid PFPeA 2706-90-3 (FASA) Perfluorohexanoic Acid PFHxA 307-24-4 6:2 Fluorotelomer Sulfonic Acid Perfluorohexanoic Acid PFHpA 375-85-9 6:2 Fluorotelomer Sulfonic Acid							
Perfluoroalkyl Carboxylic Acids (PFCA)	Perfluorohexanoic Acid	PFHxA	307-24-4	(n:2) Fluorotelomer Sulfonic Acids	6:2 Fluorotelomer Sulfonic Acid	4:2 FTSA	757124-72-4	
	Perfluoroheptanoic Acid	PFHpA	375-85-9		6:2 Fluorotelomer Sulfonic Acid	6:2 FTSA	27619-97-2	
	Perfluorooctanoic Acid	PFOA	335-67-1		8:2 Fluorotelomer Sulfonic Acid	8:2 FTSA	39108-34-4	
	Perfluorononanoic Acid	PFNA	375-95-1	N-Ethyl Perfluoroalkane	N-Ethyl Perfluorooctane Sulfonamidoacetic Acid	EtFOSAA	2991-50-6	
	Perfluorodecanoic Acid	PFDA	335-76-2	EtFASAA)				
	Perfluoroundecanoic Acid	PFUnDA	2058-94-8	N-Methyl Perfluoroalkane	N-Methyl Perfluorooctane	MeFOSAA	2355-31-9	
	Perfluorododecanoic Acid	PFDoDA	307-55-1	Sulfonamidoacetic Acids				
	Perfluorotridecanoic Acid	PFTrDA	72629-94-8	(MeFASAA)				
	Perfluorotetradecanoic Acid	PFTeDA	376-06-7					
	Perfluorobutane Sulfonic Acid	PFBS	375-73-5		ne Sulfonamides ASA)Perfluorooctane Sulfonamidemer Sulfonic Acids6:2 Fluorotelomer Sulfonic Acidmer Sulfonic Acids6:2 Fluorotelomer Sulfonic Acid8:2 Fluorotelomer Sulfonic Acid8:2 Fluorotelomer Sulfonic Acidrfluoroalkane bacetic Acids (N- ASAA)N-Ethyl Perfluorooctane Sulfonamidoacetic Aciderfluoroalkane doacetic AcidsN-Methyl Perfluorooctane Sulfonamidoacetic Aciderfluoroalkane 			
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Perfluoroalkane Sulfonic Acids (PFSA)	Perfluorohexane Sulfonic Acid	PFHxS	355-46-4	F F F F O O F F F F F F F F F F F F F F				
	Perfluoroheptane Sulfonic Acid	PFHpS	375-92-8					
	Perfluorooctane Sulfonic Acid	PFOS	1763-23-1					
	Perfluorononane Sulfonic Acid	PFNS	474511-07-4					
	Perfluorodecane Sulfonic Acid	PFDS	335-77-3					
					6:2 diPAP			







Type of Fish	Chemicals of Concern	Size of Fish (length in inches)	MI Servings per Month*	Type of Fish	Chemicals of Concern	Size of Fish (length in inches)	MI Servings per Month*
Brown Trout	PCBs	Any	1 ^{2x}	Lake Whitefish	Dioxins	Any	1 ^{2x}
Durchat	Manual	Under 18"	4	Northern Pike	Mercury	Any	2
вигрос	wiercury	Over 18"	2	Rainbow Trout	PCBs	Any	2 ^{2x}
Chinook Salmon	PCBs	Any	6 Per Year ^{2x}	Siscowet	PCBs &	Any	Limited▲
Coho Salmon	PCBs & Toxaphene	Any	4 ^{2x}	Smelt	PFOS	Any	1
Lake Herring	Mercury	Any	8	Steelhead	PCBs	Any	2 ^{2x}
Lake Trout	PCBs & Toxaphene PCBs	Under 24"	2 ^{2x}	Suckers	Toxaphene	Any	2 ^{2x}
			·	Walleye	Mercury	Any	2
		24" to 28"	$- \frac{1^{2*}}{2}$	Yellow Perch	Mercury	Any	2
		Over 28"	6 Per Year ²				



MICHIGAN'S EAT SAFE FISH PROGRAM – AUGUST 2023 UPDATE

- Eat Safe Fish new interim fish consumption guidelines for rainbow smelt and carp as of August 2023.
 - The following waterbodies have new consumption guidelines for rainbow smelt due to PFOS:
 - Lake Huron: No more than 6 MI Servings per year.
 - Lake Michigan: No more than 1 MI Serving per month.
 - Portage Lake in Houghton County: No more than **1 MI Serving per month**.
 - Gull Lake in Kalamazoo County: No more than **2 MI Servings per month.**
 - Higgins Lake in Roscommon County: No more than 4 MI Servings per month.
 - Lake Superior: 1 MI Serving per month.



