Contamination of Pesticide Products By “Forever Chemicals”; What We Know About PFAS & Pesticides

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Maine Department of Agriculture, Conservation, & Forestry

Why is the BPC talking about PFAS?

- Several PFAS chemicals have recently been associated with certain pesticide products
- Containers can react with the contents and create some PFAS

PFAS & pesticides is a very nuanced topic, we are still learning about the connection.

We’ve been using PFAS compounds in our daily lives for 60+ years

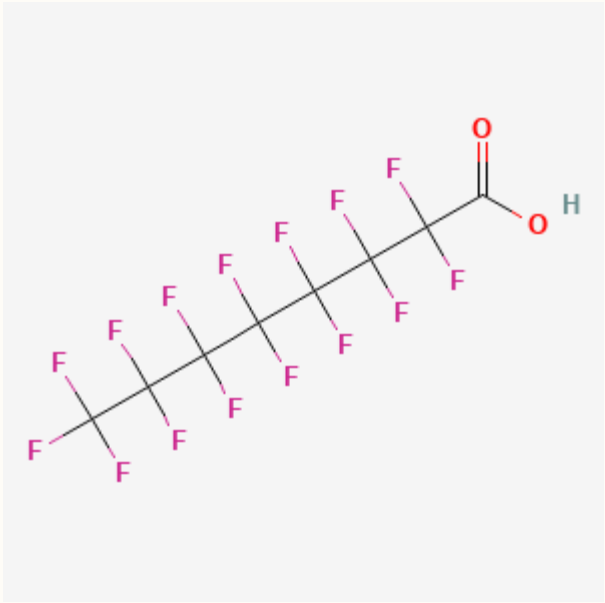
PFAS are common in our lives

Sources of PFAS?

- GoreTex / waterproof breathable clothing
- Teflon / non-stick cookware
- Dental floss / slick non-stick anything
- Fast food containers / oil proof & waterproof papers and cardboard
- Firefighting foams
- Medicines
- Refrigerants/ Aerosols
- Many industrial applications

Per- and Polyfluoroalkyl Substances (PFAS)

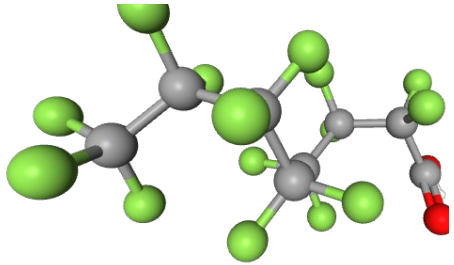
- Pronounced as “P -fas”
- Often confused with “P -foss” which is a specific type of PFAS



Perfluorooctanoic acid
C8

We will come back to this topic in a bit…

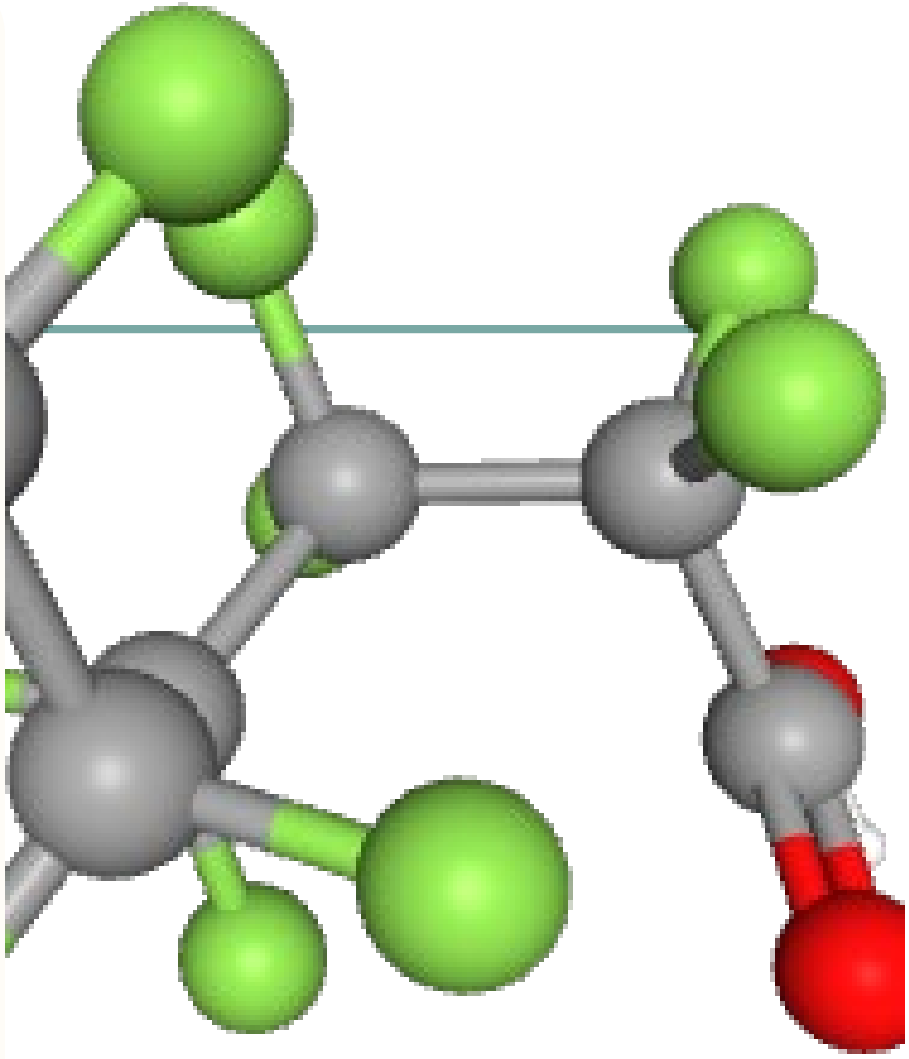
Not all molecules with fluorine are PFAS



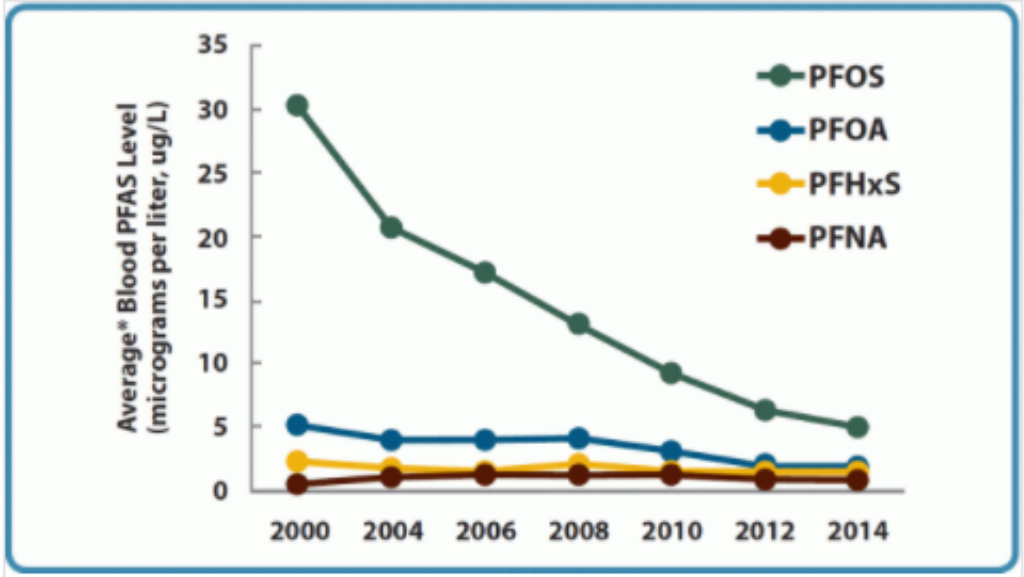
- Fluorine is a naturally occurring element, rare in organisms
- Many compounds are “organofluorines”
- Fluorocarbons
- Fluorine gas

“Forever chemicals”!?

- It is hard to generalize about a group of 10,000+ of anything, but…
- PFOA isn’t degraded by bacteria / microorganisms, or water, or sunlight; one study estimates:
  - *256 years at ocean surface*
  - *>25,000 years coastal ocean*



Blood Levels of the Most Common PFAS in People in the United States from 2000-2014



* Average = geometric mean

Data Source: Centers for Disease Control and Prevention. Fourth Report on Human Exposure to Environmental Chemicals, Updated Tables, (January 2017). Atlanta, GA: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention.

PFOA (blue) in the U.S. general population is 2.08 micrograms per liter (mcg/L) of blood

-about ½ lost every 3 years from your body

Human health effects

- Immune system
- Increased cholesterol
- Liver enzyme changes
- Increased blood pressure & pre-eclampsia
- Higher rates of testicular & kidney cancer
- Slight decrease in birth weight

The Anvil 10+10 story

Timeline

- Citizen concerned about water quality following mosquito spraying organized collection of samples of the sprayed pesticide
- Samples came back positive for several different PFAS

September 1, 2020

The Anvil 10+10 story

Timeline (side note)

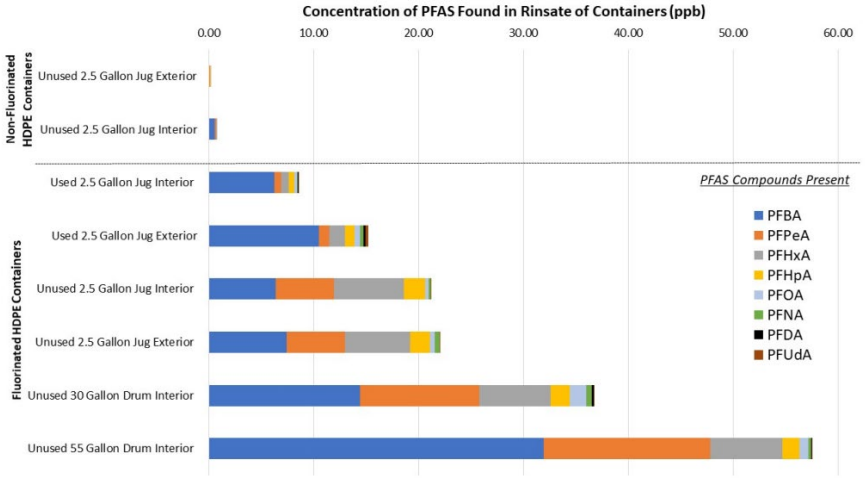
- Prior to this press release the state regulatory pesticide community had been hearing about this issue.
- In 2019, via email, EPA stated that there were no current PFAS compounds as active ingredients or as inerts

September 1, 2020

The Anvil 10+10 story

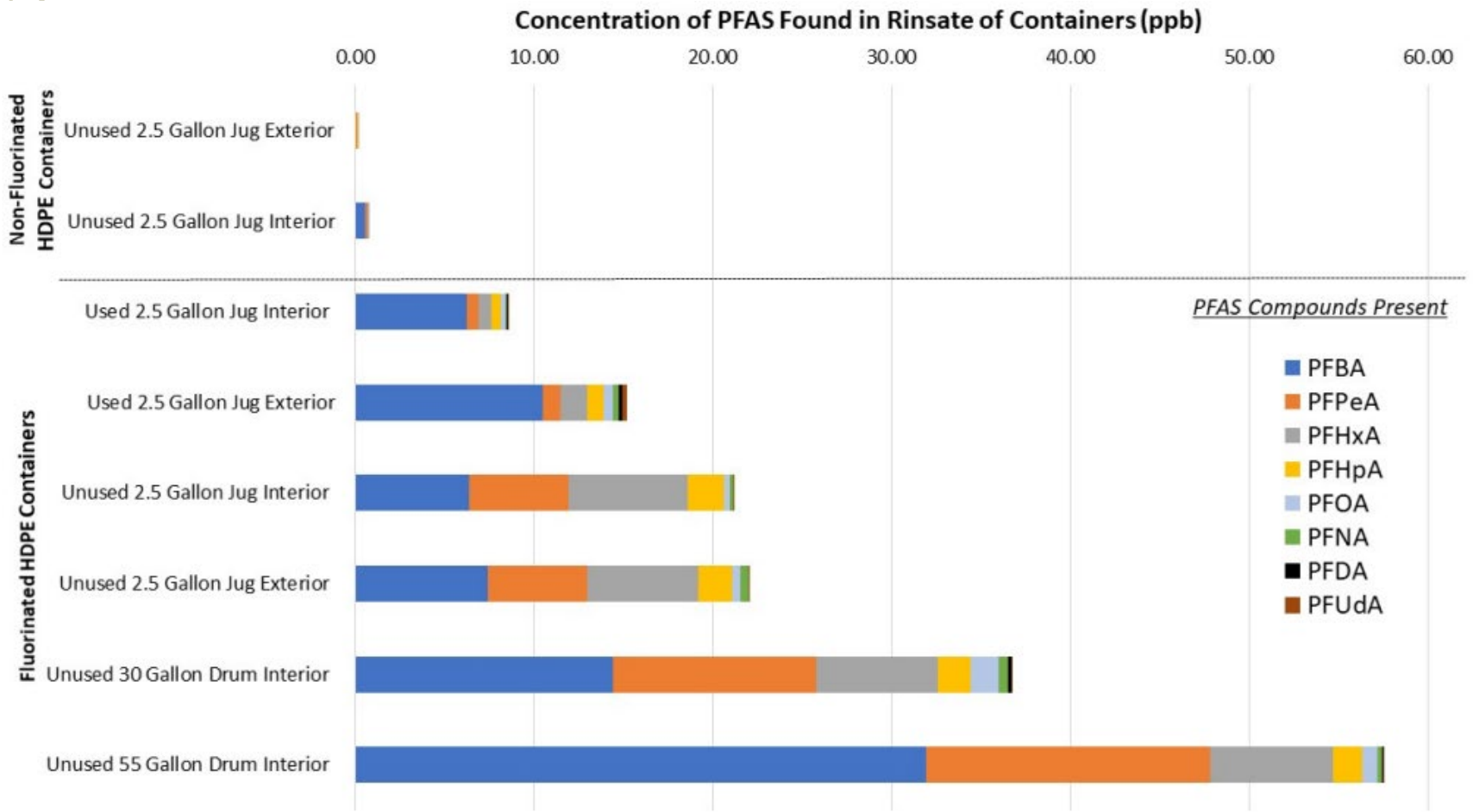
Timeline

- Mass followed up with testing, confirming PFAS
- EPA collected samples from:
  - Product as sold but unopened
  - Product prior to being packaged
  - Packaging prior to being filled



