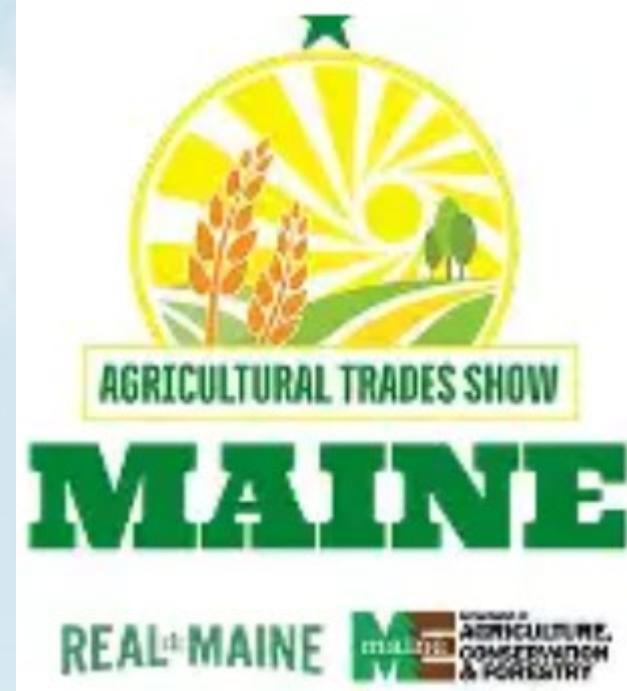




BOARD OF
PESTICIDES CONTROL

DEPARTMENT OF AGRICULTURE,
CONSERVATION & FORESTRY



PFAS-Pesticides: a tale of two toxicities

Doug Van Hoewyk, PhD. Toxicologist. Maine Board of Pesticide Control

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www.thinkfirstspraylast.org

This
Job
Last
Paint
Should
Forever.

WET PAINT
CLOSED
TODAY
COME
TO
HEAVEN!

PFAS

PFAS: Per-(or poly)fluoroalkyl substances

PFAS are molecules designed by chemists since the 1940s.

PFAS-products have altered chemical properties, which are often desirable.

However, many PFAS are extremely toxic.



Many PFAS are associated with negative health outcomes

Excerpted from ASTDR report:

<https://www.atsdr.cdc.gov/ToxProfiles/tp200-c2.pdf>

Health Effect Endpoint	PFOA	PFOS	PFHxS	PFNA	PFDA	PFUnA	PFHpA	PFBS	PFBA	PFDoDA	PFHxA	FOSA
Body weight	•	•	•	•	•	•			•			•
Respiratory	•											
Cardiovascular	•	•	•	•	•	•	•	•	•	•	•	•
Gastrointestinal		•										
Hematological	•	•										
Musculoskeletal	•	•	•	•								
Hepatic	•	•	•	•	•	•	•	•	•			
Renal	•	•	•	•	•		•		•	•		
Dermal												
Ocular												
Endocrine	•	•	•	•	•	•			•			
Immunological	•	•	•	•	•	•	•		•	•	•	
Neurological	•	•	•	•								
Reproductive	•	•	•	•	•	•	•		•	•	•	
Developmental	•	•	•	•	•	•	•	•	•			
Other noncancer	•	•	•	•	•	•	•					•
Cancer	•	•	•	•	•	•	•		•			•

FOSA = perfluorooctane sulfonamide; PFBA = perfluorobutanoic acid; PFBS = perfluorobutane sulfonic acid;
PFDA = perfluorodecanoic acid; PFDoDA = perfluorododecanoic acid; PFHpA = perfluoroheptanoic acid;
PFHxA = perfluorohexanoic acid; PFHxS = perfluorohexane sulfonic acid; PFNA = perfluorononanoic acid;
PFOA = perfluorooctanoic acid; PFOS = perfluorooctane sulfonic acid; PFUnA = perfluoroundecanoic acid

***However, not all PFAS molecules have the same toxicity.

In 2024, EPA set maximum contaminant levels for five toxic PFAS in drinking water

PFOA- 4 parts per trillion

PFOS- 4 parts per trillion

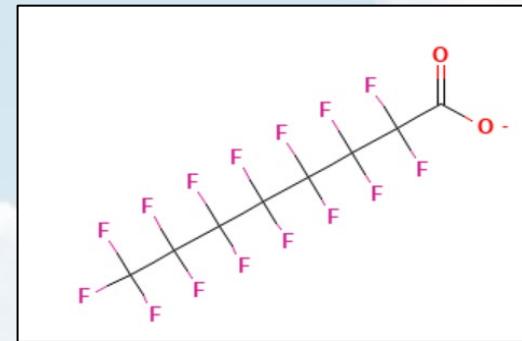
PFHxS- 10 parts per trillion

PFNA- 10 parts per trillion

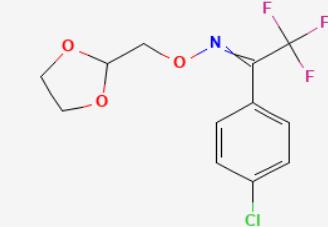
HFPO- 10 parts per trillion
(GenX)

Other states have set their own guidance on maximum contaminant levels for PFAS.

PFOA in Minnesota: 8 parts per Quadrillion



Fomesafen (herbicide) in Minnesota and Wisconsin: 20 and 25 parts per Million



Both PFOA and Fomesafen are PFAS. What explains the chemicals' nearly 9-million-fold difference in the maximum concentration level in Minnesota?

In chemistry, structure determines function.

- Structure of a chemical can also predict toxicity.

Structure also predicts function and potential hazards in modes of transport.



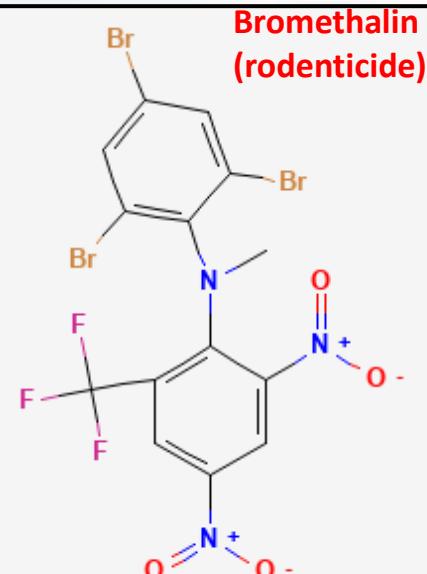
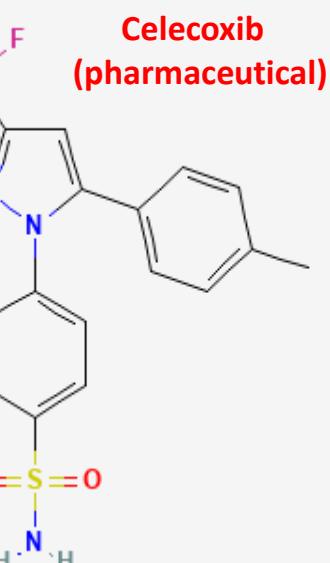
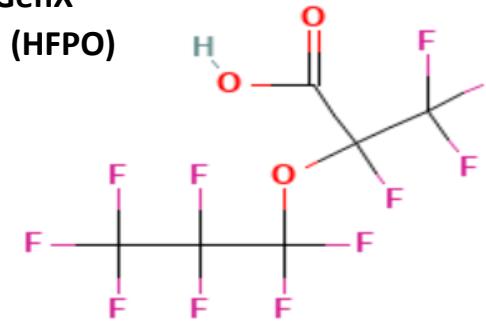
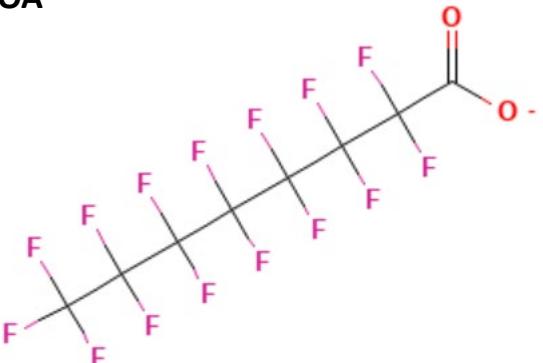
In chemistry, structure determines function.