POSSIBLE HEALTH IMPACTS

- · reduction in immunity
- · metabolic diseases like obesity & diabetes
- · thyroid disfunction
- · reduced vaccination response
- · ulcerative colitis
- low sperm count
- smaller penis size
- · affect the growth, learning, and behavior of infants and older children
- · lower a woman's chance of getting pregnant
- · interfere with the body's natural hormones
- · increased cholesterol levels
- increased risk of testicular cancer
- increased risk of prostate cancer
- · increased risk of breast cancer
- · increased risk of heart disease
- · increased risk of kidney disease
- · increased risk of liver disease
- · increased risk of osteoarthritis
- increased risk of Parkinson's disease
- increased risk of autoimmune disease



HEALTH IMPACTS OF PFOA AND PFOS

Research involving humans suggests that high levels of certain PFAS **may** lead to the following:



Increased cholesterol levels



Changes in liver enzymes



Increased risk of high blood pressure or pre-eclampsia in pregnant women



Small decreases in infant birth weights

Decreased vaccine response in children



Increased risk of kidney or testicular cancer



https://www.atsdr.cdc.gov/pfas/health-effects/index.html

- Alternatives are being used
- Bans on added PFAS
- Regulators are reducing levels of concern
- Increased monitoring
- Implementation of removal technologies



ALTERNATIVES



Human blood levels of PFOA and PFOS in the US are more than 70–85% less than they were in 1999.







SHORTER CHAIN ALKYL

the estimated half-lives for short-chain PFASs (such as PFBA, PFBS and PFHxA) were found to range from a few days to approximately one month, whereas for compounds having a long perfluoroalkyl chain length (such as PFOA, PFNA, PFDA, PFHxS or PFOS), it can be several years.



PFBA

PFBS

In 2002, 3M announced a new fluorosurfactant as an alternative to perfluorooctane sulfonic acid (PFOS). The new chemical, perfluorobutane sulfonic acid (PFBS), was a shorter chain PFAS and was believed to be less biologically accumulative than its longer chain counterpart PFOS.





Regrettable Substitution



WHAT IS BEING DONE

- Bans on added PFAS
 - California, Colorado, Hawaii, Maine, Maryland, Minnesota, New York, Oregon, Rhode Island, Vermont, and Washington have passed laws on the manufacture and selling of articles containing PFAS.

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- Regulators are reducing levels of concern
 - EPA (June 2022):
 - PFOA from 70 ppt to 0.004 ppt
 - PFOS from 70 ppt to 0.02 ppt
 - GenX chemicals to 10 ppt
 - PFBS to 2 ppb (2000 ppt)

- WHO (29 Sept 2022):
 - PFOA 100 ppt
 - PFOS 100 ppt
 - total PFAS of 500 ppt (6 compounds)

Increasingly monitoring is for total organic fluorine (TOF) due to the increasing number of possible chemicals meeting new definitions of PFAS. Specific monitoring for ~40 cmpds out of >1500 (maybe greater than 4000) potential.



IMPLEMENT REMOVAL TECHNOLOGIES





- Reduce Use of Products Known to Migrate PFAS
- Reduce PFAS Levels in the Water You Drink and Foods You Eat
 - follow advisories on fish and game from contaminated areas



REASON FOR SOME OPTIMISM



Blood Levels of the Most Common PFAS in People in the United States Over Time from National Health and Nutrition Examination Survey (NHANES) cycle 1999-2000 to 2017-2018.

Data Source

Centers for Disease Control and Prevention. National Report on Human Exposure to Environmental Chemicals, Biomonitoring Data Tables for Environmental Chemicals. Atlanta, GA: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention.

TESTING GUIDANCE

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and a share		AR			Re-	Guidance on PFAS Exposure, Testing, and Clinical Follow-Up
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New Report Calls for Expanded PFAS Testing for People With History of Elevated Exposure, Offers Advice for Clinical Treatment News Release | July 28, 2022

WASHINGTON — Testing for exposure to perfluoroalkyl and polyfluoroalkyl substances, also known as PFAS, should be offered to patients who are likely to have a history of elevated exposure — such as those exposed to PFAS through their work or who live in areas with known PFAS contamination, says a new report from the National Academies of Sciences, Engineering, and Medicine. The report finds evidence of association between PFAS exposure and increased



- Using serum or plasma concentrations of the sum of the seven PFAS considered by the committee, patients whose tests show a PFAS blood concentration below 2 nanograms per milliliter (ng/mL) are not expected to have adverse health effects.
- Patients with test results between 2 and 20 ng/mL may face the potential for adverse effects, especially in sensitive populations (such as pregnant individuals). Clinicians should encourage reduction of PFAS exposure for these patients. Following the usual standard of care, clinicians should also prioritize screening for dyslipidemia, hypertensive disorders of pregnancy, and breast cancer based on age and other risk factors.
- Patients with test results above 20 ng/mL may face a higher risk of adverse effects. Clinicians should encourage exposure reduction and prioritize screening for dyslipidemia in accordance with guidance for patients with increased risk. In addition to the care recommended for patients who test between 2 and 20 ng/ml, clinicians should also conduct thyroid function testing, and assess for signs of kidney and testicular cancer and of ulcerative colitis at all wellness visits.
- The report recommends clinicians begin with a conversation on how a patient might be exposed to PFAS, and which exposures they
 are interested in reducing including questions about occupational exposures. Clinicians should also advise patients with elevated
 PFAS in their drinking water to filter their water. The report points to a database created by NSF International to help patients
 locate water filters that can reduce PFAS.



- Rapidly changing understanding
- Reasons for caution
 - with some reasons for optimism
- Reduce exposure

Forever chemicals will not be going away.





Slides will be posted on mjphd.net/presentations soon