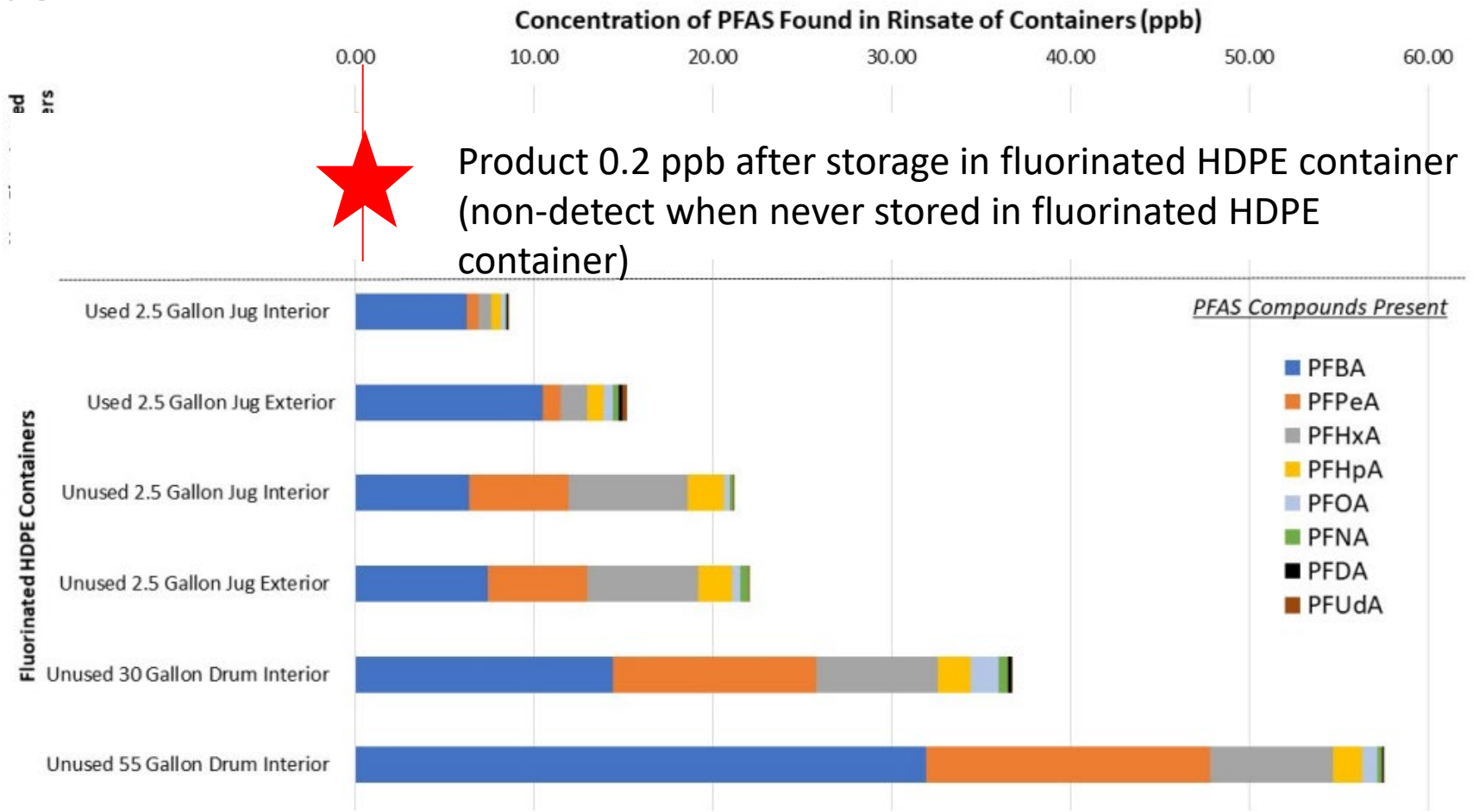
March 5, 2021

The Anvil 10+10 story



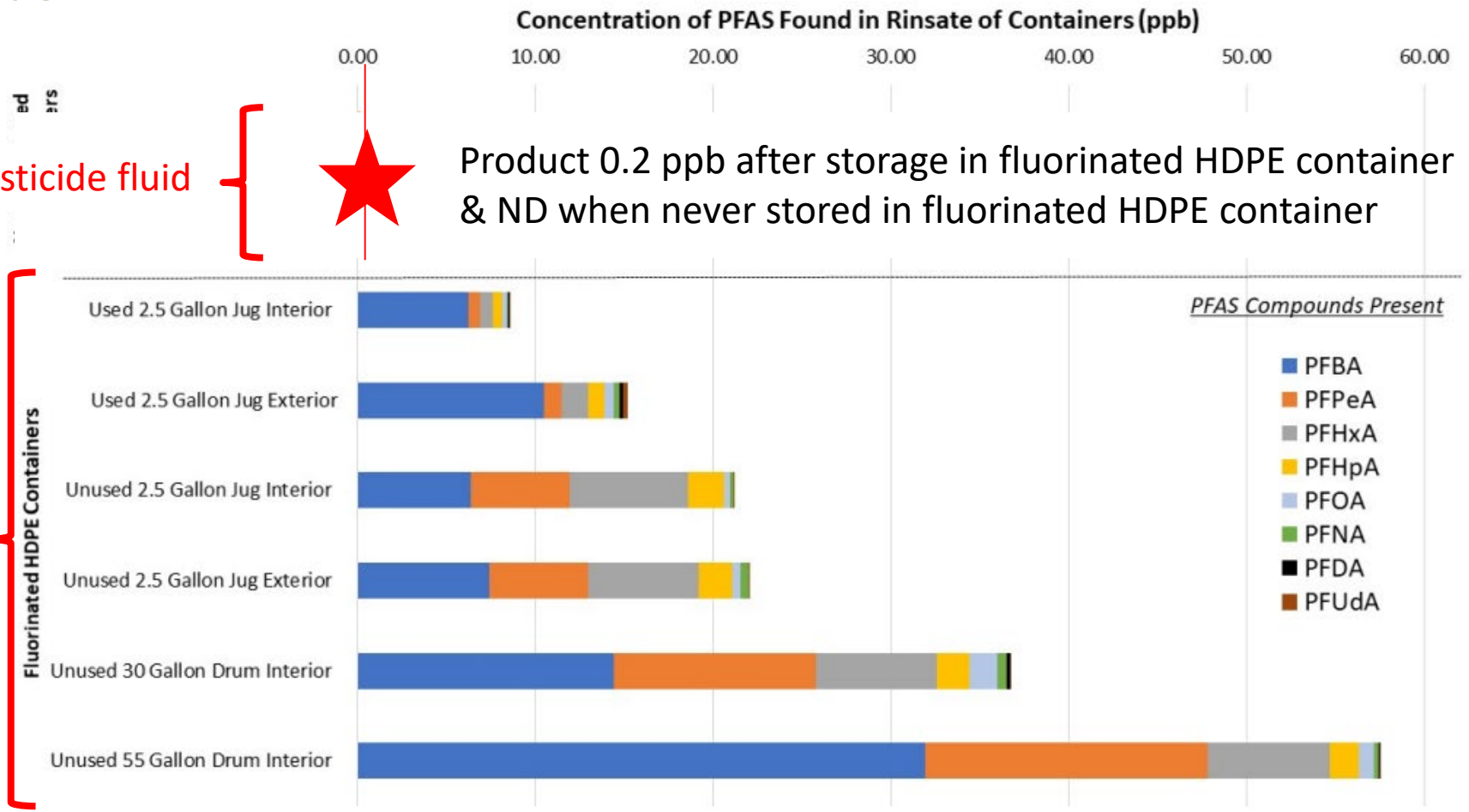
March 5, 2021

The Anvil 10+10 story



Product 0.2 ppb after storage in fluorinated HDPE container (non-detect when never stored in fluorinated HDPE container)

The Anvil 10+10 story



Rinsing pesticide container only / never any pesticide in it

The Anvil 10+10 story

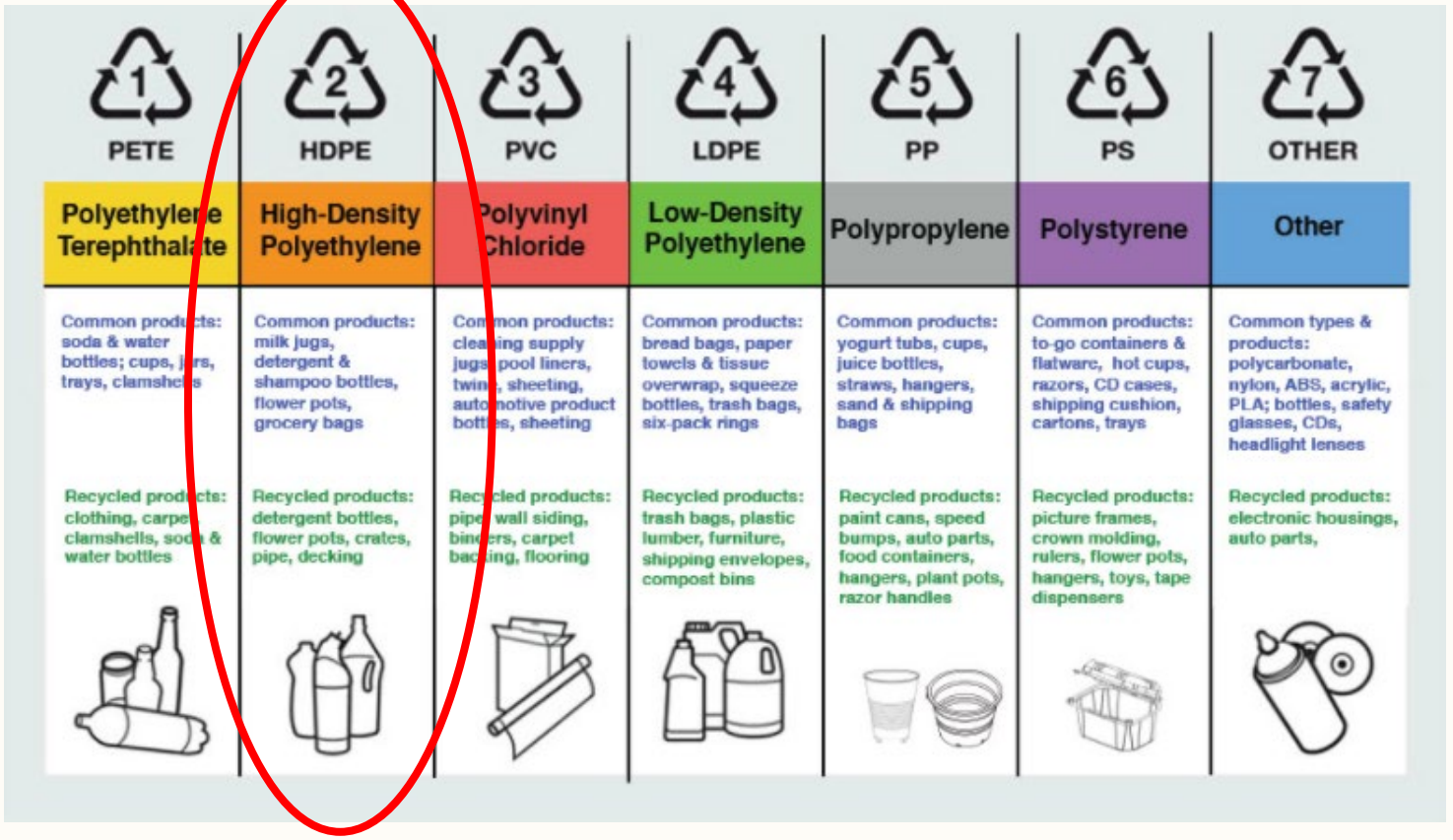
EPA confirmed there are PFAS coming from these products, but the big question then was, WHY?

- Was it added during the manufacture of the containers?
- Contamination of the containers during manufacturing?
- Fluorination of the containers

