

The Dark Matter of PFAS in Environmental Real Estate Assessments

Kenneth F. Ede, Ph.D., CHMM

Audra S. Ligenstoffer, Ph.D.

Damon Wright, M.S.

Andrew Pawlisz, D.A.B.T.

Anthony Moore

Contact Information

Kenneth F. Ede, Ph.D., CHMM

KFE & Associates, LLC

Kenede115@gmail.com

Audra Ligenstoffer, Ph.D.

Brown Environmental, LLC

Audra.Ligenstoffer@brownenviro.com

Damon Wright, MS, CHMM

QuikTrip Corporation

dawright@quiktrip.net

Andrew Pawlisz, DABT

Trihydro Corporation

apawlisz@trihydro.com

Anthony Moore

Environmental Works, Inc.

Anthony@environmentalworks.com

Thank You

Environmental Federation of Oklahoma

- **Howard (Bud) Ground**
- **Jody Reinhart**



Environmental Federation of Oklahoma

Working for Oklahoma's Economic and Environmental Future

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Today's Problem vs. Tomorrow's Problem

- A Greenpeace activist was recently asked the following question:
- Q: *“Today, why is PFAS the most prominent environmental problem?”*
- A: *“People see climate change as a tomorrow problem”*
- *“PFAS is a today problem”*
- Just one percent of voters in a recent New York Times/Siena College poll named climate change as the most important issue facing the country

PFAS the Last 12 months

➤ Question: “You gave a PFAS presentation last year. What has really changed over just the last 12 months regarding PFAS?”

One thing that has not changed!

- **Chemists are still Chemists!**
- **The rest of the world will be spending millions, billions or may be trillions of \$\$\$ DOLLARS \$\$\$ getting rid of PFAS molecules**





FLUORINATION

Fluorine-studded cube ensnares electron

Perfluorocubane can capture an electron within its interior, thanks to antibonding orbital overlap

by *Bethany Halford*

August 11, 2022 | A version of this story appeared in *Volume 100, Issue 28*

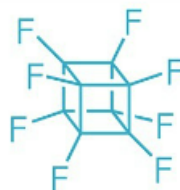
Chemists have synthesized perfluorocubane for the first time. The molecule, C_8F_8 , consists of a cube of carbon atoms with fluorine atoms attached to each of its eight vertices. The synthetic feat advances fundamental fluorocarbon science, says the University of Tokyo's Midori Akiyama, who led the research. Akiyama adds that C_8F_8 could have applications in electronic and spintronic materials.

Perfluorocubane has long interested chemists, "not only for its beautiful structure, but also for its electron acceptivity and intermolecular interactions," Akiyama says in an email.

Her team synthesized perfluorocubane using fluorine gas in a fluorinated solvent to add seven fluorines to a cubane that had a partially fluorinated ester at one of its corners. The chemists then swapped in a different ester and converted the molecule to heptafluorocubane. Finally, they replaced the heptafluorocubane's lone hydrogen with a fluorine.

Akiyama's team also showed that the position of C_8F_8 's C-F antibonding orbitals allows the molecule to hold an electron inside the cube, generating a radical anion that ultimately decomposes. Capturing an electron this way contrasts with common π -conjugated electron acceptors, which hold electrons on their surfaces (*Science* 2022, DOI: [10.1126/science.abq0516](https://doi.org/10.1126/science.abq0516)).

Karl K. Irikura, a theorist at the US National Institute of Standards and Technology, has studied the electronic properties of perfluorocubane. "It's exciting to see these molecules created in the real world, and not only studied by theory," he says in an email.



