

PFAS-Pesticides: a tale of two [potential] toxicities

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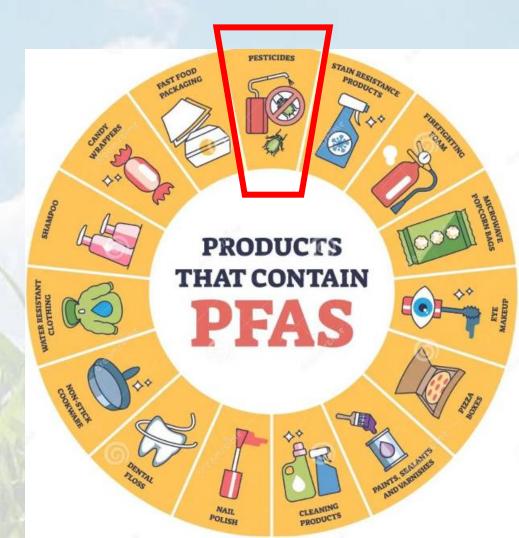


PFAS: Per-(or poly)fluoroalkyl substances

PFAS are molecules designed by chemists since the 1940s.

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

There are thousands of PFAS which exhibit a range of toxicities.



In 2024, EPA set maximum contaminant levels for five 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 <u>M</u>illion

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

Source: https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

Many PFAS are associated with negative health outcomes

erpted from ASTDR re ps://www.atsdr.cdc.g	eport: ov/ToxPr	ofiles/tp/	200-c2.pc	df		Perfluc	roalkyl						
Health Effect Endpoint			/	/ /	£17 d	ior /	Jest /	Hat &	65 A	ight phi	og P	HAT FC	SP.
Body weight		1901	1000			P(•)						*	
Respiratory								()					
Cardiovascular	3.67	5900	200		35.00	72₩8	1/ 🞳	•	•	•			ji .
Gastrointestinal													
Hematological													
Musculoskeletal													
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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 or similar risk.

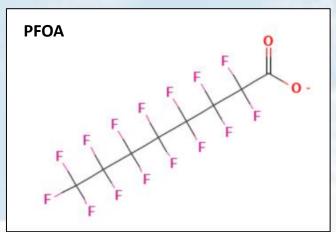
Risk= hazard x exposure

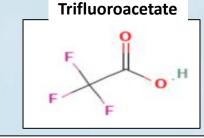
In chemistry, structure determines function.

- Structure of a chemical can also predict toxicity.

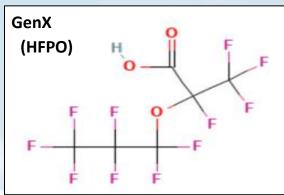
Structure also predicts function and potential hazards in modes of transport.

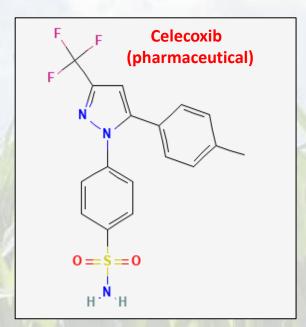


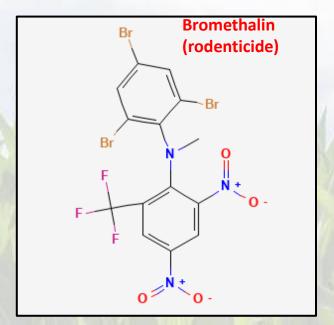




PFAS diversity







PFAS: Per-(or poly)fluoroalkyl substances

PFAS are a growing class of molecules designed by chemists.