The Anvil 10+10 story

Anvil 10+10 was packaged in
Number 2 - HDPE plastic

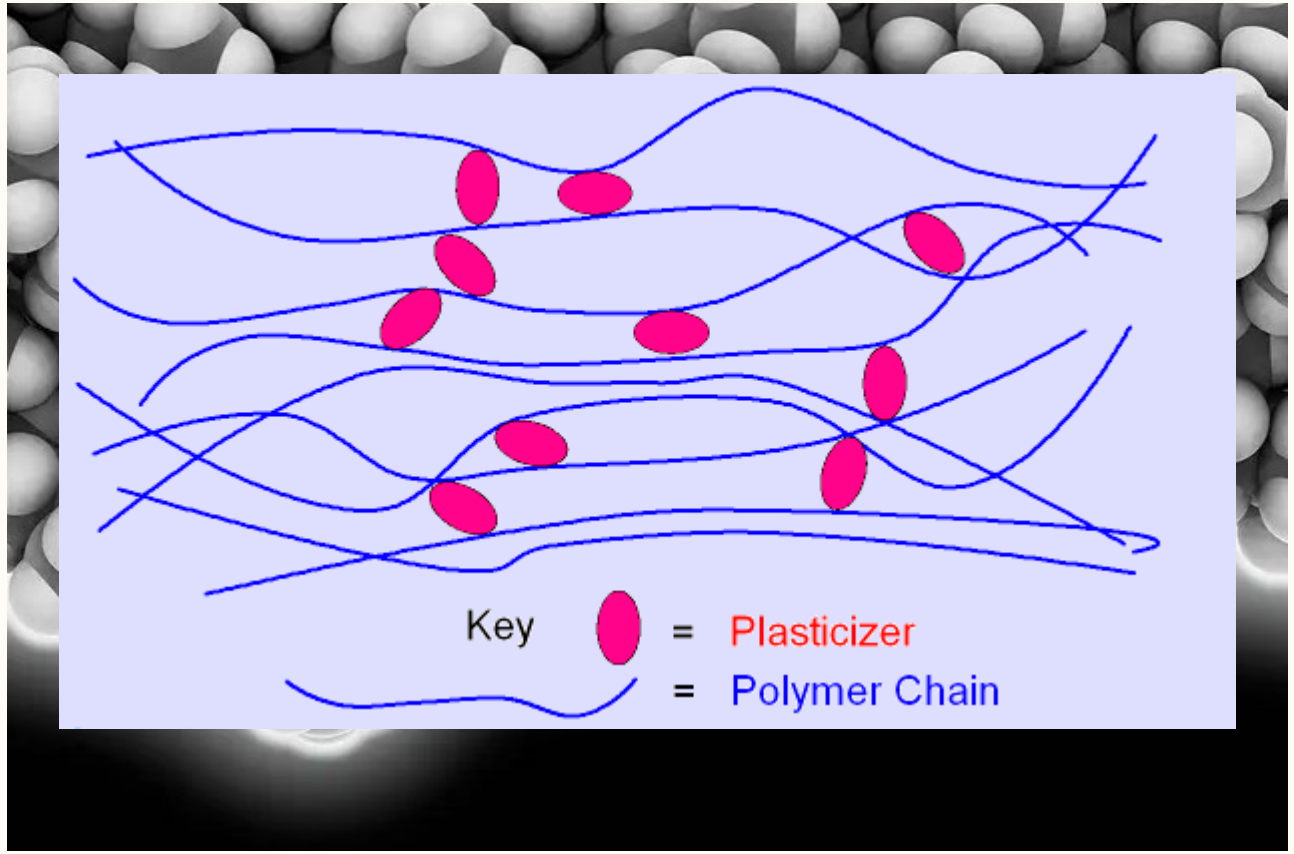
- Fluorination



1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
Polyethylene Terephthalate	High-Density Polyethylene	Polyvinyl Chloride	Low-Density Polyethylene	Polypropylene	Polystyrene	Other
Common products: soda & water bottles; cups, jars, trays, clamshells	Common products: milk jugs, detergent & shampoo bottles, flower pots, grocery bags	Common products: cleaning supply jugs, pool liners, twine, sheeting, automotive product bottles, sheeting	Common products: bread bags, paper towels & tissue overwrap, squeeze bottles, trash bags, six-pack rings	Common products: yogurt tubs, cups, juice bottles, straws, hangers, sand & shipping bags	Common products: to-go containers & flatware, hot cups, razors, CD cases, shipping cushion, cartons, trays	Common types & products: polycarbonate, nylon, ABS, acrylic, PLA; bottles, safety glasses, CDs, headlight lenses
Recycled products: clothing, carpet, clamshells, soda & water bottles	Recycled products: detergent bottles, flower pots, crates, pipe, decking	Recycled products: pipe, wall siding, binders, carpet backing, flooring	Recycled products: trash bags, plastic lumber, furniture, shipping envelopes, compost bins	Recycled products: paint cans, speed bumps, auto parts, food containers, hangers, plant pots, razor handles	Recycled products: picture frames, crown molding, rulers, flower pots, hangers, toys, tape dispensers	Recycled products: electronic housings, auto parts,

The Anvil 10+10 story

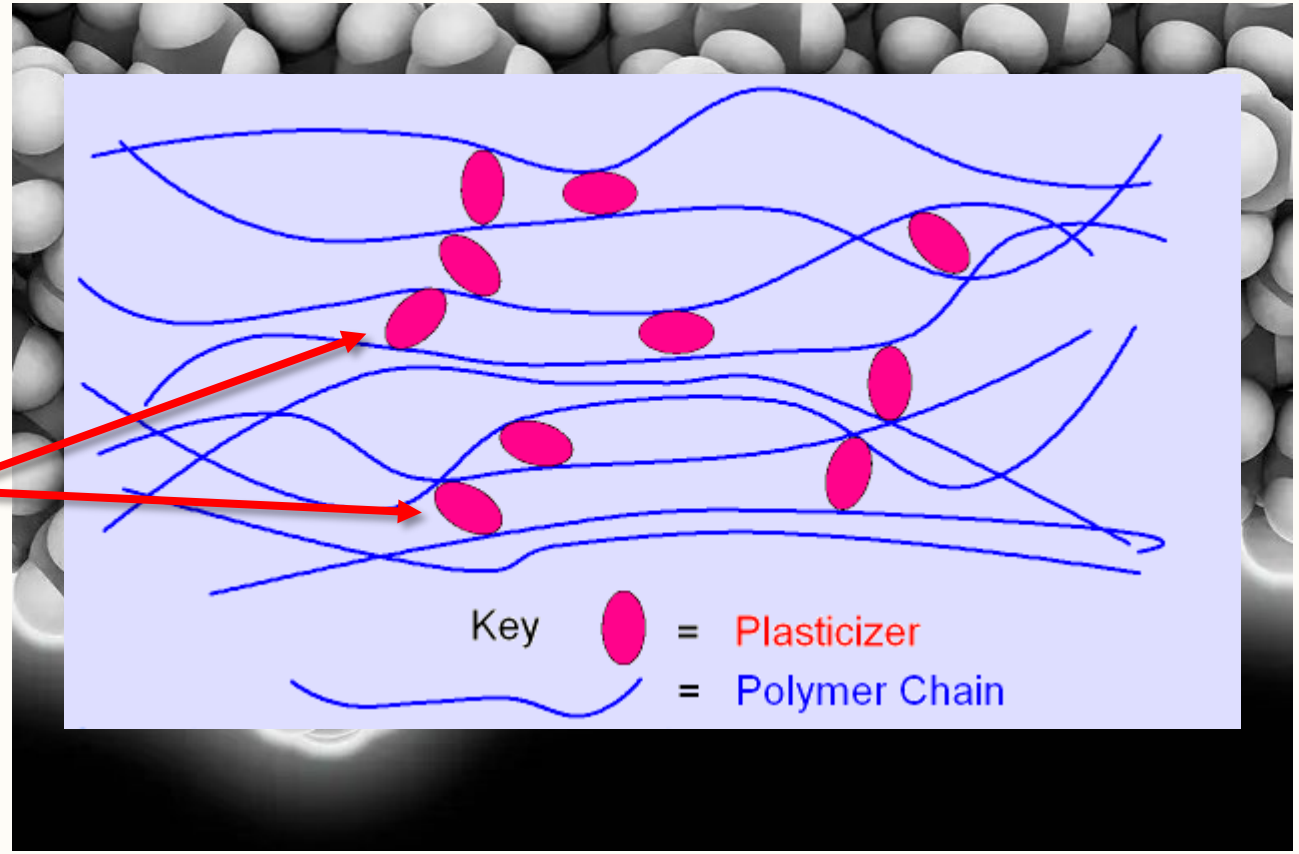
- Fluorination of plastics and what plastics are



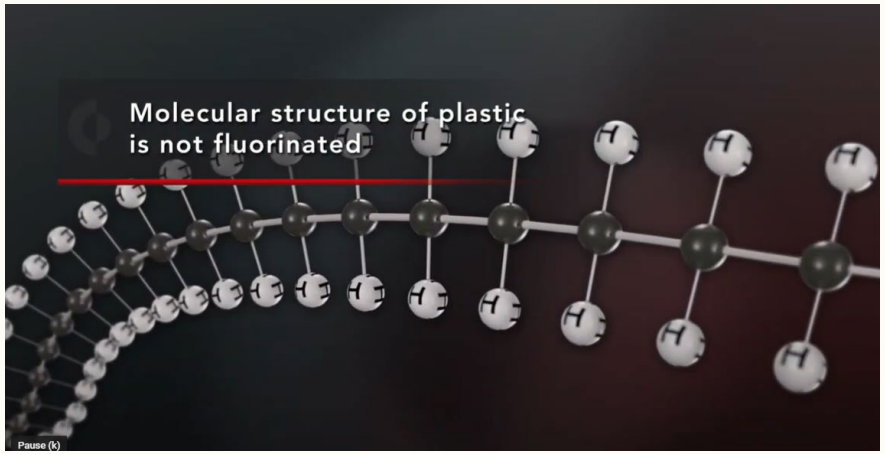
The Anvil 10+10 story

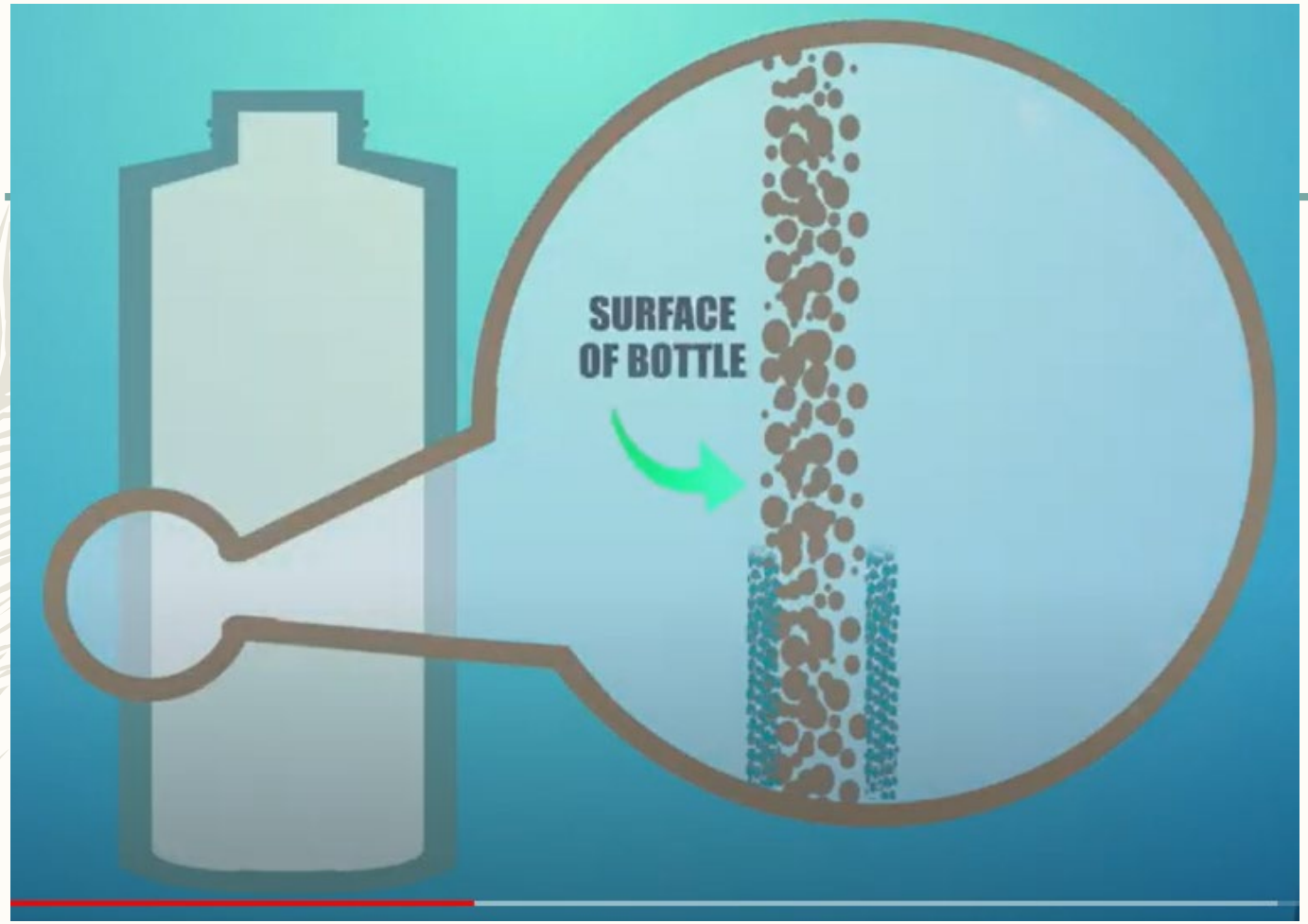
- Fluorination of plastics and what plastics are

See these plasticizers? They help the plastic sheet together. They are not well connected to the long strands.