- Structure of a chemical can also predict toxicity.

PFAS diversity



Structure also predicts function and potential hazards in modes of transport.



PFAS: Per-(or poly)fluoroalkyl substances

PFAS are a growing class of molecules designed by chemists.

Molecules: between 10,000 to >7,000,000

Pharmaceuticals: between 4 or 380 PFAS products

Pesticides: between 7 to 170 active ingredients

*** No 25(b) products are PFAS

Why is there a range in the number of PFAS molecules?



The definition of polyfluoroalkyl substances differs between agencies. But there are some commonalities.

PERIODIC TABLE OF THE ELEMENTS

The image shows the Periodic Table of the Elements with the following features:

- Group and Period Labels:** Groups 1, 2, 13-18, and 18 are labeled at the top. Periods 1-7 are labeled on the left.
- Element Properties:** A legend on the left provides information on atomic mass, element names, and symbols.
- Classification:** Elements are color-coded by category: Metal (blue), Semimetal (orange), Nonmetal (green), Alkali metal (light blue), Alkaline earth metal (light orange), Transition metals (dark blue), Chalcogens element (light green), Halogens element (medium green), Noble gas (light blue-gray), Lanthanide (light orange), and Actinide (light green).
- Standard State:** The standard state for each element is indicated: Ne - gas, Fe - solid, Hg - liquid, and Te - synthetic.
- Red Circled Element:** Fluorine (F) is circled in red.



Alkyl- molecule containing a carbon chain

Fluorine (F) atom

Rest of the molecule

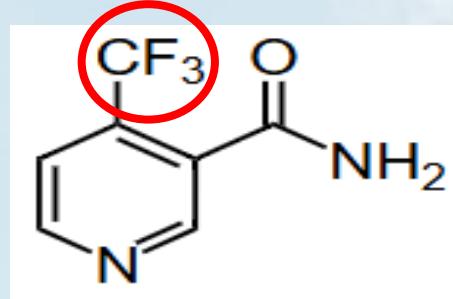
Carbon (C) atom

Rest of the Molecule

Fluorine (F) atom

PFAS definitions: the differences

Maine: "Perfluoroalkyl and polyfluoroalkyl substances" or "PFAS" means substances that include any member of the class of fluorinated organic chemicals containing at least one fully fluorinated carbon atom.



Connecticut, Minnesota, Rhode Island, Massachusetts, and several other states also define PFAS as a molecule with "fully fluorinated carbon" with minor verbiage differences.

Organization for Economic Cooperation and Development (OECD) and European Chemical Agency definition also contains reference to one "fully fluorinated carbon."

EPA OPPT: PFAS is "a structure that contains the unit R-CF₂-CF(R')(R''), where R,R',and R'' do not equal H and the carbon-carbon bond is saturated."

The definition of PFAS is timely and relevant.

PESTICIDES

Report from the American Chemical Society

4 new pesticides ignite debate over PFAS definition

Environmental advocates claim the chemicals are PFAS, but the EPA says they are not

by Britt E. Erickson

JUNE 24TH, 2025



All four pesticides proposed for registration by the US Environmental Protection Agency in the past 2 months contain at least one fully fluorinated methyl or methylene group, but the agency says they are not per- and polyfluoroalkyl substances.



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FACT CHECK: EPA Debunks False Claims that Agency Recently Approved "Forever Chemical" Pesticides

November 26, 2025

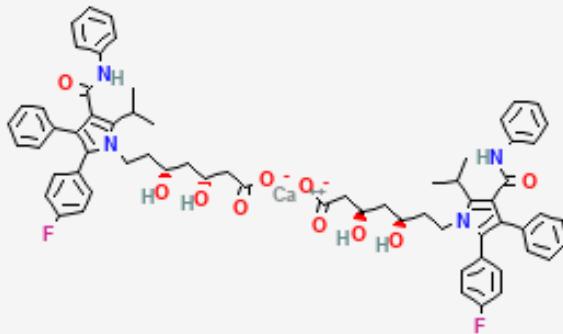
The definition of PFAS has societal implications for:

- 1. Policy Makers**
- 2. Regulatory Officials**
- 3. Public Health Officials**
- 4. Pesticide applicators**
- 5. Farmers and growers**

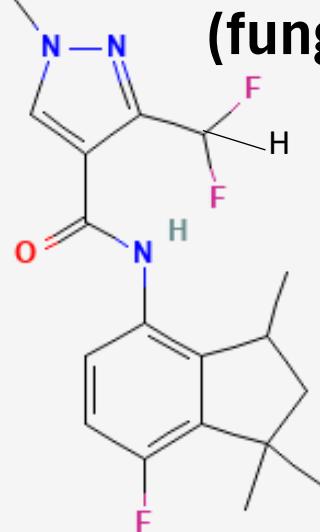
**In 2021, Maine became the first state to pass a ban on PFAS-pesticides.
This will go into effect in 2032.**

Minnesota has also enacted legislation that bans PFAS-pesticides.

A. Atorvastatin



B. Fluindapyr (fungicide)



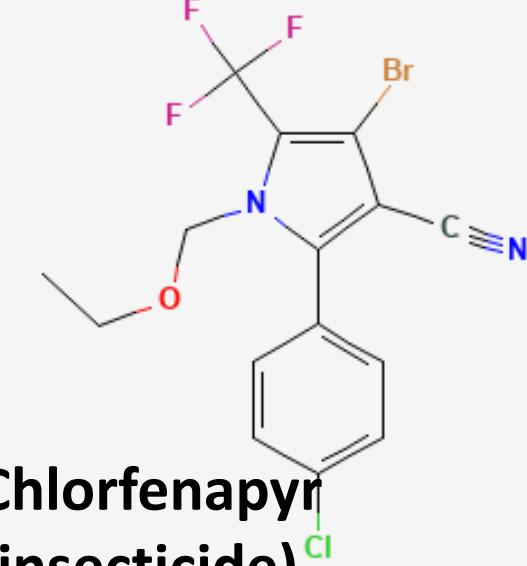
All of these are organo-fluorine molecules, because each has at least one fluorine atom.