Perfluorocubane

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[Fluorine-studded cube ensnares electron](#)

[Mechanochemists want to shake up industrial chemistry](#)

[Chemistry in Pictures: Still life of the lab](#)

[Chemists find shortcut to puffer fish poison](#)

[Nabbing nitrogen from the air to make fertilizer on the farm](#)

[Chemistry in Pictures: Complicated crystals](#)

Fluorine-studded cube ensnares electron

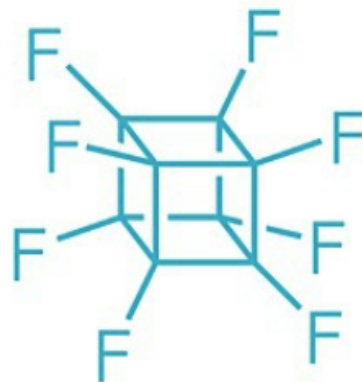
Perfluorocubane can capture an electron within its interior, thanks to antibonding orbital overlap

by **Bethany Halford**

August 11, 2022 | A version of this story appeared in **Volume 100, Issue 28**

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Perfluorocubane

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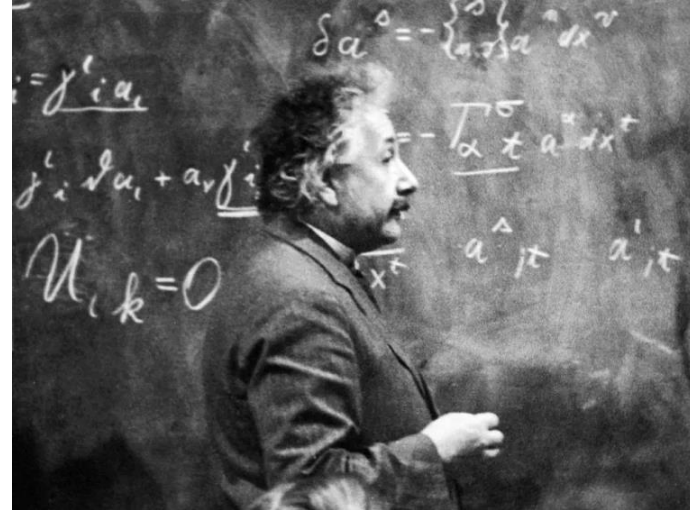
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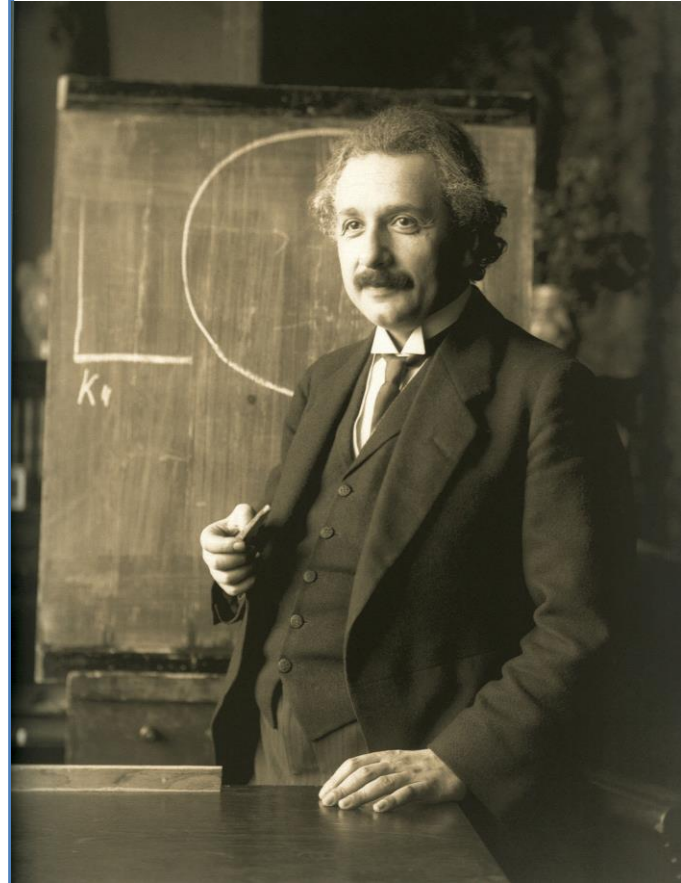
From last year to this year!