Fluorination of containers

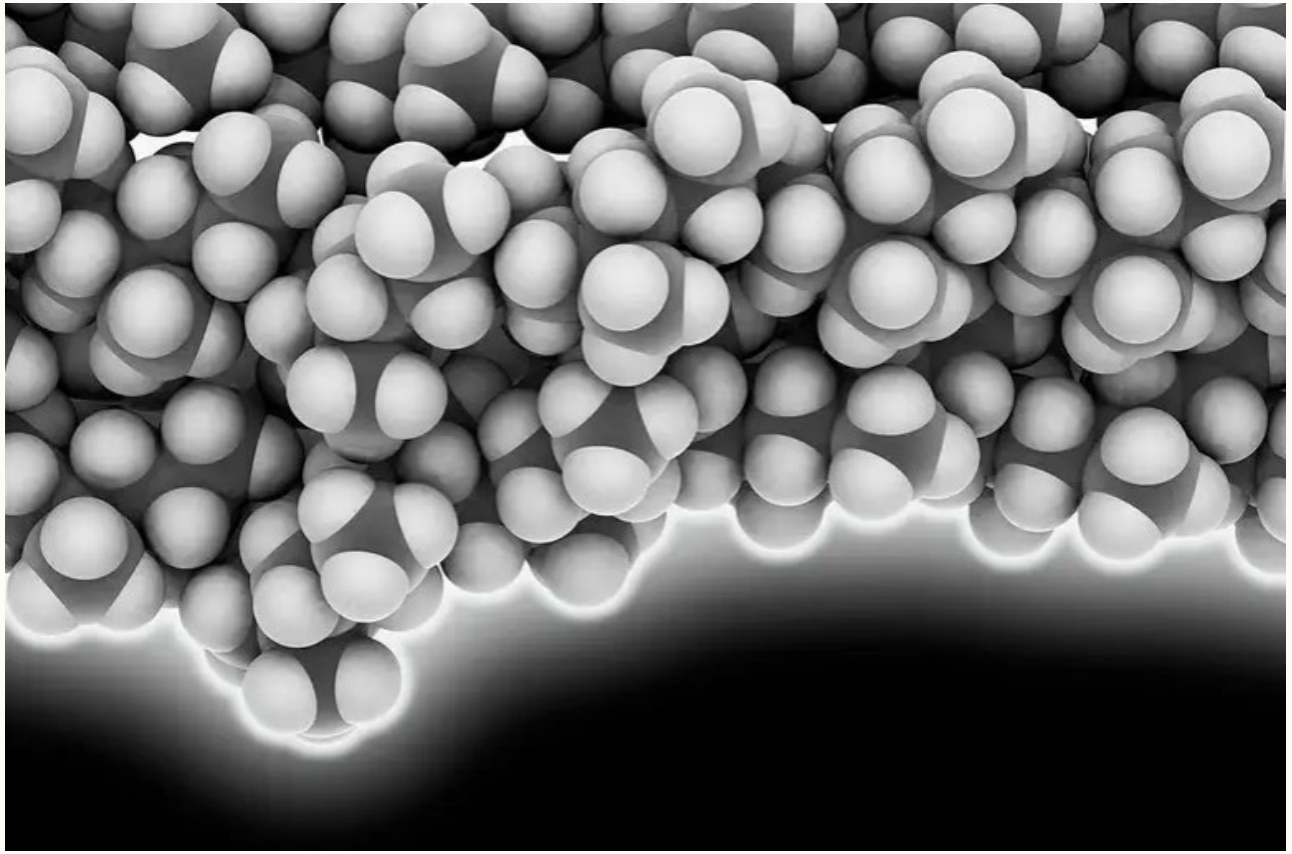



SURFACE
OF BOTTLE


fluorinated
un-fluorinated
1:52

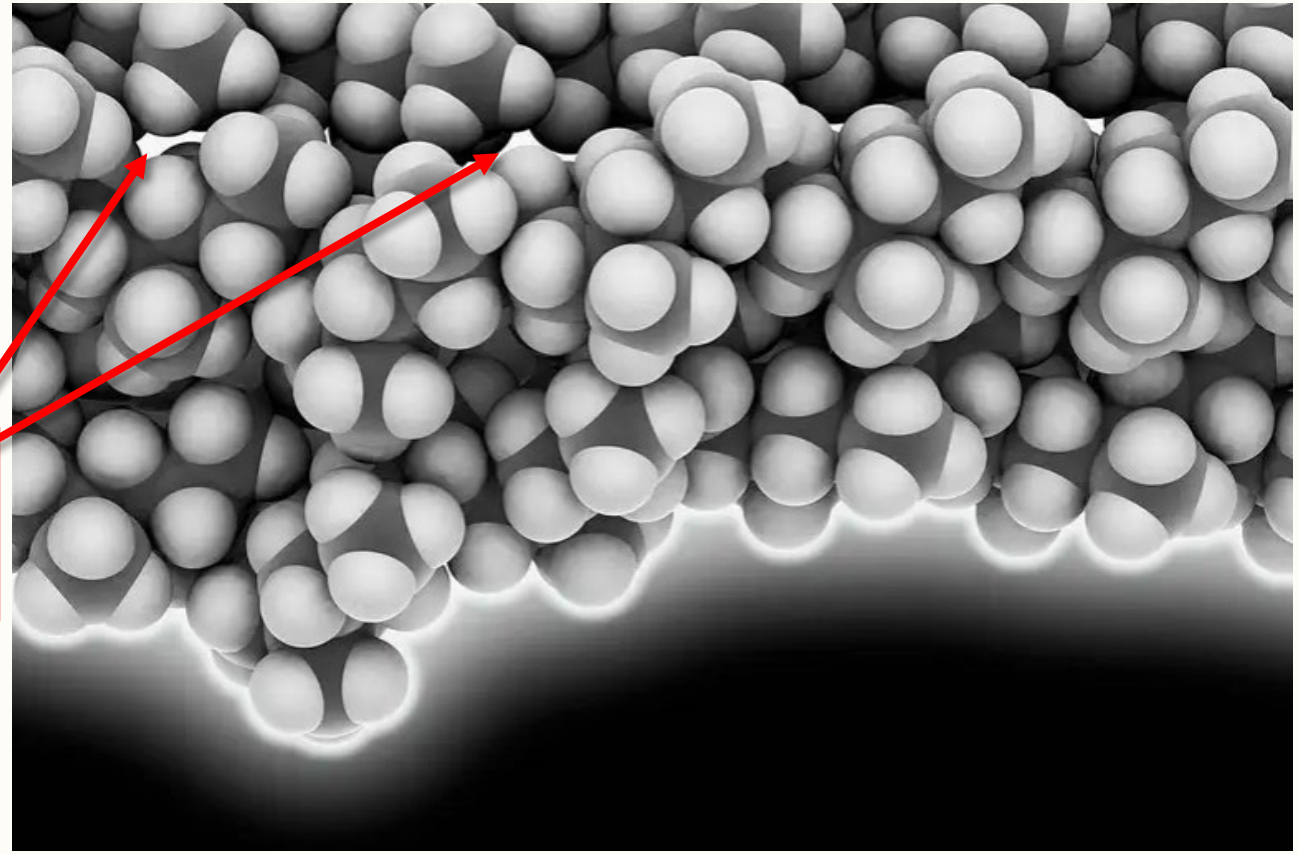
The Anvil 10+10 story

- Fluorination of plastics and what plastics are

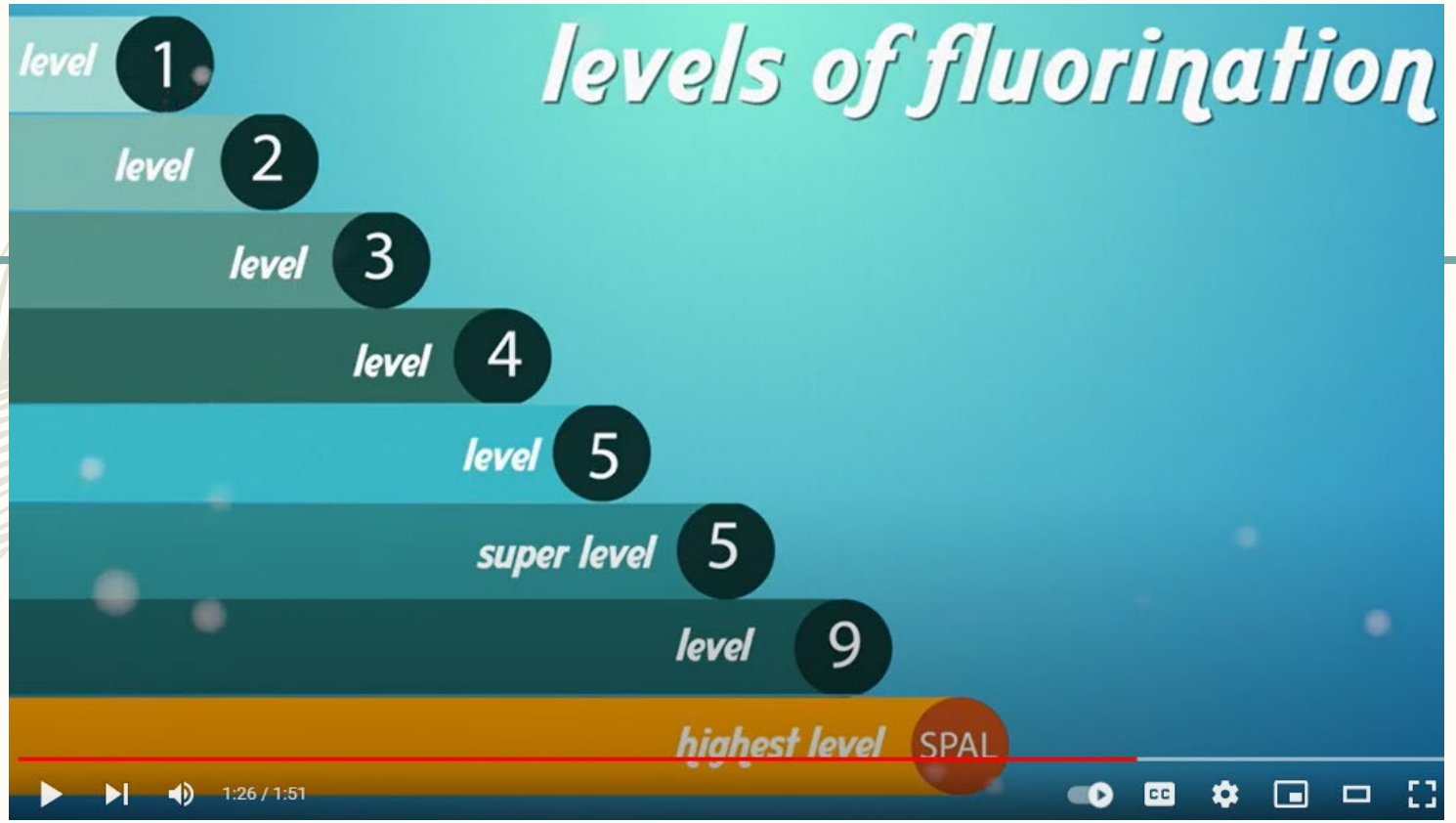


The Anvil 10+10 story

- Fluorination of plastics and what plastics are



See these gaps? These gaps let oxygen in and flavors out. This is what fluorination fixes.


levels of fluorination
level 1
level 2
level 3
level 4
level 5
super level 5
level 9
highest level
SPAL
1:26 / 1:51

We have been fluorinating containers since the 1970s

FDA, as promulgated in 1983, allows fluorination of plastic food-contact materials that produces up to 5,000 parts per billion (ppb) of total fluorine in the food.

That’s fluorine not PFAS

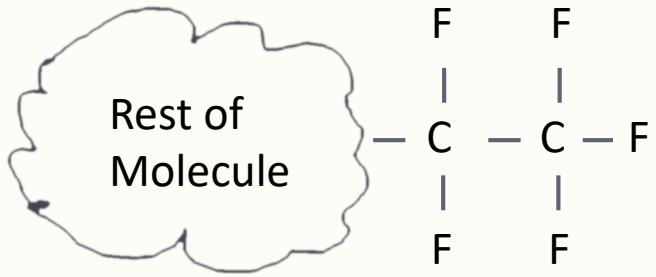
EPA's Response

- Timeline
- Test methods
- Test results
- Links to other information

EPA Q & A

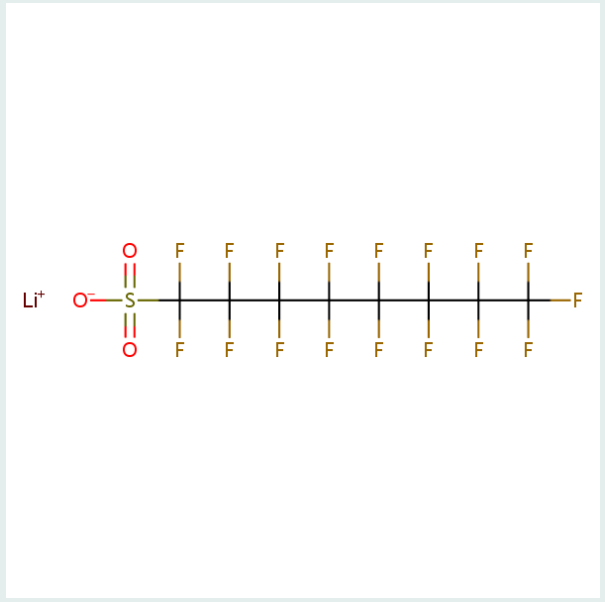
1. What is the definition of a PFAS compound in the context of pesticides?

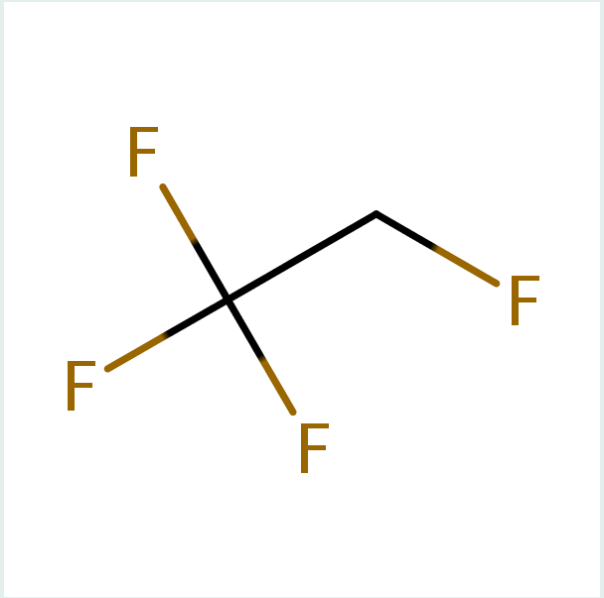
- R-CF2-CF(R1)(R2) where R, R1, and R2 do not equal H and the carbon to carbon bond is saturated

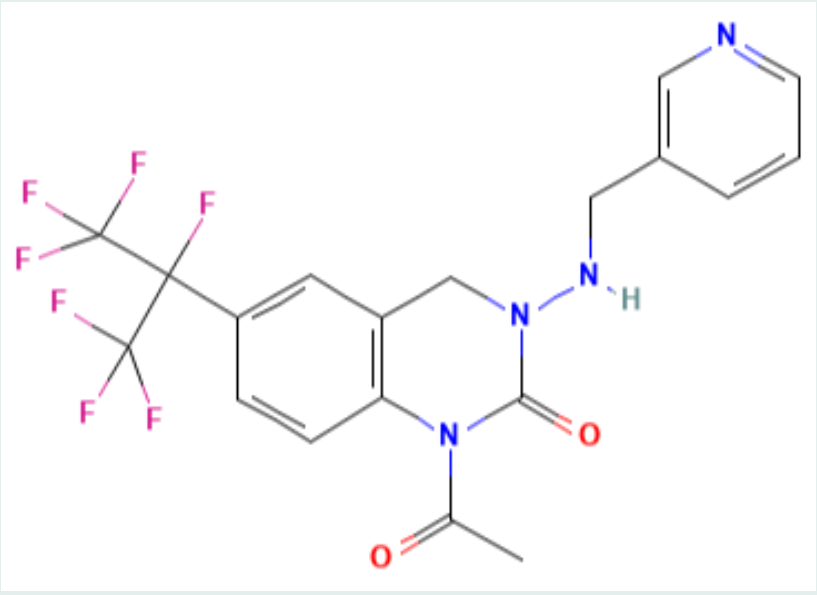


EPA Q & A

1. What is the definition of a PFAS compound in the context of pesticides?







EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- September 1, 2020, Public Employees for Environmental Responsibility (PEER) contacted the Massachusetts Reclamation Board, the Massachusetts Department of Agricultural Resources' (MDAR) Division of Pest Services, and other state agencies claiming that there were unspecified PFAS in a pesticide used for mosquito control. EPA Region 1 was notified that same day.

EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- January 13, 2021, to minimize risks to human health and the environment, EPA asked states with existing stock of the mosquito product distributed in fluorinated HDPE containers to discontinue use and hold until its final disposition is determined.

EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- January 13, 2021, …cont…The pesticide manufacturer has notified all its customers regarding management of the product, voluntarily stopped shipments of all products in fluorinated HDPE containers and is now using non-fluorinated containers.

EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- January 14, 2021, EPA issued a TSCA subpoena to the company that fluorinates the containers supplied to the manufacturer of the pesticide in which PFAS was discovered to learn more about the fluorination process used on the HDPE containers.

EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- EPA is actively working with the Food and Drug Administration, the U.S. Department of Agriculture, and industry and trade organizations to raise awareness of this emerging issue and discuss expectations of product stewardship. For example, EPA is coordinating with the Ag Container Recycling Council, the American Chemistry Council, Crop Life America, the Household & Commercial Products Association, and the National Pest Management Association.

EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- The Agency is also testing different brands of fluorinated containers to determine whether they contain and/or leach PFAS, and if so, learn the conditions affecting leaching.

EPA Q & A

2. When did EPA first learn of this contamination? What steps have been taken since initial PFAS discovery in the pesticide product?

- Testing method published appropriate for oily pesticide mixtures

EPA Q & A

4. What should pesticide registrants do if they find PFAS in their production lines?

- Under FIFRA Section 6(a)(2), pesticide registrants should report to EPA additional factual information on unreasonable adverse effects, including metabolites, degradates, and impurities (such as PFAS).

EPA Q & A

6. Does EPA allow pesticide manufacturers to include PFAS in their formulations as inert ingredients which do not have to be reported?

- No, EPA requires all inert ingredients in pesticide formulations to be reported as part of the Confidential Statement of Formula.

EPA Q & A

2. What PFAS compounds were detected on or in the containers?

Abbreviated	Full Name
PFBA	Perfluoro-butanoic acid
PFPeA	Perfluoro-pentanoic acid
PFHxA	Perfluoro-hexanoic acid
PFHpA	Perfluoro-heptanoic acid
PFOA	Perfluoro-octanoic acid
PFNA	Perfluoro-nananoic acid
PFDA	Perfluoro-decanoic acid
PFUdA	Perfluoro-undecanoic acid

Levels ranging from 20 to 50 parts per billion

EPA Q & A

4. Do we know to what degree long term storage or hot/cold storage conditions might affect the concentration of PFAS leaching?

- EPA is planning to conduct a study to determine under what conditions, generally, PFAS compounds will leach from container walls into the pesticide products.

EPA Q & A

5. What consideration, if any, is being given to pesticide container recycling programs in regard to the fluorinated HDPE containers?

- EPA has been in contact with the Ag Container Recycling Council.

EPA Q & A

6. Should people be concerned about the possibility of being exposed to PFAS from pesticide container contamination? What about other containers?

- The PFAS detections in rinsate from the tested containers do not represent PFAS concentrations in the environment or human exposure to PFAS.
- While EPA is early in its investigation, the Agency will use all available regulatory and non-regulatory tools to determine the scope of this emerging issue and its potential impact on human health and the environment.

EPA Q & A

8. Do the data requirements for containers require information about fluorination to be submitted if containers are fluorinated?

- Yes, EPA's storage and stability/corrosion characteristics data requirements require registrants to provide details on the type of container used to distribute the product commercially, which can include fluorinated High Density Polyethylene (HDPE) containers.

EPA Q & A

9. Do existing FIFRA container regulations address the use of fluorinated HDPE containers?

- FIFRA pesticide container regulations do not specifically address the fluorination of plastic containers, i.e., the regulations do not require fluorination, nor do they prohibit fluorination of plastic pesticide containers.
- However, some of the Department of Transportation requirements that are referred to and adopted in the pesticide container regulations may impact a pesticide manufacturer's decision to fluorinate containers.

EPA Q & A

2. What are the alternatives to Anvil 10+10 for mosquito spray, and are the alternative pesticide products stored the same way?

- Fluorinated polyethylene and HDPE are used for numerous applications such as food packaging and containers for chemical storage, including pesticides.
- This is the first time that EPA has been aware of fluorinated HDPE container use as a potential source of PFAS contamination in a pesticide.
- EPA is using its authorities under FIFRA and TSCA to obtain more information about the potential scope of this contamination and to evaluate whether other regulated products may be affected.

EPA Q & A

3. What should states and others do with existing stock of Anvil 10+10?

4. Will affected products be placed under Stop Sale/Stop Use by EPA or State Lead Agencies?

- EPA asked states with existing stock of the mosquito product distributed in HDPE containers to discontinue use and contact the manufacturer about their product exchange program.
- EPA will respond to any additional PFAS supply-chain contamination issues on a case-by-case basis. For example, EPA worked with the mosquito product manufacturer to remove contaminated product from the supply chain.

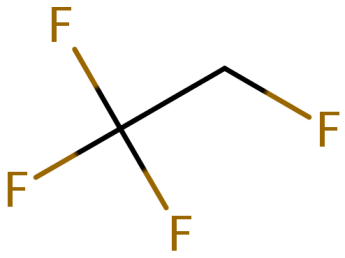
EPA Q & A -Summary

- New issue, working on it.
- None of the product that is known to have PFAS has been used -all of it was withdrawn and replaced by manufacturer.
- All of the big federal agencies are working to determine the scope of this issue.

State of Maine actions

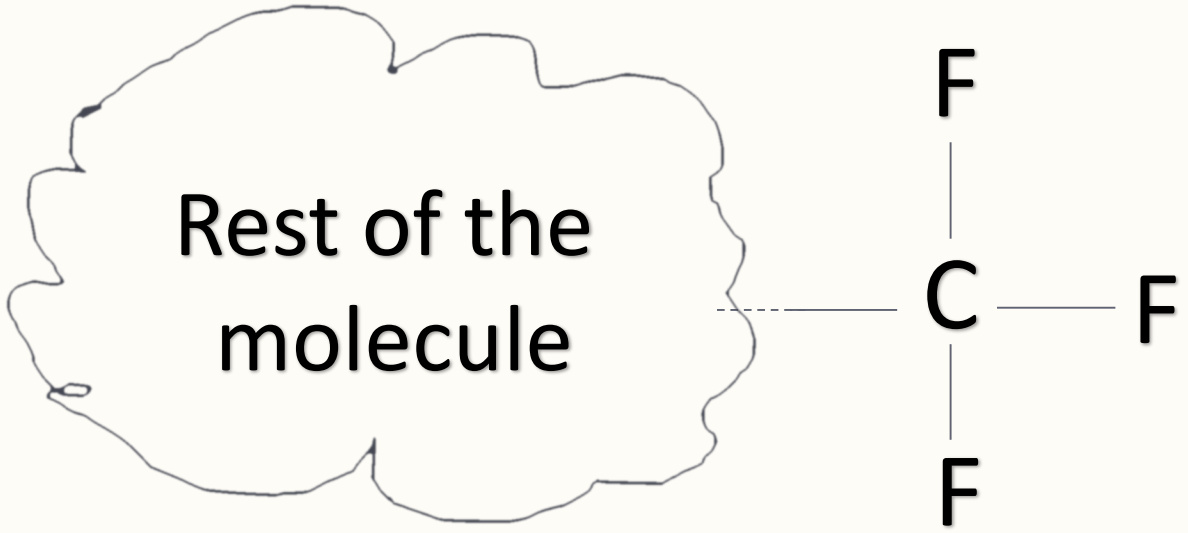
LD 1503 defines PFAS as:

F. "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.



State of Maine actions

This definition is close to other definitions but different.



-CF3

State of Maine actions

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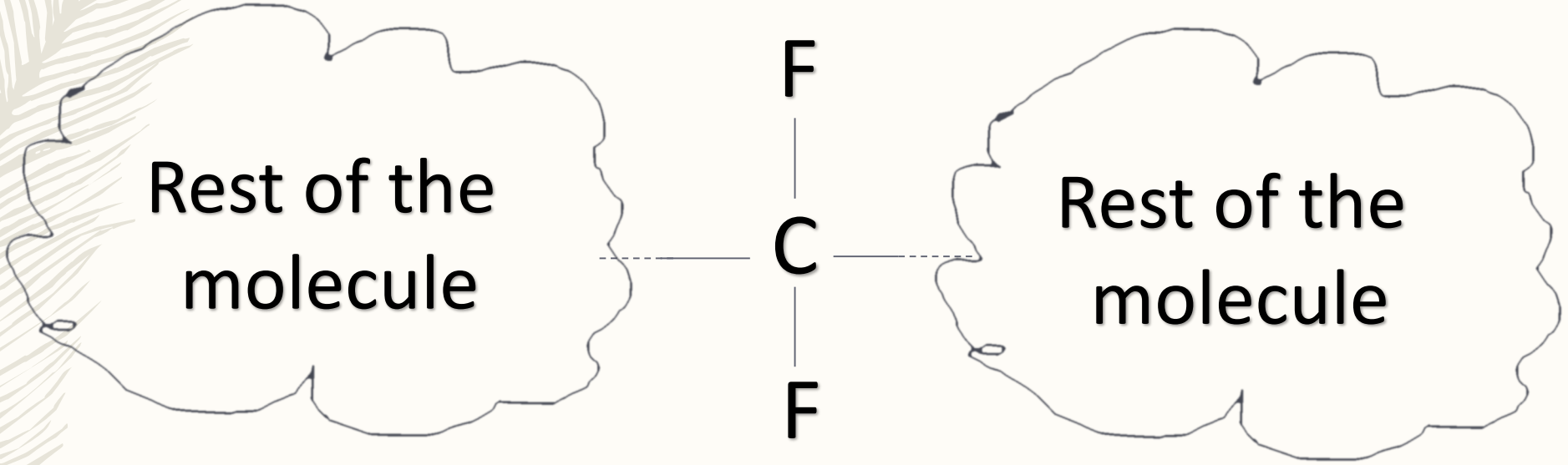
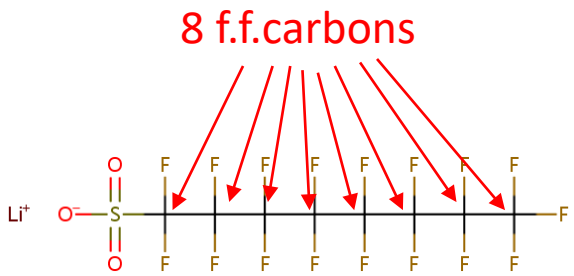
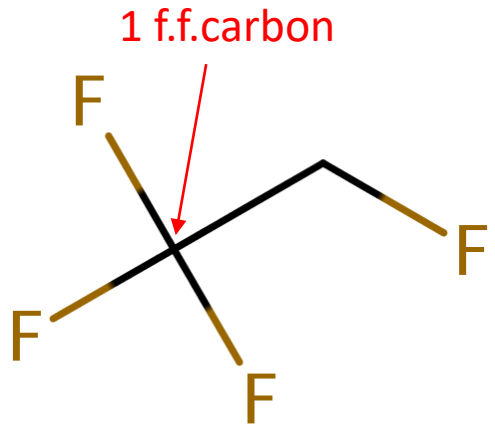


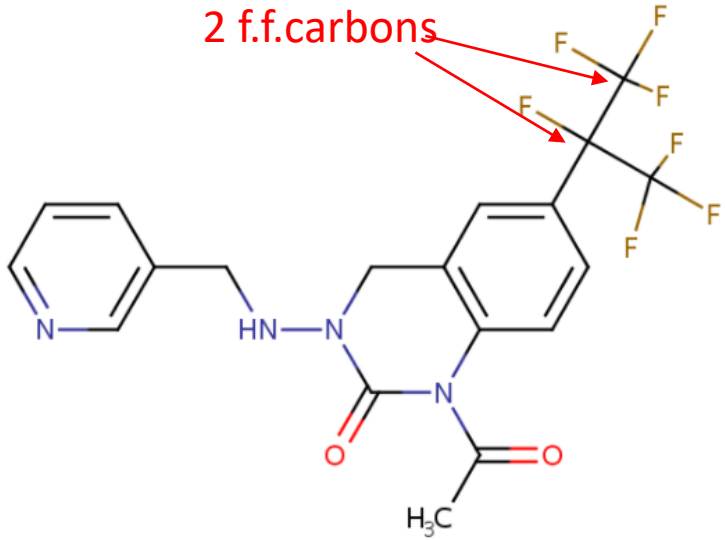
-CF2-

PFAS classification

- Depending on the definition between a few hundred to 12,000+ chemicals classified as PFAS

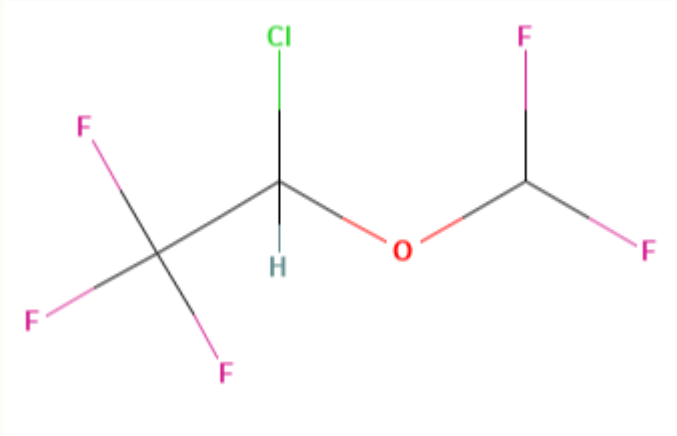






How does the State of Maine definition of PFAS change things?