But which chemical is a PFAS according to the OECD/Maine definition?
“fully fluorinated carbon”

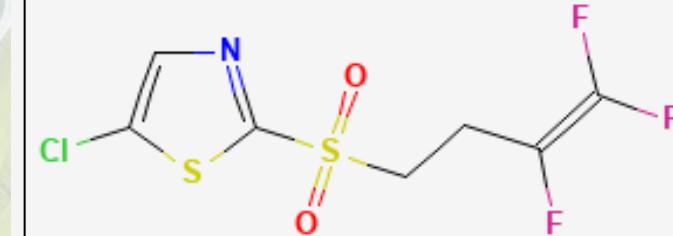
>>>Hint: Fluorine (F) is depicted in purple. The fully fluorinated carbon must:

- 1) Have at least two F
- 2) Not contain H,Cl,Br,I
- 1) Be a single bond (not double bond)

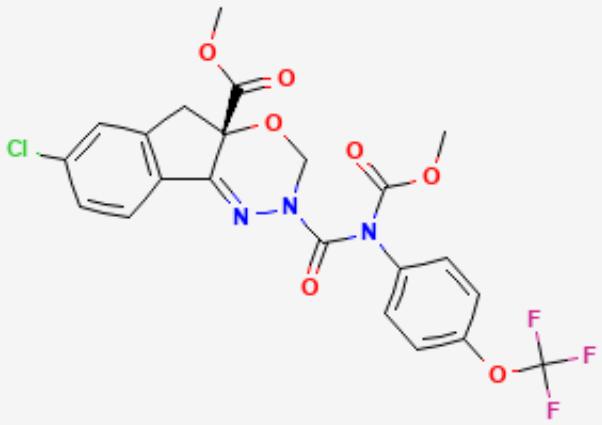
C. Chlorfenapyr (insecticide)



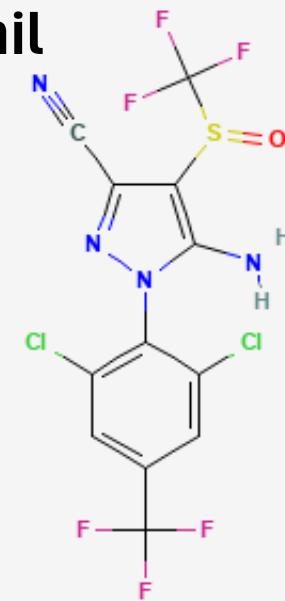
D. Fluensulfone (insecticide)



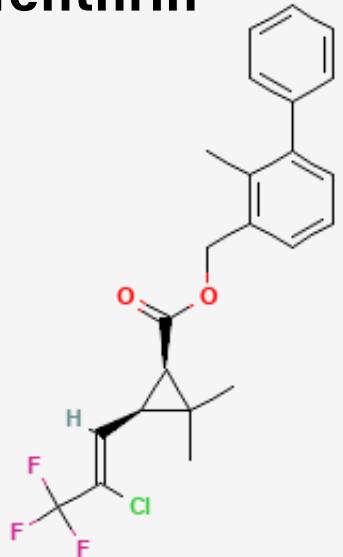
Indoxacarb



Fipronil



Bifenthrin



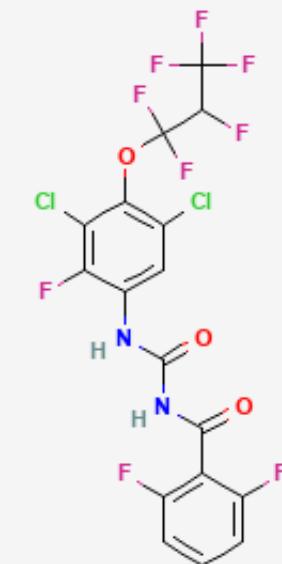
All these insecticides are PFAS according to the OCED/Maine “fully fluorinated” definition, but only one is a PFAS according to EPA’s definition.

Which one is it?

>>> Hint: EPA requires more than a single “fully fluorinated carbon.”

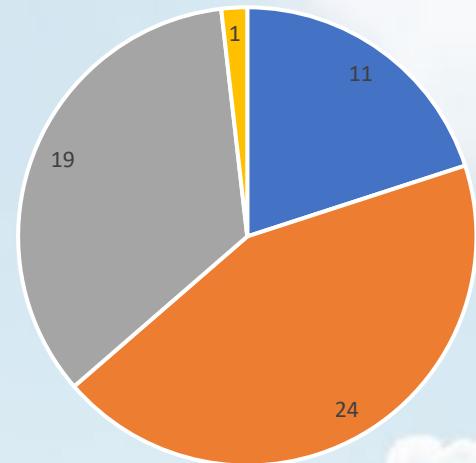


Noviflumuron

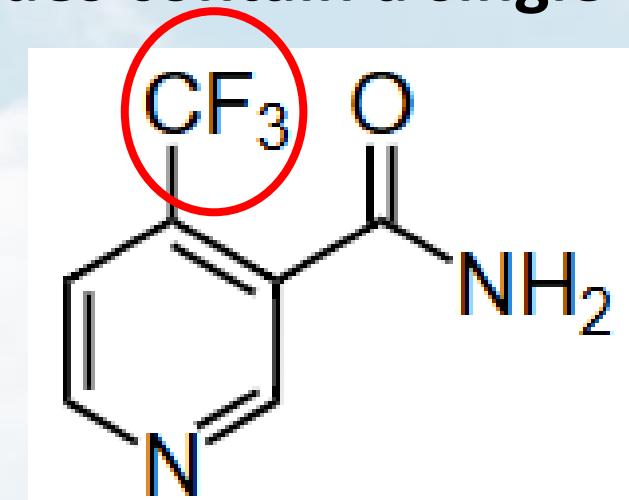


Using the Maine PFAS definition, there were 58 PFAS-active ingredient in 2022.

PFAS-Pesticide by category



80% of PFAS pesticides contain a single CF3 group.



From 2020-2025, EPA registered 21 new active ingredients.

~75% are fluorinated, and 53% are PFAS.

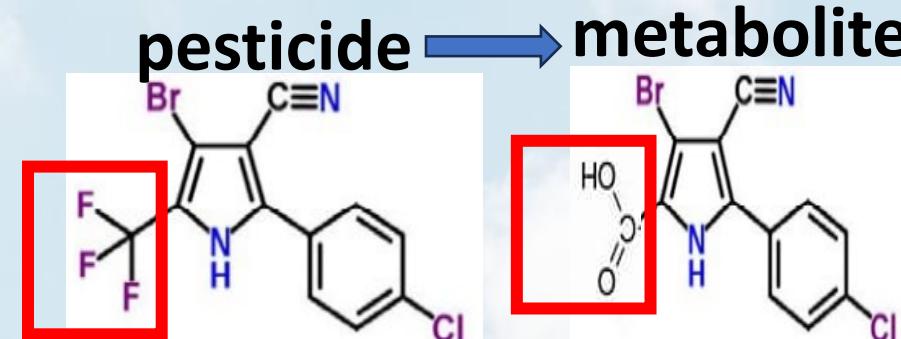
From 2020-2025, 87 novel chemicals with pesticidal properties were given names.

~ 50% are PFAS. These chemicals represent the “pesticide pipeline.”

Why are pesticides fluorinated: a case study

Defluorination of a PFAS-insecticide decreases toxicity, but comes at a cost.