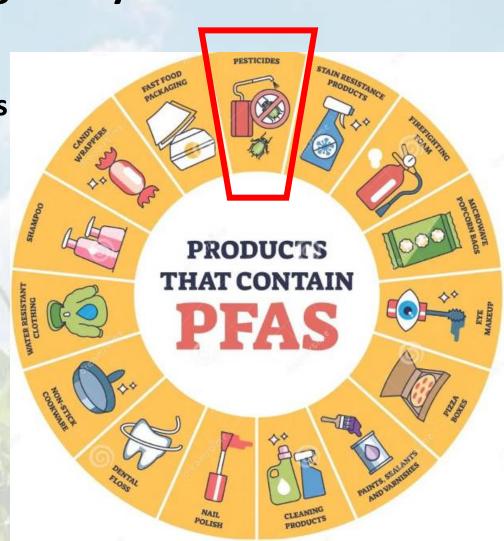
Molecules: between 10,000 to >7,000,000

Pharmaceuticals: between 4 or 380 PFAS products

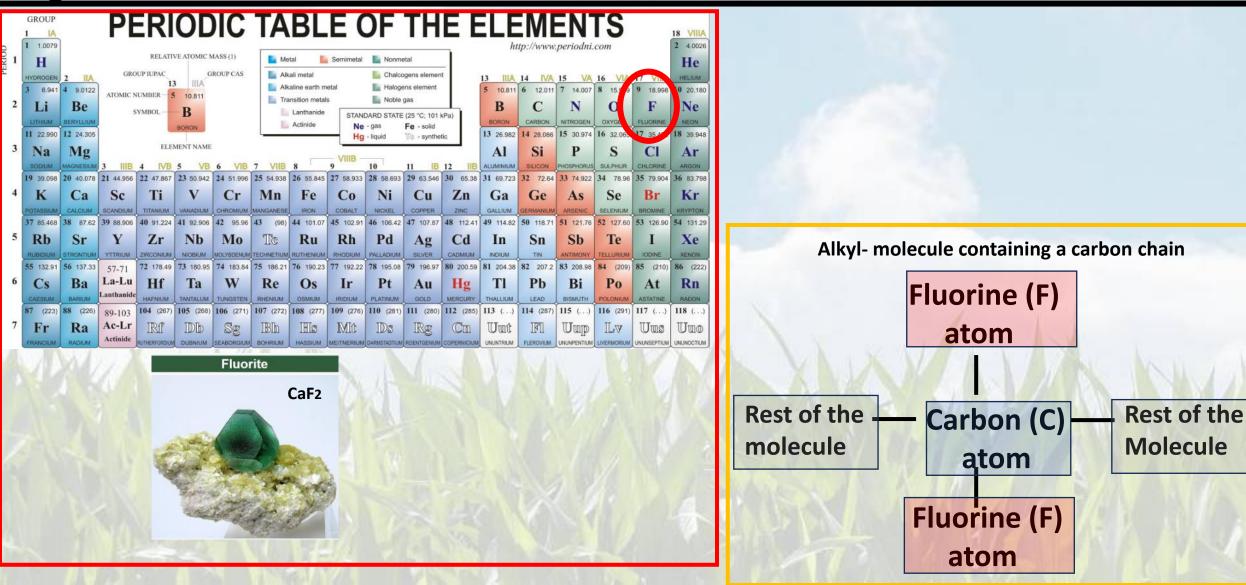
Pesticides: between 7 to 170 active ingredients

*** 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.



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 <u>least one fully fluorinated carbon atom.</u>

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

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

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.

Report from the American Chemical Society

PESTICIDES

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



Shutterstock

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.



The definition of PFAS has societal implications for:

- 1. Policy Makers
- 2. Regulatory Officials
- 3. Public Health Officials
- 4. Pesticide applicators

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

Massachusetts, Maryland, and Minnesota have also enacted legislation that bans PFAS-pesticides.

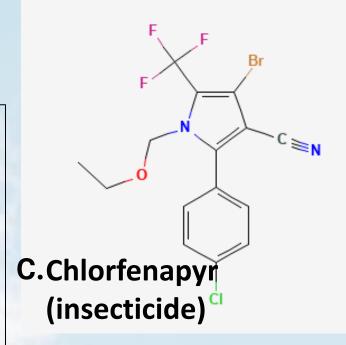
A. Atorvastatin

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 fluorinated carbon must be a single bond, contain at least two F, and not contain H,Cl,Br,I



D. Fluensulfone (insecticide)

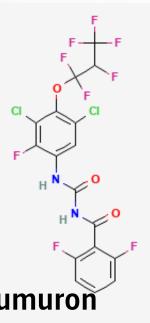
Indoxacarb

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."