- Chemicals not previously classified as PFAS will become “PFAS”
- Unknown number of pesticides and inert/other ingredients



Isoflurane: general anesthetic and muscle relaxant activities

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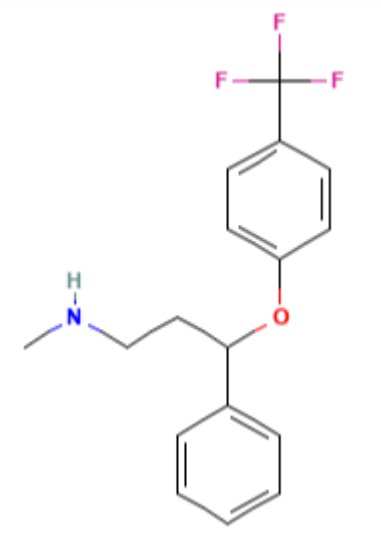
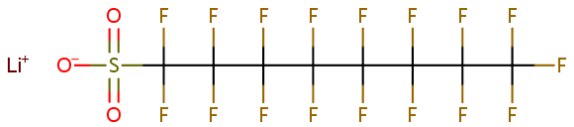


fluoxetine: selective serotonin reuptake inhibitor (SSRI) widely used as an antidepressant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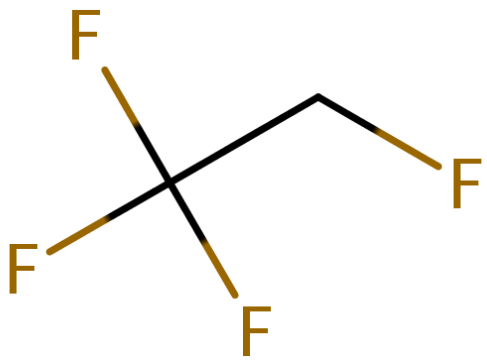
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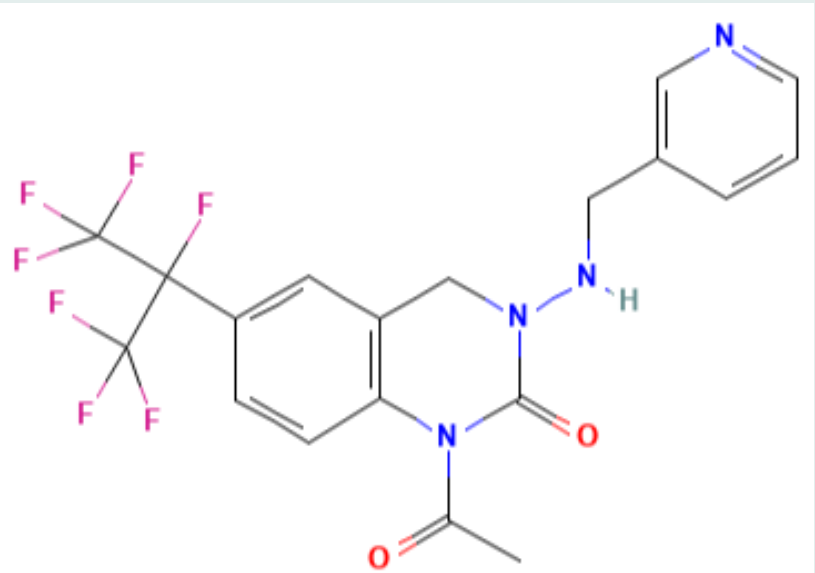
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OECD PFAS Discussion on How to Define PFAS…

OECD definition:

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

The points they make about this definition:

- …The decision to broaden the definition compared to Buck et al. is not connected to decisions on how PFASs should be grouped in regulatory and voluntary actions….

OECD PFAS Discussion on How to Define PFAS…

OECD definition:

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The points they make about this definition:

- …The term “PFASs” is a broad, general, non-specific term, which does not inform whether a compound is harmful or not, but only communicates that the compounds under this term share the same trait for having a fully fluorinated methyl or methylene carbon moiety…

As we discuss this important to distinguish between

- **Adulterants**
  - Typified by “classic PFAS”
  - May or may not be well classified by risk assessment (PFOA)

Vs.

- **Intentionally added**
  - Definition changes the scope
  - In pesticides, accompanied by a risk assessment

Pesticide risk assessments address many of the issues of “classic” PFAS

- Soil half-life
- Aquatic half-life
- Bioaccumulation potential
- Major degradation products
- Leaching potential
- Suite health effects studies

The attributes that make PFAS so difficult environmentally/health effects are all included as parts of the required data collection during registration.

How big of a deal is container adulteration?

- How much do pesticide containers add PFAS to the environment? and
- Is that ok?

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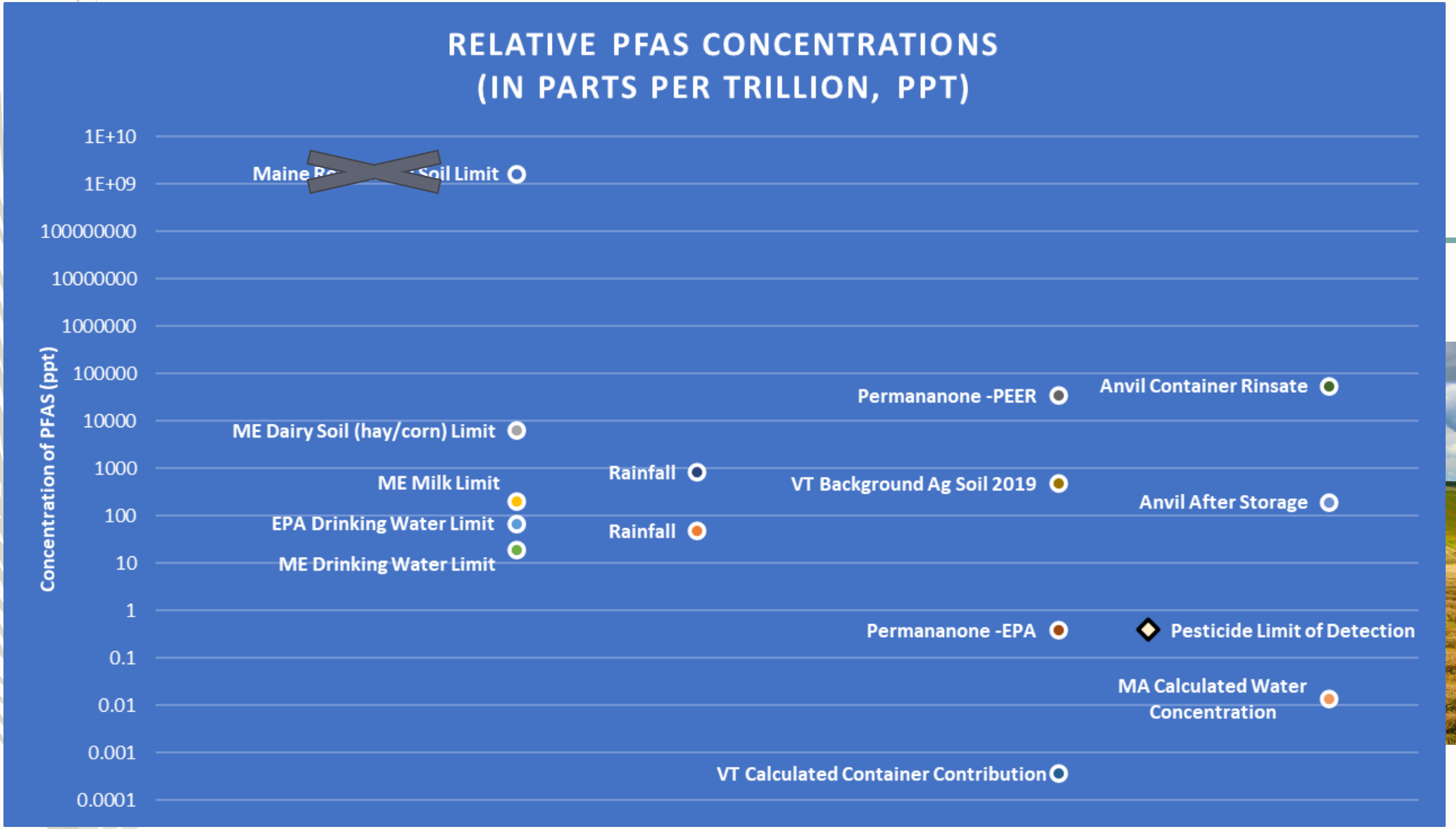
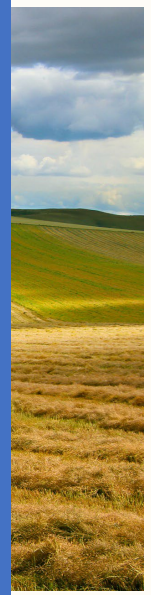
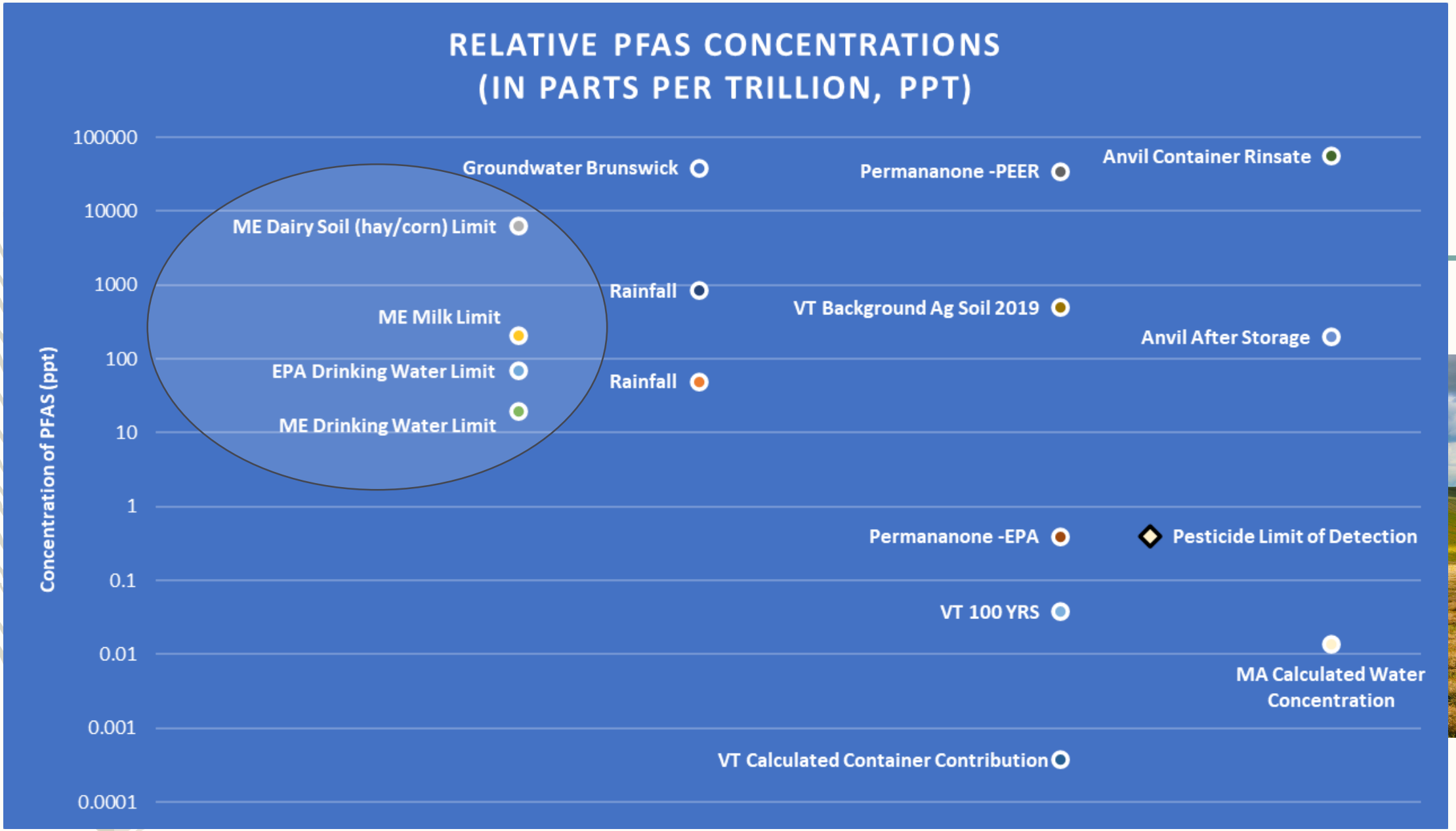

RELATIVE PFAS CONCENTRATIONS
(IN PARTS PER TRILLION, PPT)
Concentration of PFAS (ppt)
1E+10
1E+09
100000000
10000000
1000000
100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Maine [illegible] Soil Limit
ME Dairy Soil (hay/corn) Limit
ME Milk Limit
EPA Drinking Water Limit
ME Drinking Water Limit
Rainfall
Rainfall
Permananone -PEER
VT Background Ag Soil 2019
Permananone -EPA
VT Calculated Container Contribution
Anvil Container Rinsate
Anvil After Storage
Pesticide Limit of Detection
MA Calculated Water Concentration