Docket Number EPA-HQ-OPP-2013-0217
www.regulations.gov



species (toxic dose)	tralopyril	CL 322,250	fold-difference
Water flea (21 d) ppb	0.2	300	1500
Eastern oyster (96h) ppb	0.56	310	554
Mysid shrimp (96h) ppb	1	550	550
Rainbow Trout LC50 (11 d) ppb	1.3	520	400
Amphipod <i>Hyalellia azteca</i> (10d)	2.2	35	16
Mallard duck LC50 (96h) ppm	10.8	962	89
Sheepshead minnow (96h) ppb	24	950	40

Active ingredients are just one source of PFAS in Pesticides

I. Intentionally added

1. Active ingredients- at least 58 using the Maine definition

2. Inerts

II. Unintentionally added

3. Fluorinated containers

2. Inerts and Adjuvants

Surfactants:
dispersants,
Emulsifiers,
Wetting agents,
Penetrants,
Spreaders,
Foaming agents,
Antifoaming
agents,
Stabilizers,
anticoagulants

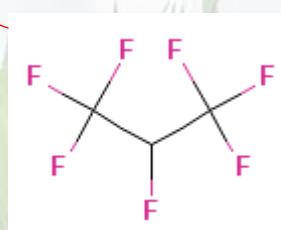
Non surfactants:
Diluents,
Solvents,
Co-solvents,
Carriers,
Fillers,
antistatic agents,
Anticaking agents,
Phytotoxicity
relievers,
Antifreeze agents,
pH regulators,
Propellants,
synergists

Table 1 Functions and types of pesticide adjuvants

Adjuvant function	Representative adjuvant
Disperse and dilute active ingredients	Dispersants, emulsifiers, solvents, diluents, fillers and carriers
Benefit targets' contact and absorption of pesticides	Wetting agents, penetrants and spreaders
Enable the pesticides to take effect, and to prolong and enhance their efficacy	Stabilizing agents, release control adjuvants and synergists
Increase safety and facilitate application	Drift control agents, pesticide hazard mitigation agents, antifoaming agents and foaming agents

2. PFAS INERTS: EPA revoked the approval of twelve PFAS inerts in 2022

- 2-Chloro-1,1,1,2-tetrafluoroethane (CAS Reg. No. 2837-89-0).
- α -(Cyclohexylmethyl)- ω -hydropoly(difluoromethylene) (CAS Reg. No. 65530-85-0).
- Dichlorotetrafluoroethane (CAS Reg. No. 1320-37-2).
- Ethane, 1,1,1,2,2-pentafluoro- (CAS Reg. No. 354-33-6).
- Hexafluoropropene, polymer with tetrafluoroethylene (CAS Reg. No. 25067-11-2).
- Montmorillonite-type clay treated with polytetrafluoroethylene (No CAS Reg. No.).
- Poly(difluoromethylene), α -chloro- ω -(1-chloro-1-fluoroethyl) (CAS Reg. No. 131324-06-6).
- Poly(difluoromethylene), α -chloro- ω -(2,2-dichloro-1,1,2-trifluoroethyl)-(CAS Reg. No. 79070-11-4).
- Poly(difluoromethylene), α -(2,2-dichloro-2-fluoroethyl)-, ω -hydro- (CAS No. 163440-89-9).
- Poly(difluoromethylene), α -fluoro- ω -[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]- (CAS Reg. No. 65530- 66-7).
- Poly(oxy-1,2-ethanediyl), α -hydro- ω -hydroxy-, ether with α -fluoro- ω -(2-hydroxyethyl) poly(difluoromethylene) (1:1) (CAS Reg. No. 65545-80-4).
- **Propane, 1,1,1,2,3,3,3-heptafluoro-** (CAS Reg. No. 431-89-0).



2. PFAS INERTS: these inerts meet Maine's PFAS Definition, but not the EPA's

Chemical Name
Siloxanes and silicones, Me 3,3,3-trifluoropropyl
1-Butanol, 4-(ethoxyloxy)-, polymer with chlorotrifluoroethene, (ethoxyloxy) cyclohexane and ethoxyethene
Ethene, 1,1-difluoro-, homopolymer
5H-1,3-Dioxolo[4,5-f]benzimidazole, 6-chloro-5-[(3,5-dimethyl-4-isoxazolyl)sulfonyl]-2,2-difluoro
2-Naphthalenesulfonic acid, 6-amino-4-hydroxy-5-{{2-(trifluoromethyl)phenyl}azo}-, monosodium s
Pigment red 242
Poly(oxy(methyl(3,3,3-trifluoropropyl)silylene)), alpha-(trimethylsilyl)-omega((trimethylsilyloxy)-)
Fluxofenim ¹ Herbical safener
p-Chlorobenzotrifluoride
Trans-1,3,3,3-tetrafluoroprop-1-ene
Teflon ¹
1,1,1,2-Tetrafluoroethane

Primary Hazards

LD₅₀ in rats= 670 mg/kg

CAS

Synonyms

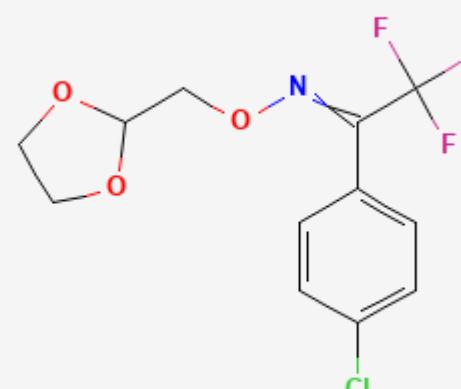
Acute Toxic

Irritant

Environmental Hazard

Fluxofenim

Fluxofenim



Chemical structure of Fluxofenim: A 2D chemical structure showing a 1,3-dioxolane ring connected to a 2,2-difluoro-1-(4-chlorophenyl)-3-(trifluoromethyl)propanoyl group via an amide linkage (-CONH-). The amide nitrogen is also bonded to a methyl group.

Data were mined from <https://ordspub.epa.gov/ords/pesticides/f?p=INERTFINDER:1:0::NO:1::>

Active ingredients are just one source of PFAS in Pesticides

I. Intentionally added

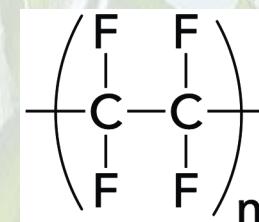
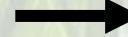
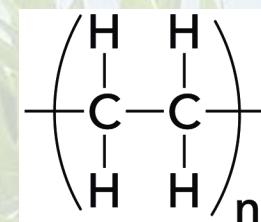
1. Active ingredients- at least 55 using the Maine definition

2. Inerts

II. Unintentionally added

3. Fluorinated containers: replace a carbon-hydrogen bond with a carbon-fluorine bond.

These plastics have improved structure, life-span, and chemical resistance.