Fipronil



Using Maine PFAS definition, there are 55 Pesticides containing a **PFAS-active ingredient. PFAS-Pesticide by category** Bromethalin insecticide rodenticide fungicide herbicide Bifenthrin **PFAS-Insecticides approved for** Broflanilide Chlorfenapyr indoor/structural use Gamma-cyhalothrin Lamdda-cyhalothrin **Fipronil** 8 Hexaflumuron-termiticide approved Hydramethylnon 11 Indoxacarb Novaluron Noviflumuron-termiticide

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



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,

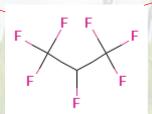
synergists

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 synergist			
Increase safety and facilitate application	Drift control agents, pesticide hazard mitigation agents antifoaming agents and foaming agents			

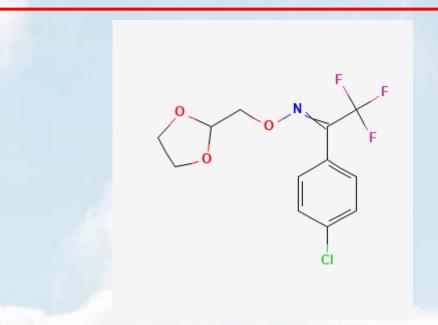
PFAS INERTS: EPA revoked the approval of these 12 inerts in 2022

- 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).



PFAS INERTS: List of PFAS-inserts that meet the OECD PFAS Definition, but not the EPA's

	Chemical Name
Siloxanes an	d silicones, Me 3,3,3-trifluoropropyl
I-Butanol, 4 and ethoxye	-(ethenyloxy)-, polymer with chlorotrifluoroethene, (ethenyloxy) cyclohexand thene
thene, 1,1-	difluoro-, homopolymer
5H-1,3-Dioxo difluoro	olo[4,5-f]benzimidazole, 6-chloro-5-{(3,5-dimethyl-4-isoxazolyl)sulfonyl]-2,2-
2-Naphthale monosodium	nesulfonic acid, 6-amino-4-hydroxy-5-{{2-{trifluoromethyl)phenyl}azo}-, n.s
Pigment red	242
	thyl(3,3,3-trifluoropropyl)silylene)), alpha-(trimethylsilyl)- ethylsilyl)oxy)-
Fluxofenim	Herbicidal safener
o-Chloroben	zotrifluoride
Frans-1,3,3,3	3-tetrafluoroprop-1-ene
l'eflon¹	
1.1.1.2-Tetra	fluoroethane





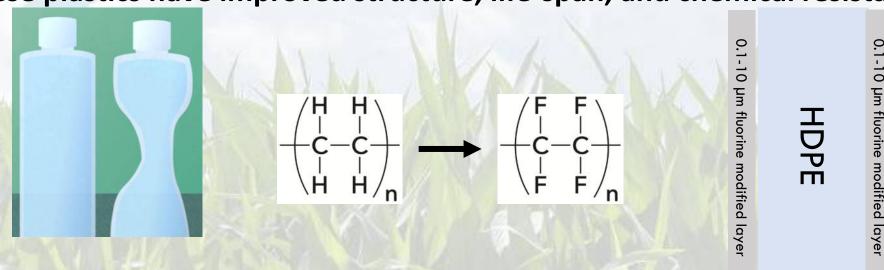
Data were mined from https://ordspub.epa.gov/ords/pesticides/f?p=INERTFINDER:1:0::NO:1::