- **1942: Albert Einstein was teaching a graduate-level class in theoretical physics**
- **After Einstein passed out an examination, his teaching assistant, realized that Dr. Einstein gave the exact same examination to the exact same students just one year ago**



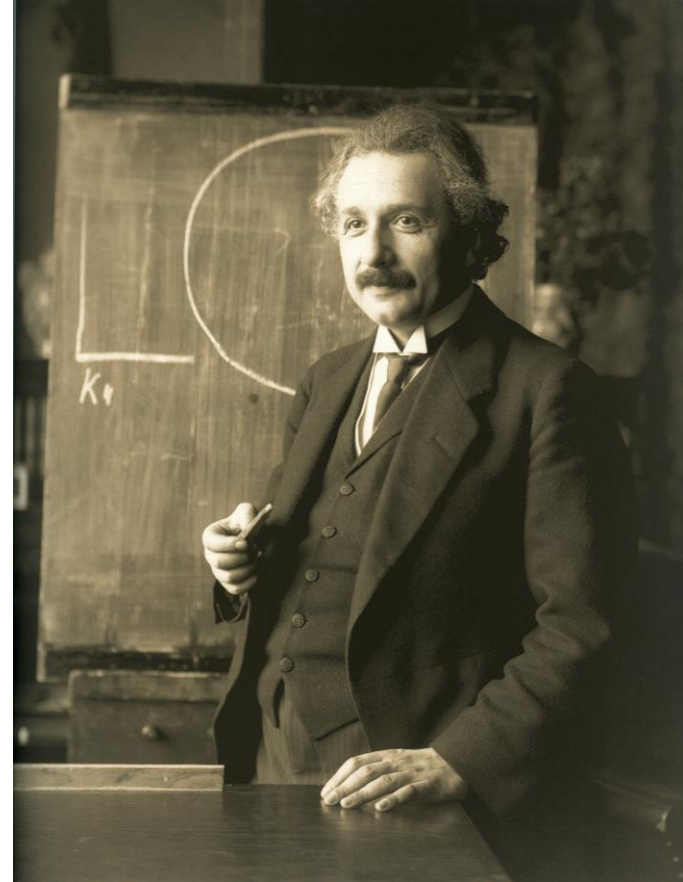
Albert Einstein

- The teaching assistant was alarmed at what he saw and thought that this mistake was the result of the professor's absentmindedness
- *"Excuse me, sir, Dr. Einstein, I'm not sure if you realize it, but you gave out this same examination to the same students last year"*



Albert Einstein

- Einstein paused to think for a moment, then said,
- *“Yes, it is the same examination, it is the same questions, however*
- *the answers have changed.”*



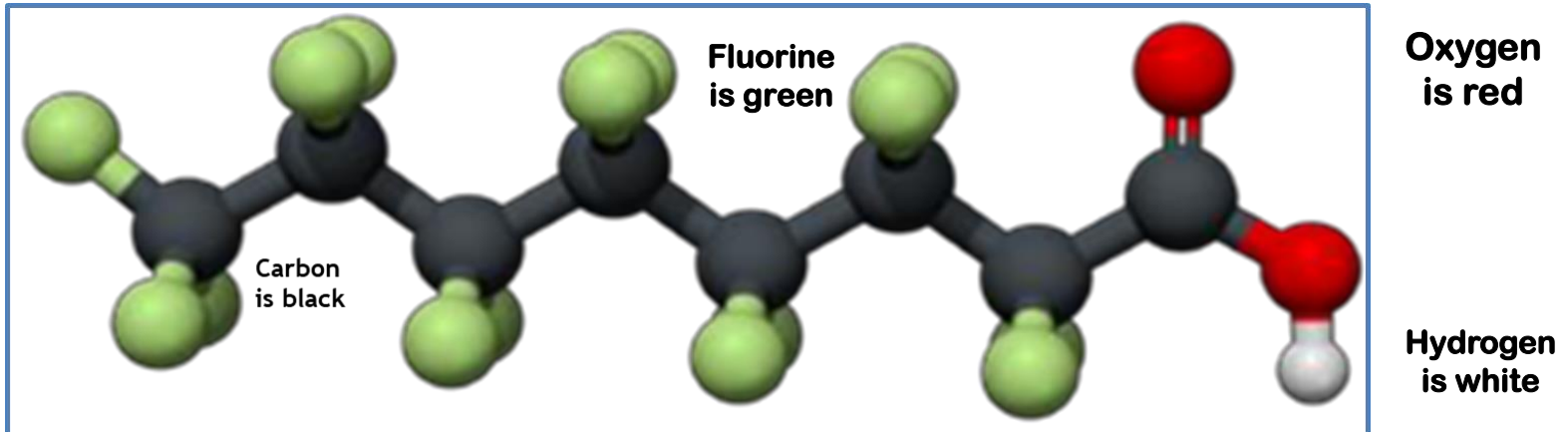
Q&A vs. Lecture

- **Rather than lecture about PFAS, I want to address specific questions I receive on a weekly basis**
- **By the way, please feel free to contact me with any additional questions:**
- **Kenede115@gmail.com**

What is PFAS?