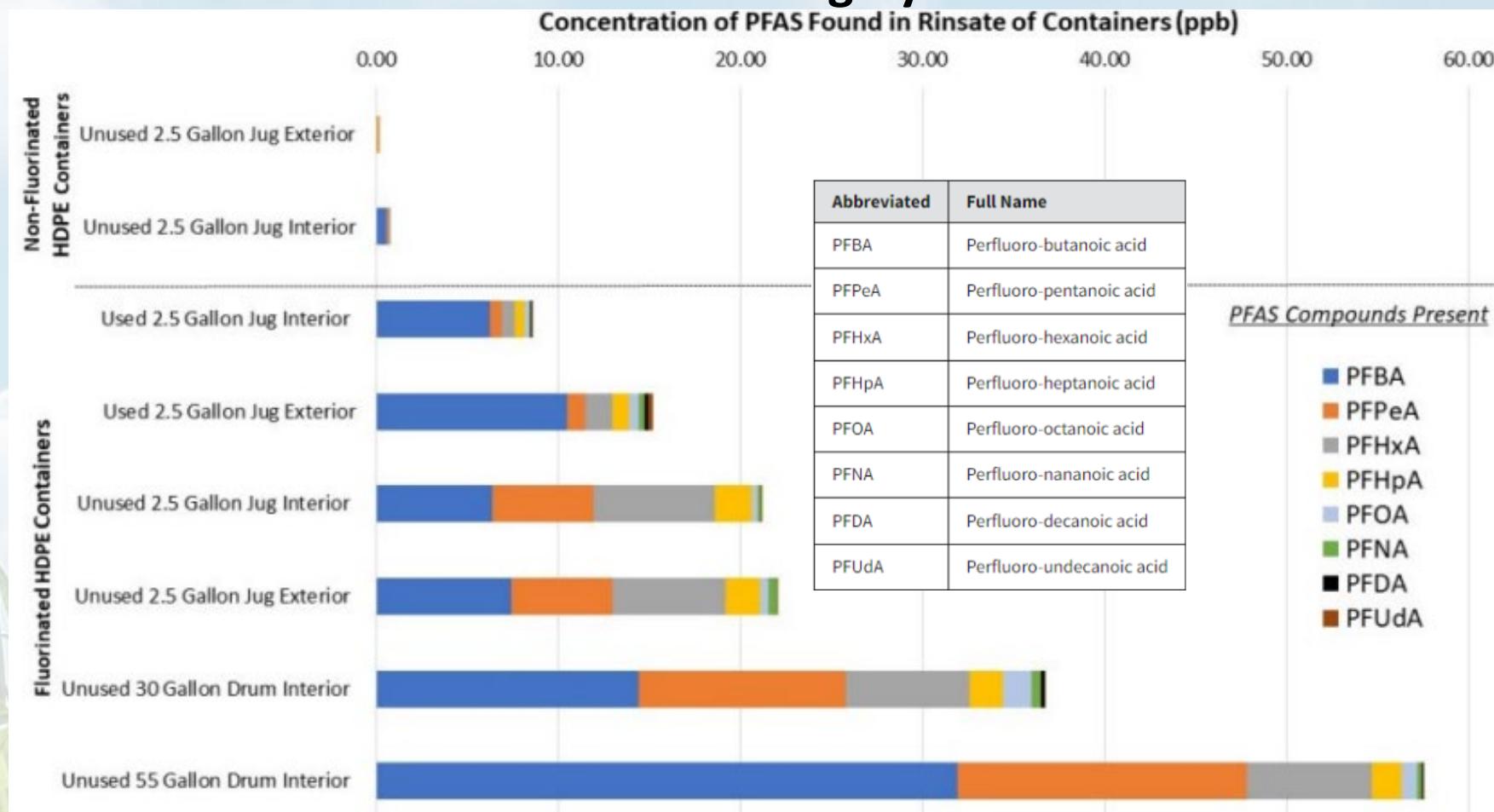
0.1-10 μm fluorine modified layer

HDPE

0.1-10 μm fluorine modified layer

3. PFAS sources: Fluorinated containers

In 2021, EPA identified eight PFAS in pesticides that were derived from the containers that were fluorinated. These include notorious PFAS that are highly toxic.

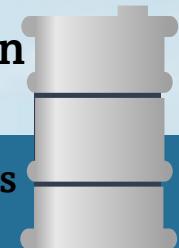


3. PFAS sources: Fluorinated containers

In 2022, the EPA banned the fluorination of containers.



Pesticide Product Contamination



Contamination of pesticide products is prohibited by federal and state law.

The **Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)** ensures consumer protections for pesticide products and mandates that the products contain exactly what was approved when they were registered with EPA, no more and no less. The entire product ingredient list is reviewed by EPA prior to allowing a pesticide product on the market.

Federal: 7 U.S.C. 136(j) (FIFRA Section 12(a)(1)(c))
Establishes as an unlawful act: composition that differs at the time of distribution or sale from its composition as described ... with its registration

Federal: 7 U.S.C. 136(d) (FIFRA Section 6(a)(2)) & 12(a)(1)(c)
Requires registrants to report impurities and prohibits composition of the product that differs from that registered with the Agency

Federal: 40 CFR § 159.179(b)
As per its current PFAS-Packaging website EPA states, "EPA considers any level of PFAS to be potentially toxicologically significant."



Federal: 40 CFR § 159.155(a)(5)
Information about impurities must be received by EPA no later than the 30th calendar day after the registrant first possesses or knows of the information



Federal: 40 CFR § 158.167
Requires all impurities of toxicological significance to be reported and accepted as part of product registration

Federal: EPA PR Notice 96-8
Establishes certain allowable contaminants of pesticide products by other pesticide active ingredients within established concentrations

Federal: 7 U.S.C. §136v(b) Authority of States:
(b) Such State shall not impose... any requirements for labeling or packaging in addition to or different from... this subchapter **Relevant Definition 40 CFR 152.3** Packaging means... the immediate container... in which the pesticide is contained for distribution, sale, consumption, use, or storage

Maine: 7 MRSA §606, sub-§1
1. Unlawful distribution. A person may not distribute in the State any of the following: ...
H. A pesticide that has been contaminated by perfluoroalkyl and polyfluoroalkyl substances

Maine: 7 MRSA §606, sub-§2 2. Unlawful alteration, misuse, divulging of formulas, transportation, disposal and noncompliance.
A person may not:...
H. Use or cause to be used any pesticide container inconsistent with rules for pesticide containers adopted by the board.

Health risks of PFAS-pesticide active ingredients

Risk= toxicity x exposure

1. Toxicity

PFAS-pesticides in Maine (n=58)

Oral LD₅₀ in rats:

- Range is 2 - >10,000 mg/kg.
- Median value is 2,000 mg/kg.
- Geometric mean is 1,220 mg/kg.

For comparison

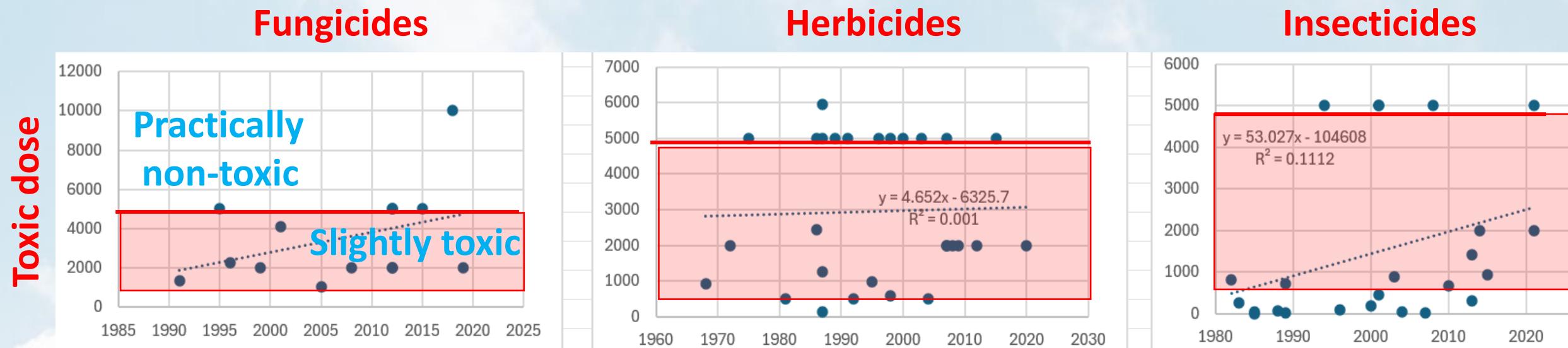
	rat (mg/kg)
cyanide	3.6
DDT	87
aspirin	250
table salt	3000
22 PFAS pesticides	>5000

ACUTE TOXICITY CATEGORIES FOR PESTICIDE PRODUCTS

Hazard Indicators	Highly toxic	Moderately toxic	Slightly toxic	practically nontoxic
	I	II	III	IV
Oral LD ₅₀	Up to and including 50 mg/kg	>50 thru 500 mg/kg	>500 thru 5,000 mg/kg	>5,000 mg/kg

[eCFR :: 40 CFR 156.62 -- Toxicity Category.](#)

PFAS pesticides have become less toxic and less bioaccumulative through the years (1960-2023).