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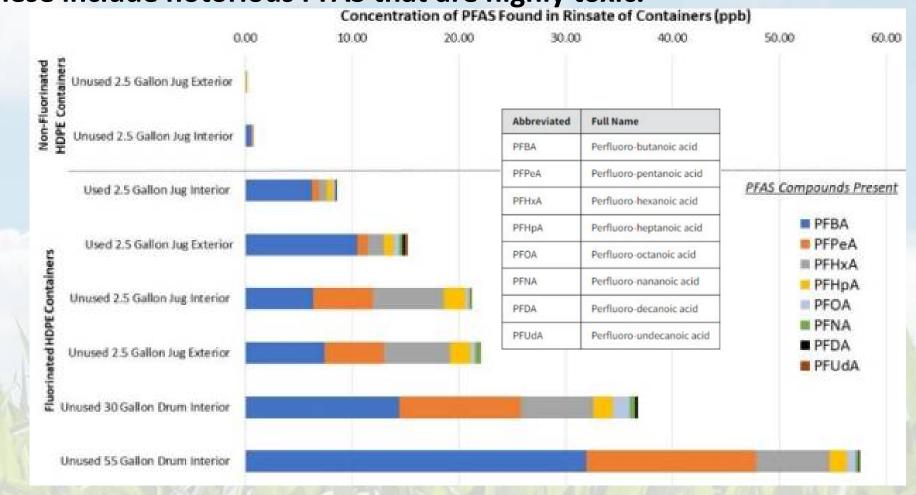
II. Unintentionally added

- Fluorinated containers: replace a carbon-hydrogen bond with a carbon-fluorine bond. These plastics have improved structure, life-span, and chemical resistance.



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.



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) (FIFRRA 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."

te T

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=55)

Oral LD₅₀ in rats:

- Range is 2 >5000 mg/kg.
- Median value is 2,000 mg/kg.
- Geometric mean is 1,220 mg/kg.

	Highly toxic	Moderately toxic	Slightly toxic	practically
Hazard Indicators	1	II	Ш	nontoxic IV
Oral LD ₅₀	Up to and including 50	>50 thru 500 mg/kg	>500 thru 5,000 mg/kg	>5,000 mg/kg

Indoor use PFAS-insecticides (n=11):

Mean LD₅₀=402 mg/kg

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

Toxicity (LD₅₀ values in rats)

Indoor use PFAS-insecticides

Bifenthrin

Broflanilide

Chlorfenapyr

gamma Cyhalothrin

lambda-Cyhalothrin

Fipronil

Hexaflumuron

Hydramethylnon

Indoxacarb

Novaluron

Noviflumuron

* Not all of these are approved for indoor use *Top-selling non-PFAS-insecticides in 2012