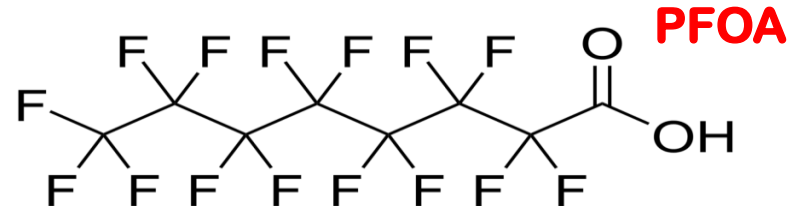
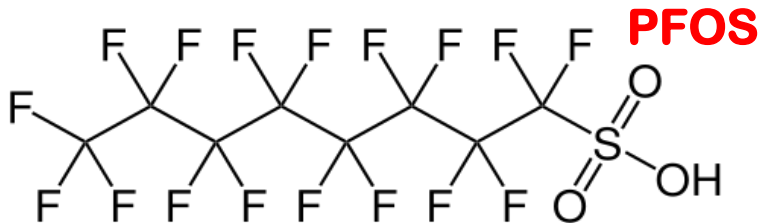
Per- & Poly-Fluoro-AlkySubstances (PFAS)

- Per- or Poly: All or more than one
- Fluoro: contains fluorine
- Alkyl: Contains carbon



PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

- **PFAS: Umbrella term**
- **PFAS are family of > 12 000 manmade chemicals**
- **PFOS, PFOA, etc..... X 12 000**
- **Most common names: Teflon (PTFE), Kynar, Gore-Tex, Scotchgard, AFFF, etc.**



PFAS: One tree with 12 000 leaves

PFOS

PFOA

PTFE
(TEFLON)

PFAS

Q: How many PFAS substances are there?

- **A: The number have changed over the years:**
- **200 → 500 → 1000 → 5000 → 10 000**
- **Presently > 12 000 different molecules**

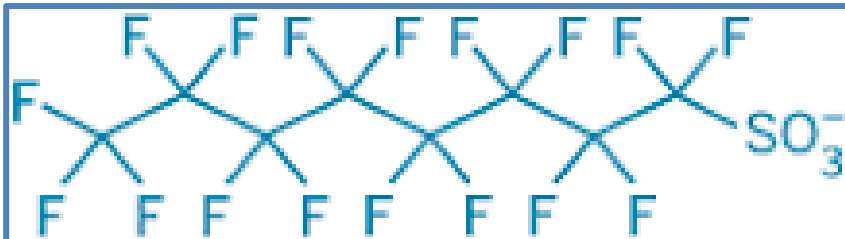
Q: Why does the PFAS number keep growing?

- FR September 6, 2022:
- EPA is proposing to designate both PFOA and PFOS, including their salts and structural isomers -- as hazardous substances under the CERCLA, also known as Superfund

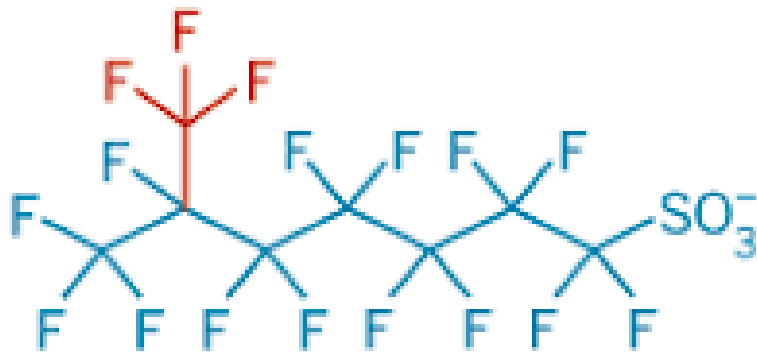
Q: Why does the PFAS number keep growing?