RELATIVE PFAS CONCENTRATIONS
(IN PARTS PER TRILLION, PPT)
Concentration of PFAS (ppt)
100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
Groundwater Brunswick
ME Dairy Soil (hay/corn) Limit
Rainfall
ME Milk Limit
EPA Drinking Water Limit
Rainfall
ME Drinking Water Limit
Permananone -PEER
Anvil Container Rinsate
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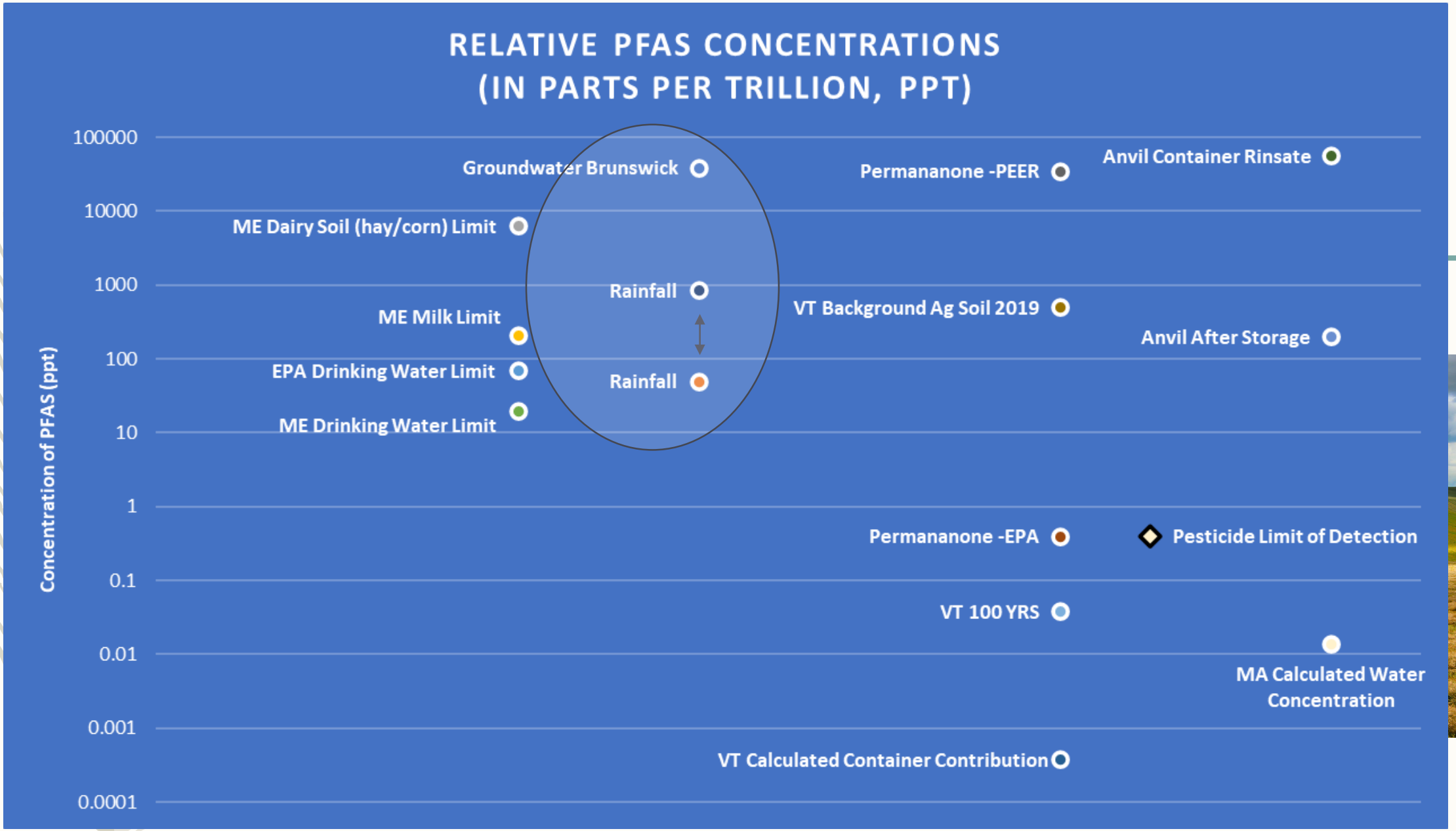
Pesticide Limit of Detection
VT 100 YRS
MA Calculated Water Concentration
VT Calculated Container Contribution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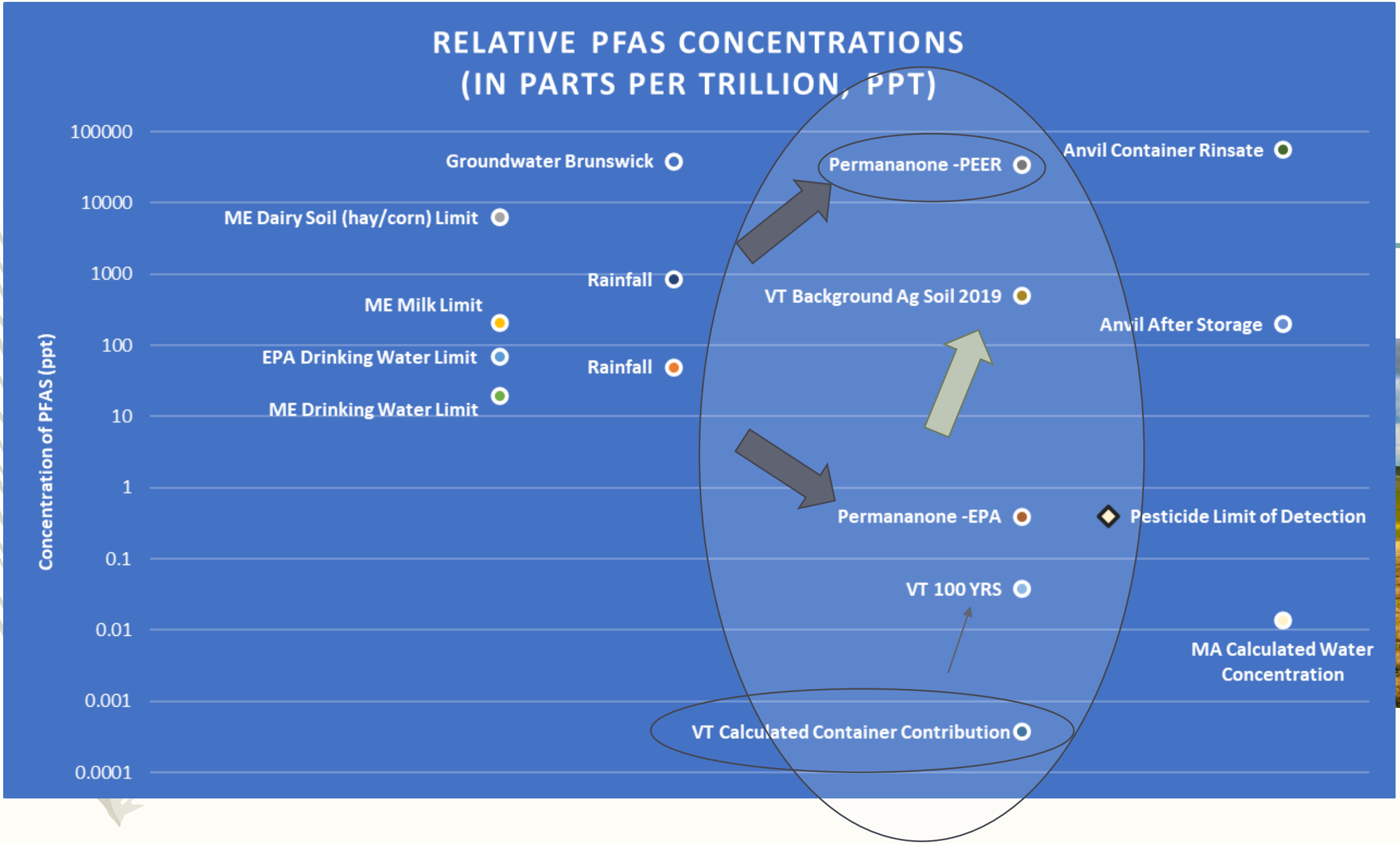

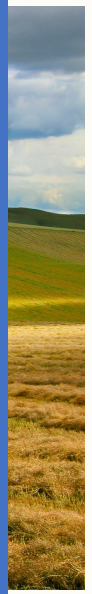

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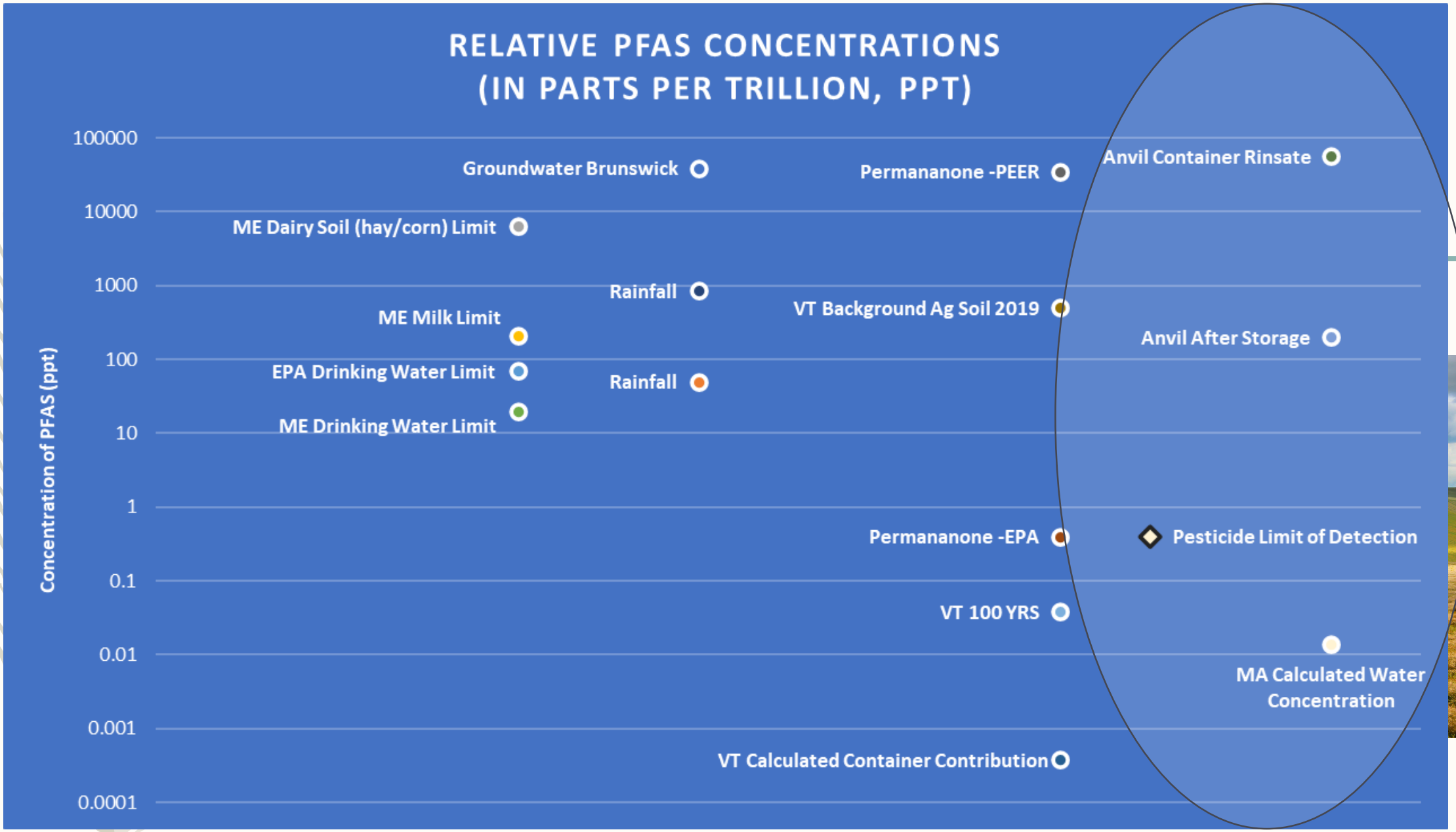
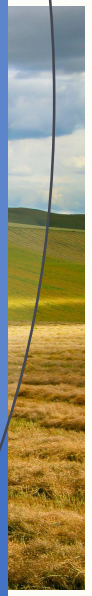




My contact information

Pam Bryer

Pesticides Toxicologist

Maine Board of Pesticides Control

pamela.j.bryer@maine.gov

Main line:

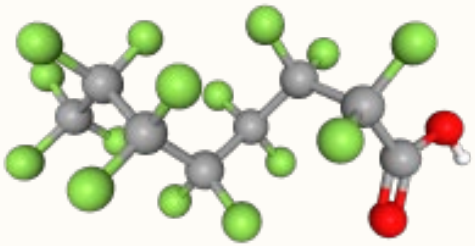
207-287-2931

pesticides@maine.gov

-or- just reach out to our office

Per- and Polyfluoroalkyl Substances (PFAS)

- Pronounced as “P -fas”
- Often confused with “P -foss” which is a specific type of PFAS
- Also hear: “P -foe-ah” which is another specific type of PFAS



Perfluorooctanoic acid (PFOA)
C8

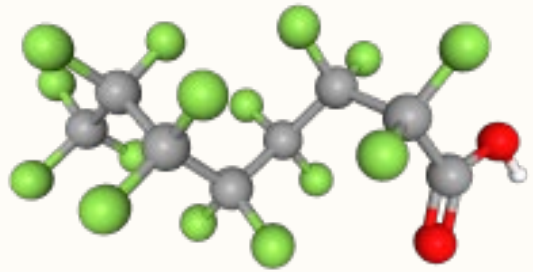
Per- and Polyfluoroalkyl Substances (PFAS)

Fluorine = Green

Carbon = Gray

Oxygen = Red

Hydrogen = White



Perfluorooctanoic acid
C8

Per- and Polyfluoroalkyl Substances (PFAS)

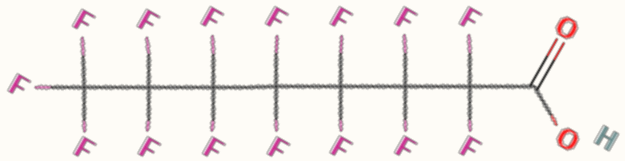
Fluorine = Green

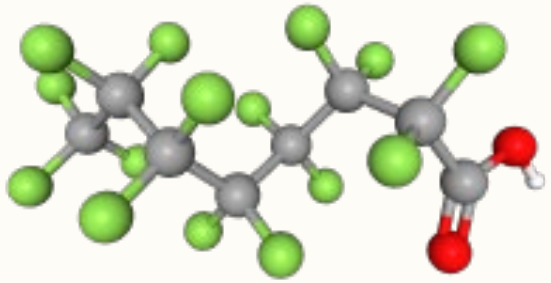
(sometimes purple)