PFAS-Insecticide Toxicity (LD₅₀ values in rats)

Indoor use PFAS-insecticides

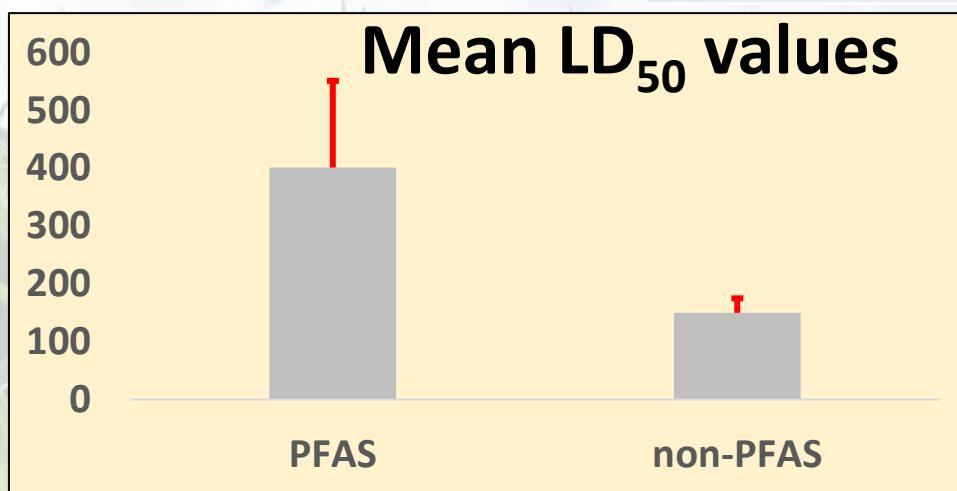
Bifenthrin
Broflanilide
Chlorfenapyr
gamma Cyhalothrin
lambda-Cyhalothrin
Fipronil
Hexaflumuron
Hydramethylnon
Indoxacarb
Novaluron
Noviflumuron

*Non-PFAS insecticides

imidacloprid
chlorpyrifos
carbaryl
acephate
dimethoate
thiamethoxam
malathion
zeta-cypermethrin
permethrin

* Not all of these are approved for indoor use

*Top-selling non-PFAS-insecticides in 2012

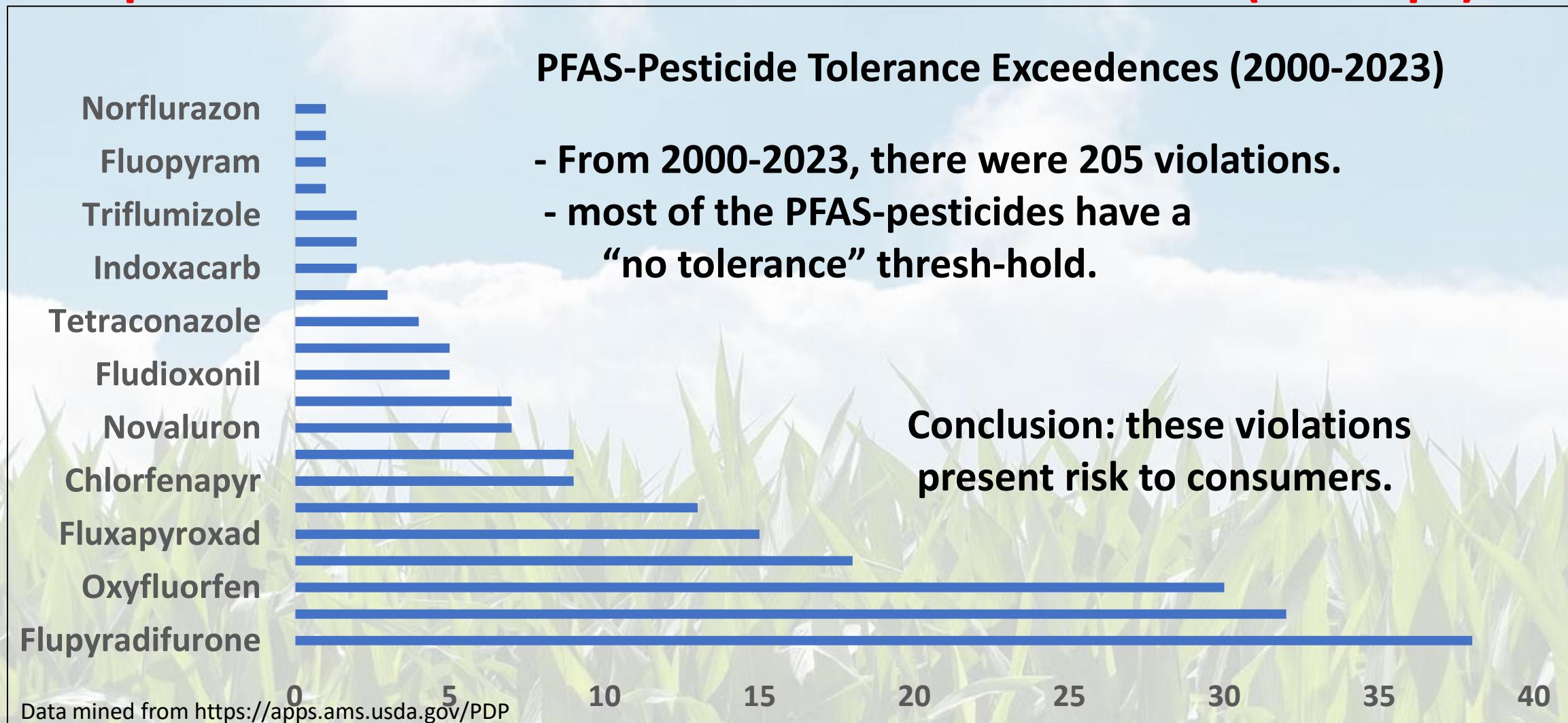


In this case, PFAS-insecticides are less-toxic than non-PFAS insecticides.
Student's unpaired t-test, $p = 0.043$