- Therefore, EPA has included:
All Isomers: Chemicals with the same chemical formula, but different molecular structures
- Therefore, a PFAS isomer contains the same number of atoms of each element, but have different arrangements of their atoms

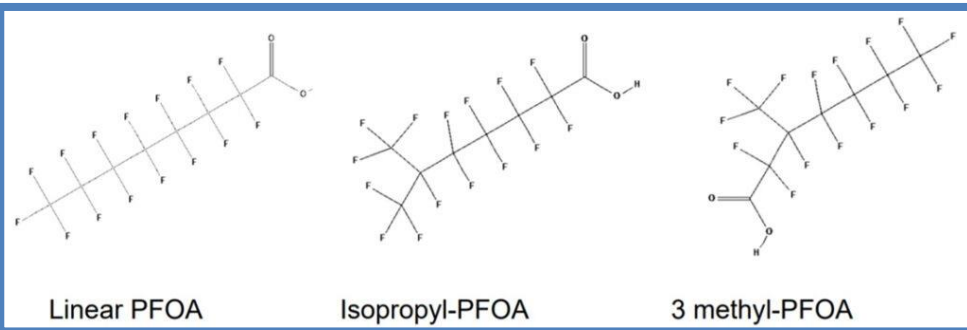
Q: Why does the PFAS number keep growing?



PFOS linear isomer



PFOS branched isomer



PFOA Isomers

Q: Why does the PFAS number keep growing?

- In addition, EPA including their salts
- PFAS can exist in various ionic states
- Neutral (no charge) or
- Anion (negatively charged) or
- Cation (positively charged) or
- Zwitterions (both positively and negatively charged dipolar molecules),
- PFAS can exist in different salts including sodium, lithium, potassium, or ammonium
- Each of these salts will have a different CAS number

Q: We tested our wastewater and found PFAS, however none of Safety Data Sheets (SDS) show PFAS? Is the laboratory wrong?

➤ A. No, at the present time, PFAS substances are not considered a known carcinogen, therefore the manufacturer of the chemical* does not need to report as an active ingredient unless it exceeds 1%

***Appendix A to § 1910.1200**

Q: SDSs & PFAS

- **1% \approx 10 000 PPM (parts per million) =**
- **10 000 000: Parts per Billion (PPB) =**
- **10 000 000 000: 10 BILLION parts per Trillion**
- **Therefore:**
- **1% \approx 10 000 000 000 PPT**
- **And does NOT need to be reported on the SDS!**
- **EPA's health advisories for PFOA = 0.004 PPT**

Q: SDSs & PFAS

- **Look at the products in question**
- **Does it bead-up water? (hydrophobic)**
- **Does it make it stain resistant, waterproof, water resistant, leak-proof or slick?**
- **Does the chemical make it fireproof, fire-retardant or antifog?**
- **It probably contains PFAS!**

PFAS found on Mt. Everest

Science

'Forever chemicals,' other pollutants found around the summit of Everest



A long queue of mountain climbers find a path on Mount Everest in Nepal. Snow samples around the summit showed traces of toxic chemicals known as PFAS. (Rizsa Alsz/AP)

By Murray Carpenter

April 17, 2021 | Updated April 17, 2021 at 9:34 a.m. EDT

From an elevation of 27,600 feet, just below the summit of Everest, researcher Mariusz Potocki could see one of the planet's most dramatic scenes — the snow-capped Himalayas against a deep blue sky. He was on a mission to gather snow and ice samples at the summit, but just above him was another startling sight: a line of climbers so dense that a photo of it went viral.

[Everest's massive climber traffic jam](#)

His team had stopped at a resting spot climbers call "The Balcony," and the snow there was littered with feces, oxygen bottles and other trash. But he wanted to gather what samples he could, so he ascended a short distance to find some cleaner snow off to the side of the trail. "I just pulled out the bottles and took samples," he said.