imidacloprid

chlorpyrifos

carbaryl

acephate

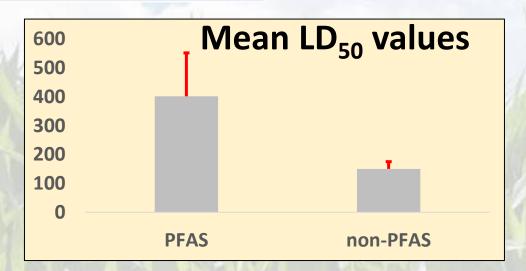
dimethoate

thiamethoxam

malathion

zeta-cypermethrin

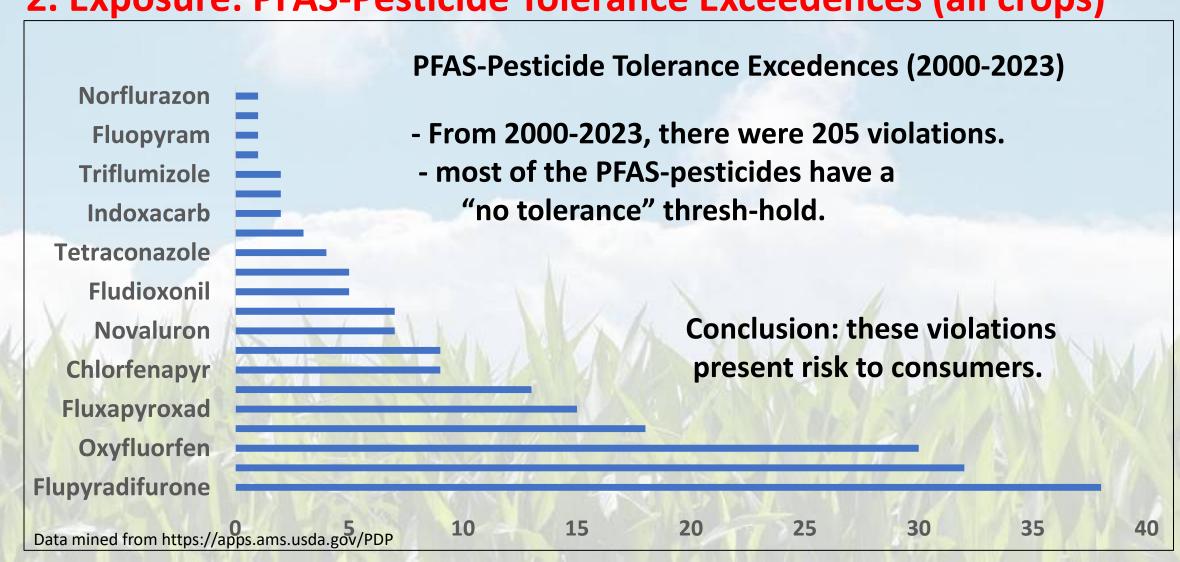
permethrin



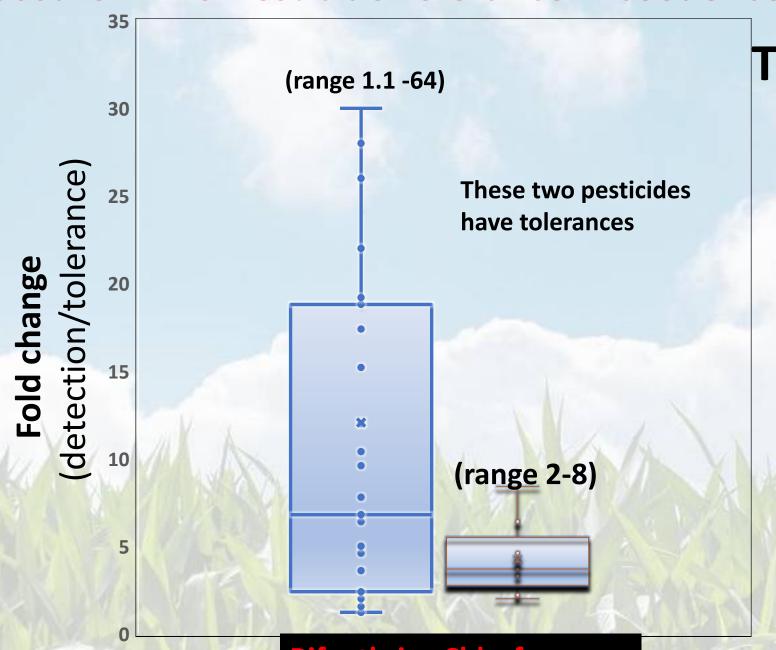
There is a significant difference in the oral toxicity between these two groups of insecticides. Student's unpaired t-test, p = 0.043