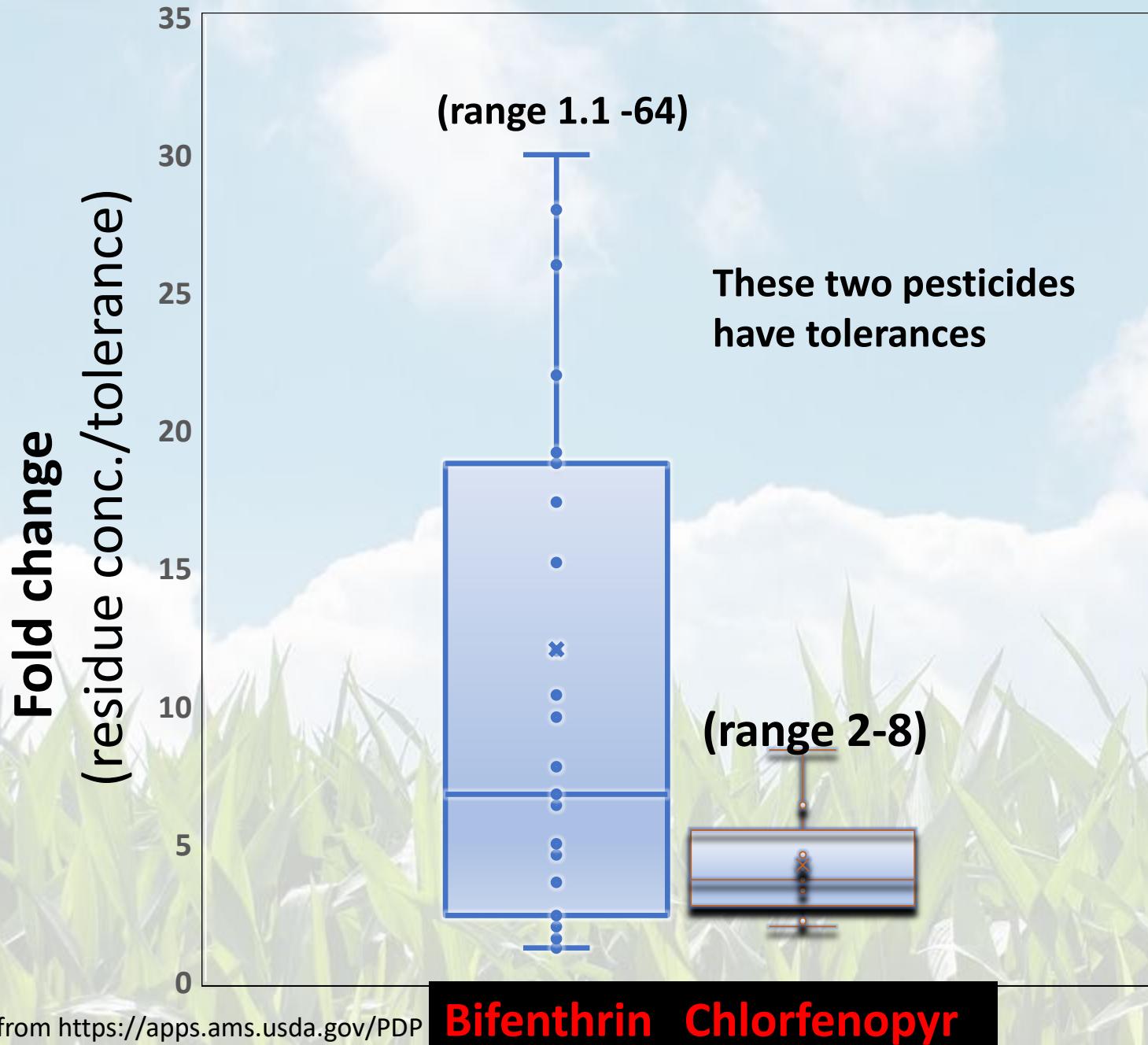
Health risks of PFAS-pesticide active ingredients

Risk= toxicity x exposure

2. Exposure: PFAS-Pesticide Tolerance Exceedences (all crops)



Exposure: PFAS-Pesticide Tolerance Exceedences in Crops



This risk is amplified in some extreme cases.

Exposure: PFAS-pesticides in municipal wastewater/drinking water

PNAS

RESEARCH ARTICLE
2025

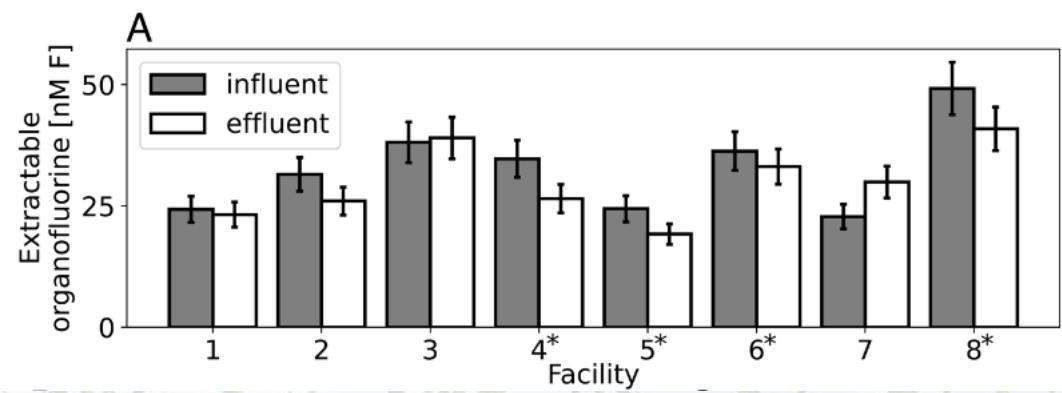
ENVIRONMENTAL SCIENCES

OPEN ACCESS

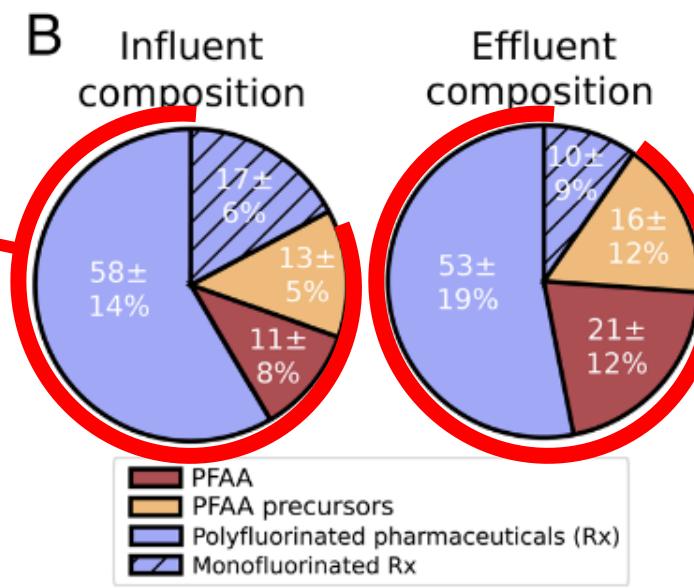


High organofluorine concentrations in municipal wastewater affect downstream drinking water supplies for millions of Americans

Bridger J. Ruyle^{a,b,c,1} , Emily H. Pennoyer^d , Simon Vojta^e, Jitka Becanova^e, Minhazul Islam^f , Thomas F. Webster^d, Wendy Heiger-Bernays^d , Rainer Lohmann^e, Paul Westerhoff^f , Charles E. Schaefer^g , and Elsie M. Sunderland^{a,h,i}