Is automation

CLIMBING

SKILLS

NEWS

GEAR

PLACES

PEOPLE

PHOTOS

VIDEOS

OLYMPICS

PODCAST

Tents, clothing, boots, ropes, food packaging



Why Are There Harmful Chemicals on Mount Everest?

McDonalds (PPT)



Bag for French Fries	250 300 000
Bag for Cookies	250 000 000
Bag for Chicken McNuggets	219 000 000
Container for Big Mac	195 300 000
Wrapper for Double Cheeseburger	15 000 000
Container for Chicken McNuggets	13 500 000

<https://www.consumerreports.org/pfas-food-packaging/dangerous-pfas-chemicals-are-in-your-food-packaging-a3786252074/#allResults>

EPA has established a lifetime health advisory level for **PFOA = 0.004 PPT**

Burger King (PPT)



Bag for Cookies, French Toast Sticks	345 700 000
Wrapper for Whopper	249 700 000
Bag for Chicken Nuggets	165 000 000
Container for French Fries	13 000 000
Container for Chicken Sandwich	12 000 000

<https://www.consumerreports.org/pfas-food-packaging/dangerous-pfas-chemicals-are-in-your-food-packaging-a3786252074/#allResults>

EPA has established a lifetime health advisory level for PFOA = 0.004 PPT



Chick-fil-A (PPT)



Wrapper for Sandwich Wrap	553 500 000
Bag for Sandwich, Foil-lined	10 500 000
Container for Sides	8 500 000

<https://www.consumerreports.org/pfas-food-packaging/dangerous-pfas-chemicals-are-in-your-food-packaging-a3786252074/#allResults>

EPA has established a lifetime health advisory level for PFOA = 0.004 PPT

Taco Bell (PPT)



Paper Bag for Chips	145 000 000
Wrapper for Taco	10 000 000
Wrapper for Burrito	9 300 000

<https://www.consumerreports.org/pfas-food-packaging/dangerous-pfas-chemicals-are-in-your-food-packaging-a3786252074/#allResults>

EPA has established a lifetime health advisory level for PFOA = 0.004 PPT

Q: If PFOA & PFOS become a CERCLA hazardous substances, will they also be controlled under US DOT?

- **Yes, CERCLA requires that US DOT regulate all listed “hazardous substances” as hazardous materials in transportation**
- **Once a new hazardous substance is added to the CERCLA list, it also becomes a regulated hazardous material for transportation purposes with a RQ of 1 pound**

Q: Assume we have just a 1% PFOA solution in one of our carwash products or fire extinguishers, how much can we spill without reaching a CERCLA Reportable Quantity of 1 pound?

1. CONVERT: mg/L to pounds

$$\frac{\text{\# gal.}}{\text{\# mg}} \times \frac{1 \text{ L}}{1000 \text{ mg}} \times \frac{1 \text{ gram}}{454 \text{ g}} \times \frac{3.78 \text{ liters}}{1 \text{ gallon}} = \text{Lbs spilled}$$

$$\text{\textcolor{red}{X}} \text{ gal} \times \frac{10\,000 \text{ mg}}{1 \text{ L}} \times \frac{1 \text{ gram}}{1000 \text{ mg}} \times \frac{1 \text{ pound}}{454 \text{ g}} \times \frac{3.78 \text{ liters}}{1 \text{ gallon}} = \text{\textcolor{red}{1} pound}$$

\text{\textcolor{red}{X}} = 12 gallons within a 24-hour period

Q: If PFOA & PFOS CERCLA HS?

- Therefore, if you have just a 1% solution of PFAS and you spill or ship 12 pounds or more you have a REPORTABLE QUANTITY
- CERCLA (SPILL REPORTING): For a SPILL that reaches a RELEASE VALUE WITHIN 24 HOURS to the ENVIRONMENT this report is phoned to the National Response Center, **ASAP**
- DOT: NOTE ON MANIFEST: RQ, Proper shipping name

Fire Suppressant Foams







TUESDAY | 7:43 a.m.