Health risks of PFAS-pesticide active ingredients Risk= toxicity x exposure

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

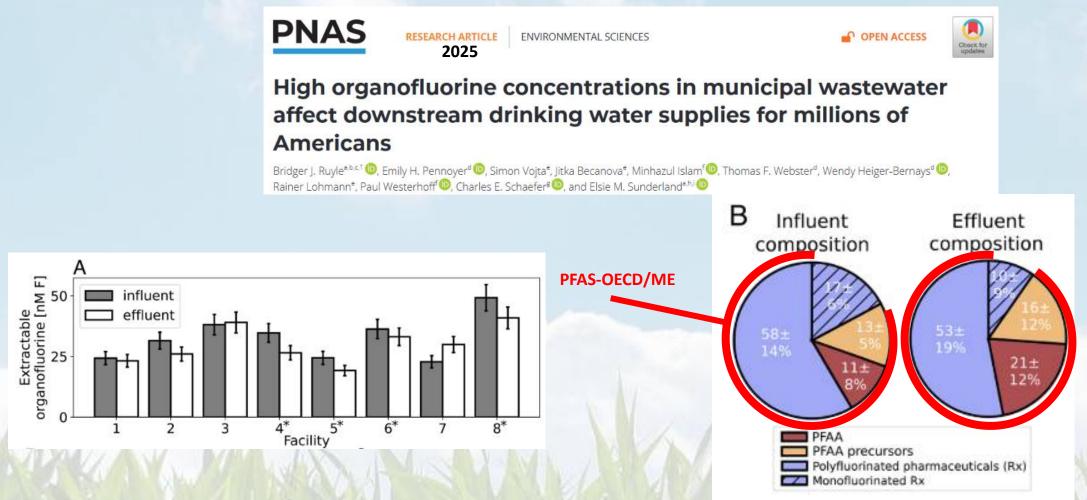


Exposure: PFAS-Pesticide Tolerance Exceedences in Crops



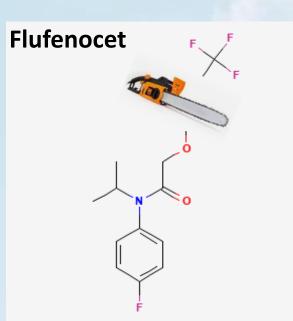
This risk is amplified in some extreme cases.

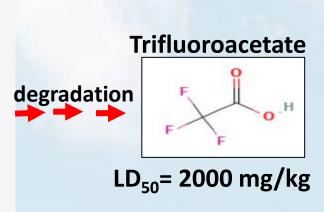
Exposure: PFAS-pesticides in municipal wastewater/drinking water



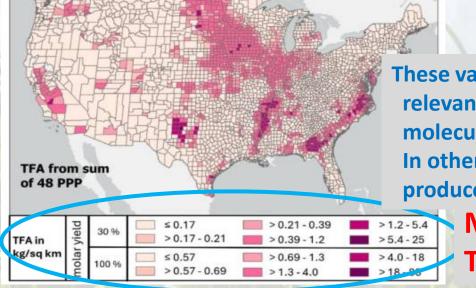
- Only 8% of total influent contains the six PFAS regulated by the EPA. Most PFAS were pharmaceuticals.
- A total of 202 organofluorine pesticides were screened, including 55 PFAS-pesticides. Not a single pesticide was detected in the influent or effluent.

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









Potential for TFA accumulation

based on PFAS-pesticide usage

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



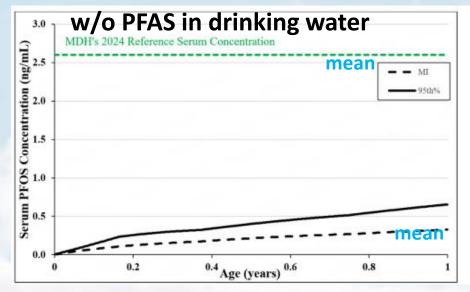
Goal: detect PFAS in infant formula and to assess their risk to infants

Methods: sampled 17 different infant formulas for 10 different PFAS

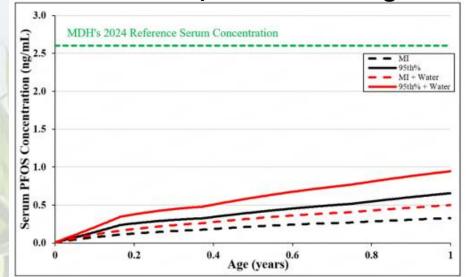
Scientific Conclusion: only 1 formula had a single PFAS. In the worst-case scenario, dietary consumption of this infant formula does not pose a significant source of overall PFAS or risk to infants under 12 months.

Question: Could other organizations make a different conclusion?

PFAS-contaminated infant formula



Infant formula w/ PFAS in drinking water





Questions?

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