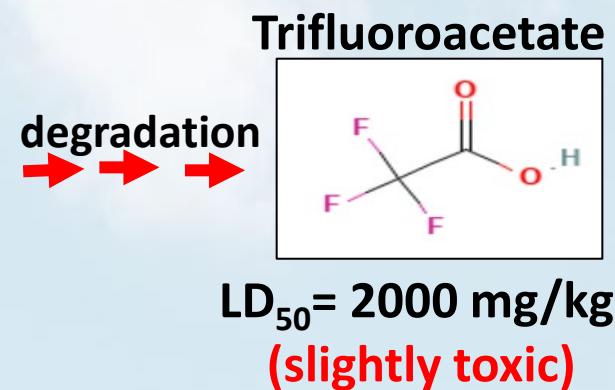
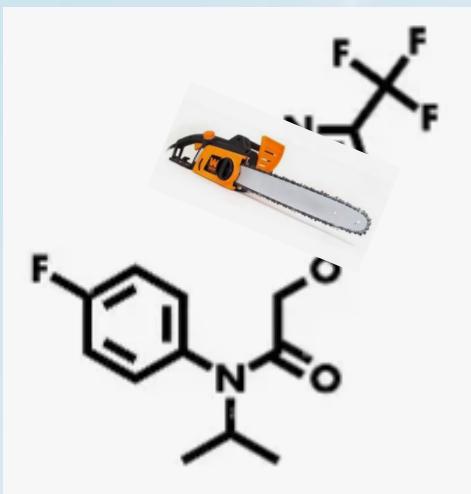
PFAS-OECD/ME



- Only 11% of total influent contains the six PFAS regulated by the EPA. Most PFAS were pharmaceuticals.
- A total of 202 organofluorine pesticides were screened, including 58 PFAS-pesticides. Not a single pesticide was detected in the influent or effluent.

Indirect risks of PFAS-pesticides: transformation into trifluoroacetate (TFA)

Flufenacet



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Perspective

The Global Threat from the Irreversible Accumulation of Trifluoroacetic Acid (TFA)

Hans Peter H. Arp,^{*§} Andrea Gredelj,[§] Juliane Glüge, Martin Scheringer, and Ian T. Cousins

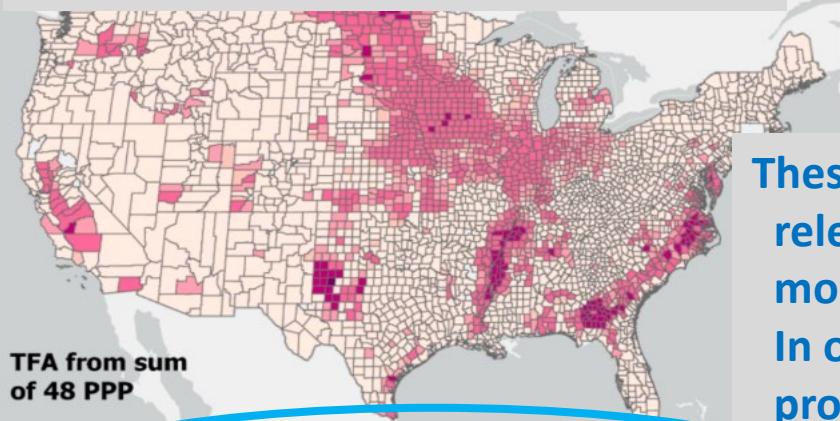


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Potential for TFA accumulation based on PFAS-pesticide usage



TFA in kg/sq km	molar yield	30 %	100 %
≤ 0.17	≤ 0.17	≤ 0.21	≤ 0.57
> 0.17 - 0.21	> 0.17 - 0.21	> 0.21 - 0.39	> 0.39 - 1.2
≤ 0.57	≤ 0.57	> 0.39 - 1.2	> 0.69 - 1.3
> 0.57 - 0.69	> 0.57 - 0.69	> 0.69 - 1.3	> 1.3 - 4.0
		> 1.2 - 5.4	> 4.0 - 18
		> 5.4 - 25	> 18 - 83

These values are not environmentally- or chemically-relevant, as experimental data for only a few PFAS-molecules show the molar yield is closer to 8-12%. In other words, a majority of the degradates will not produce TFA.

More research needed on this topic.
Too many unknowns.

Communicating the health risks of PFAS is challenging

So many unknowns.

PFAS vary in function, structure, and toxicity.

It's hard to classify 10,000 molecules in a single statement or sentence.

Humans are passionate about their health (and environment).

Communicating the health risks of PFAS is challenging: a timely example

Bogdan et al. *J Environ Expo Assess* 2024;3:14
DOI: 10.20517/jeea.2024.08

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Per- and polyfluoroalkyl substances (PFAS) in powdered infant formula: potential exposures and health risks

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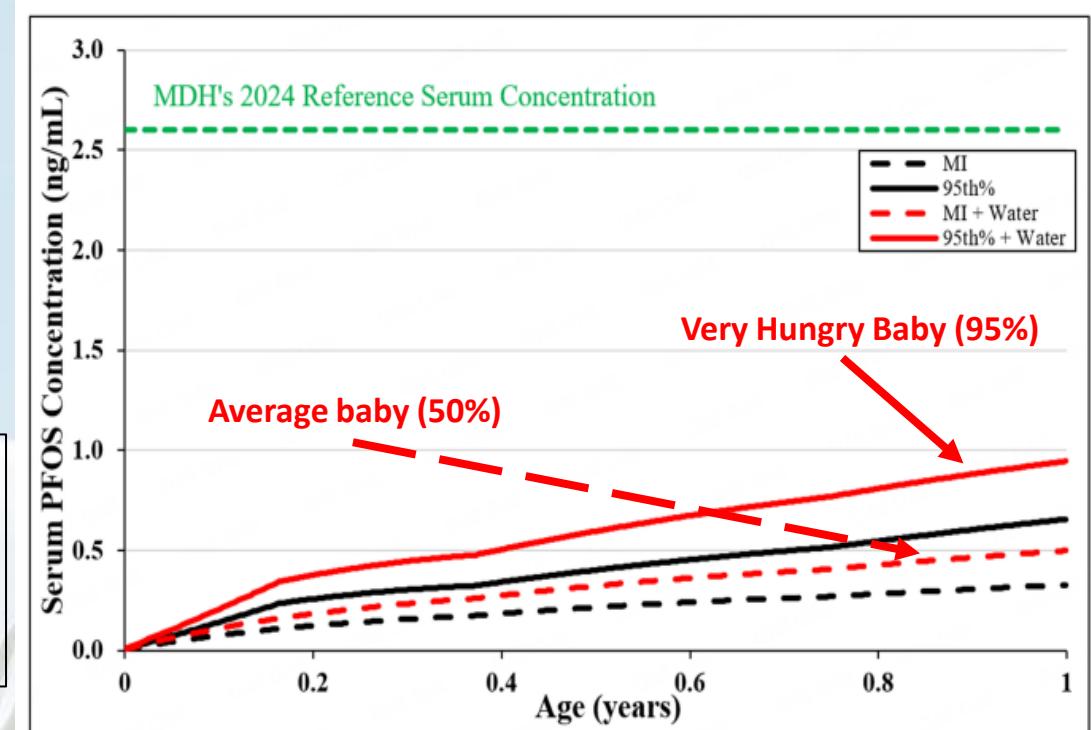
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Goal: detect PFAS in infant formula and to assess their risk to infants

Methods: sampled 17 different infant formulas for 10 different PFAS

PFAS-contaminated infant formula made with PFAS-contaminated drinking water at max limit.



Scientific Conclusion: only 1 formula had a single PFAS. In the worst-case scenario, dietary consumption of this infant formula does not pose a significant source of overall PFAS or risk to infants under 12 months.

Question: Could other organizations make a different conclusion?



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CONSERVATION & FORESTRY

Questions?

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