Carbon = Gray

Oxygen = Red

Hydrogen = White

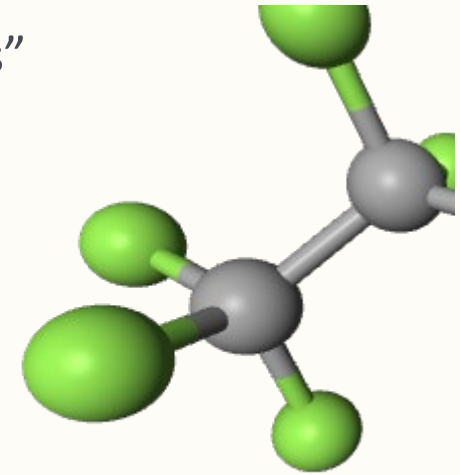




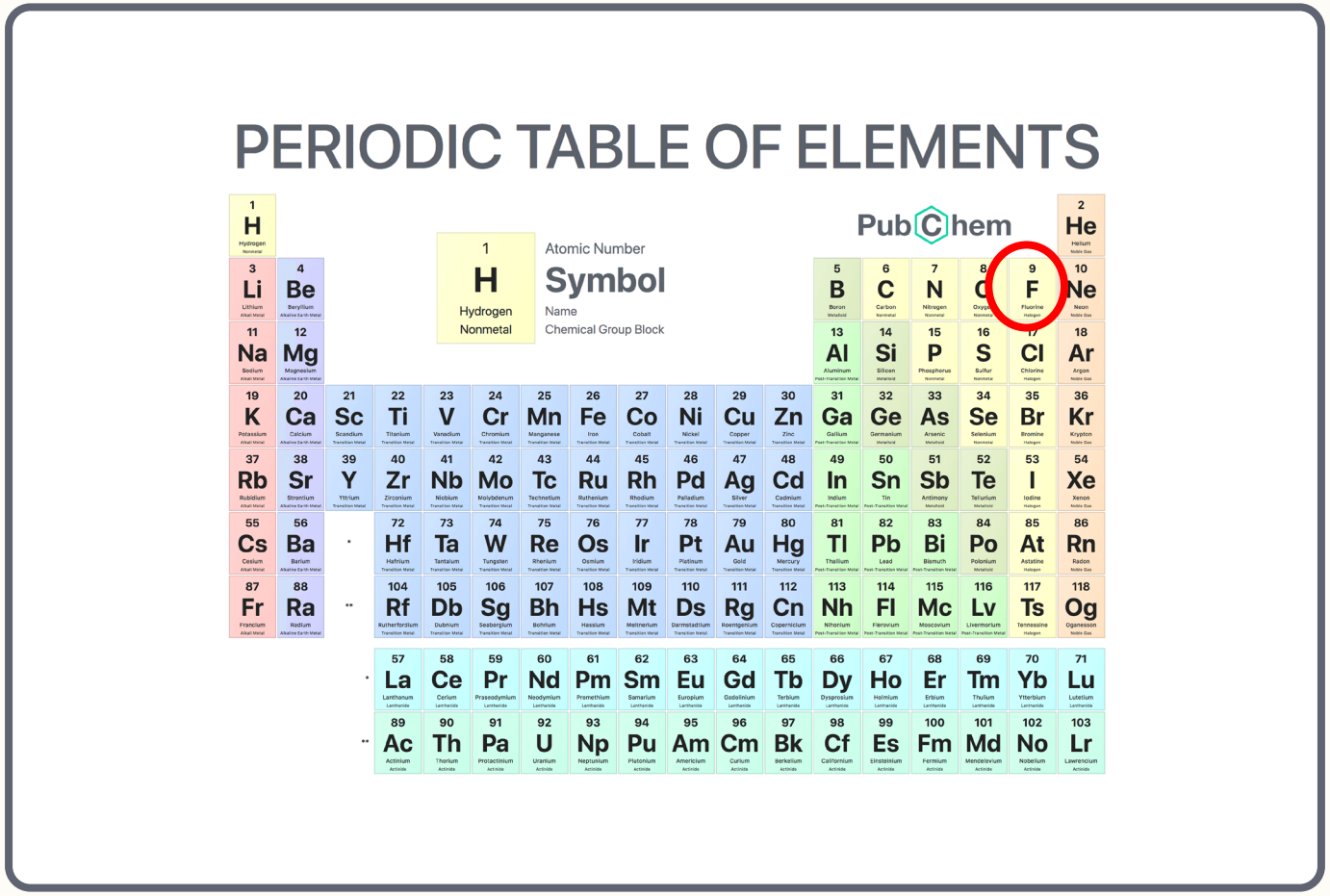
Perfluorooctanoic acid
C8

Per- and Polyfluoroalkyl Substances (PFAS)

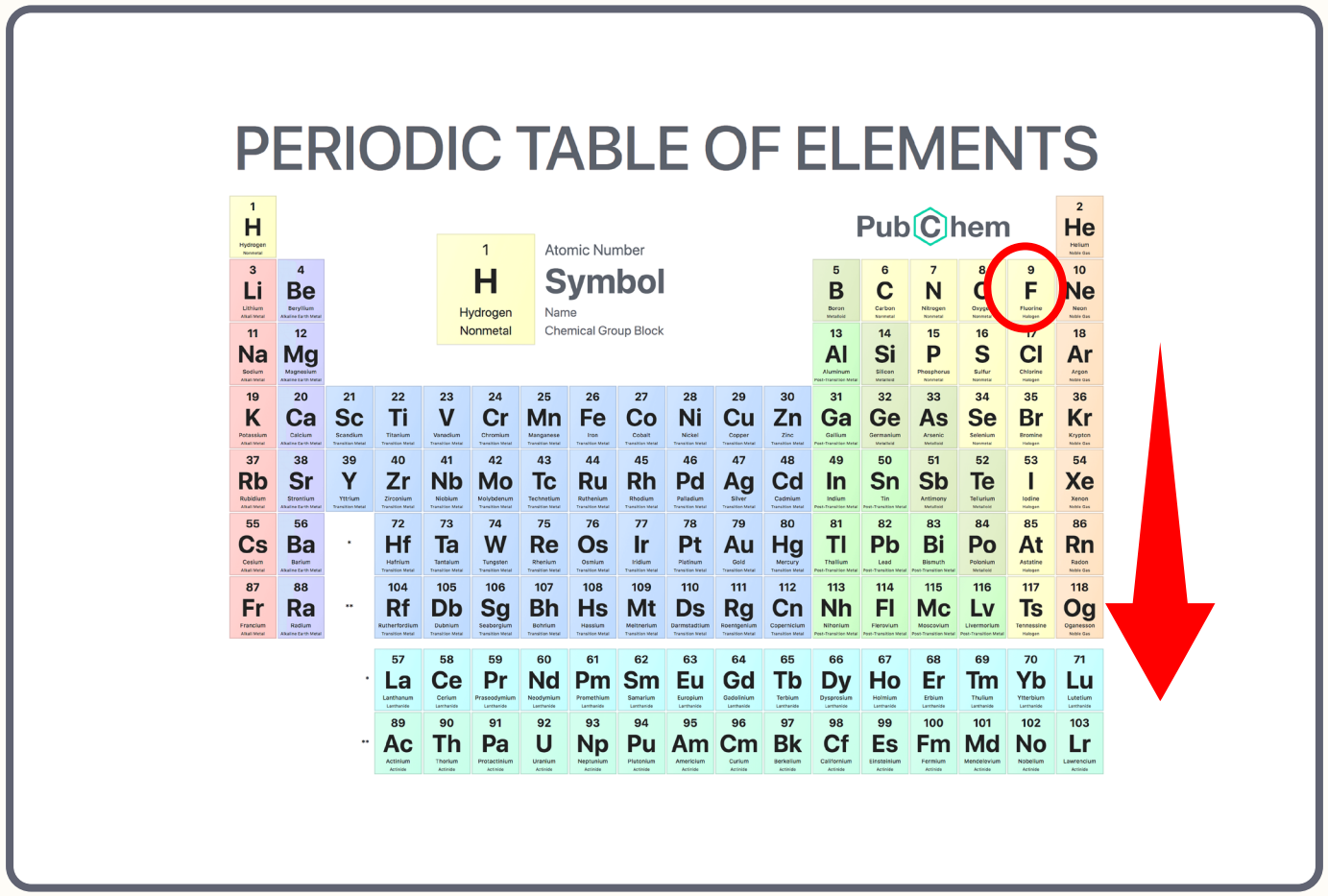
- Fluorine to Carbon bond is one of the strongest chemical bonds
- This is why they are called “forever chemicals”
- Takes a lot of energy to break the fluorine off of the carbon



Fluorine molecules hold other molecules tight & close



- Fluorine is a small molecule (top of the table)
- Fluorine has strength (same as others in the column)



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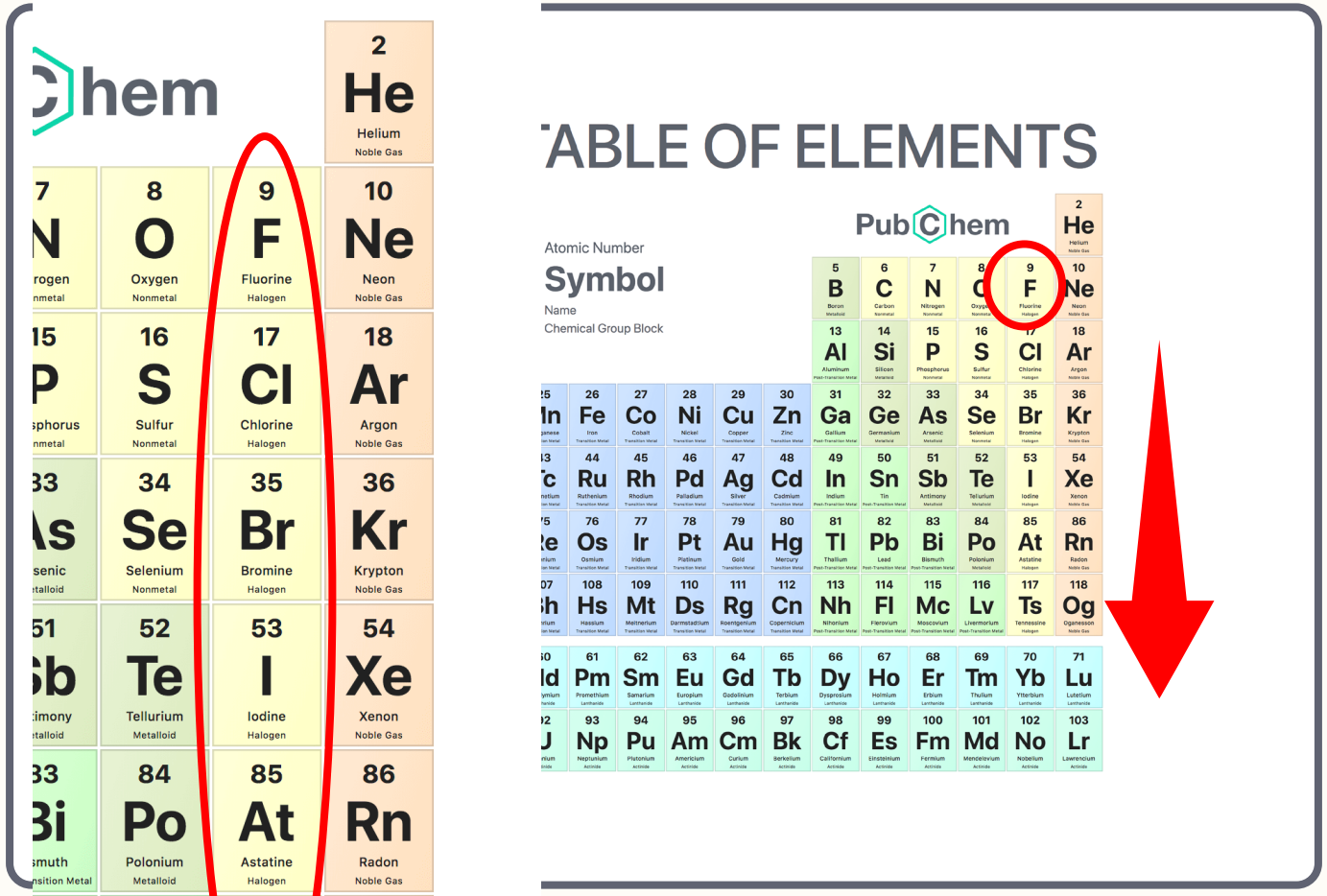

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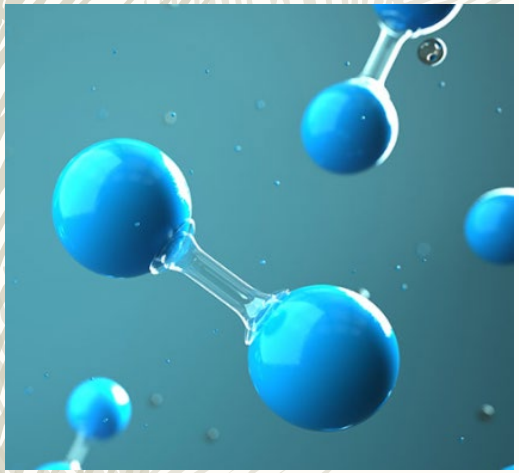

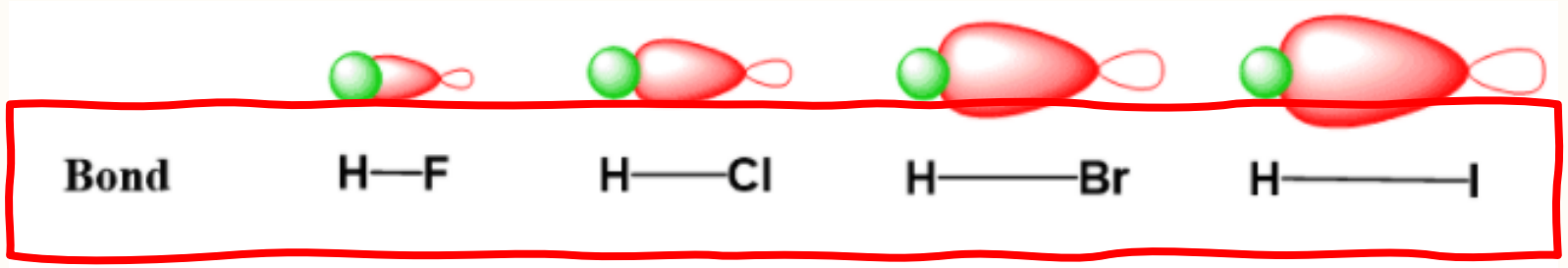

Bond	H—F	H—Cl	H—Br	H—I
Length	0.917 Å	1.275 Å	1.415 Å	1.609 Å
Strength	136 kcal/mol	103 kcal/mol	87 kcal/mol	71 kcal/mol
	571 kJ/mol	432 kJ/mol	366 kJ/mol	298 kJ/mol

https://www.sciencenewsforstudents.org/

https://www.chemistrysteps.com/bond-lengths-and-bond-strengths/

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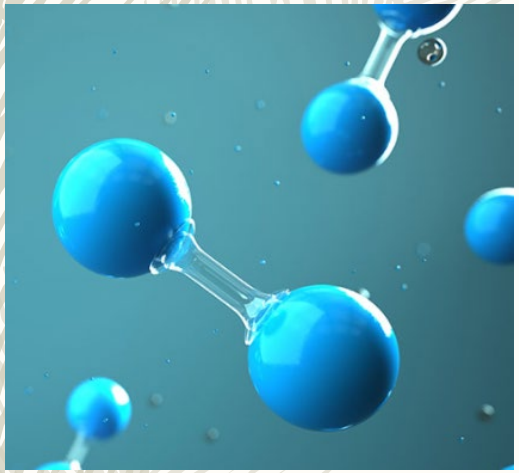

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