Deer Park, Texas, Incident Date:
March 17, 2019





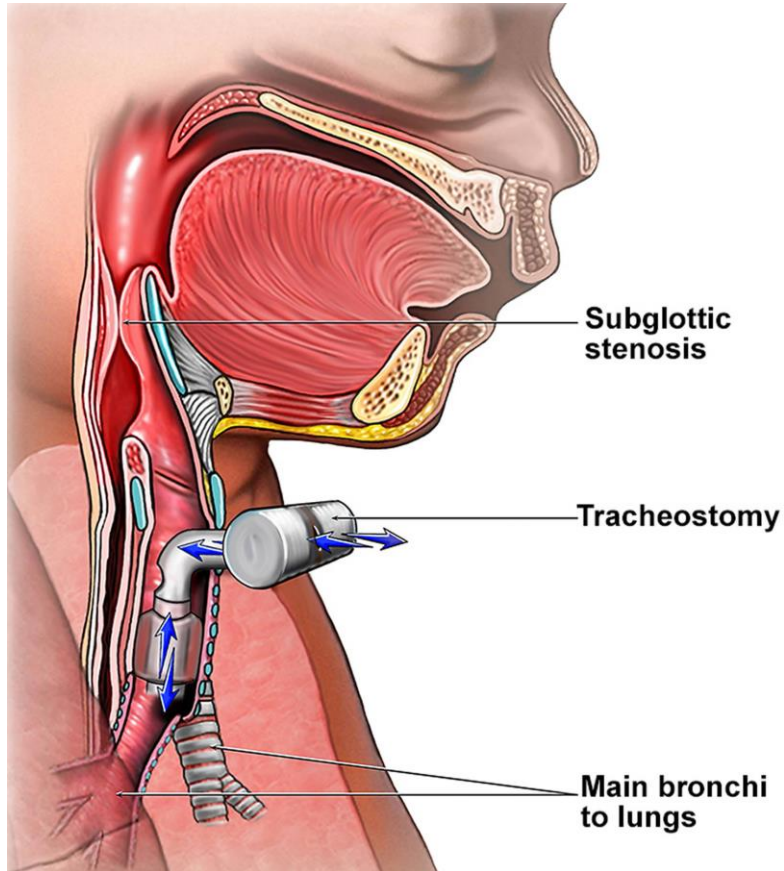






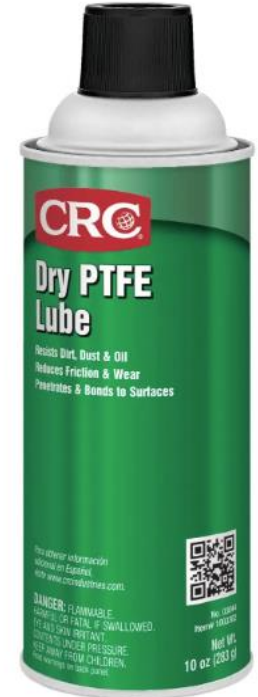


Tracheostomy



PFAS Products

Amazon > 10 000 products with PTFE





Chick-fil-A (PPT)



Wrapper for Sandwich Wrap	553 500 000
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EPA has established a lifetime health advisory level for PFOA = 0.004 PPT

Q: After PFOA & PFOS become a CERCLA hazardous substances, what will be the next set of molecules to be regulated under CERCLA?

- **Hexafluoropropylene oxide dimer acid and**
- **Its ammonium salt (HFPO-DA) AKA =**
- **“GenX Chemicals”**
- **Perfluorononanoic acid (PFNA)**
- **Perfluorohexanesulfonic acid (PFHxS)**
- **Perfluorobutanesulfonic acid (PFBS)**

Q: According to USEPA what are the adverse human health effects of PFOA & PFOS?

- High Cholesterol**
- Changes in Liver Enzymes**
- Decreased Immune Response to Vaccination**
- Thyroid Disorders,**
- Pregnancy-induced Hypertension**
- Preeclampsia**
- Cancer (Testicular, Kidney, Liver, Thyroid)**

Which PFAS Analysis should I use?

Method
USEPA 533
USEPA 537.1
USEPA Method 1633
USEPA SW-846 Method 3512
USEPA SW-846 Method 8327
DoD AFFF01
ISO 21675:2019
ISO 25101:2009
ASTM D7979-20
ASTM D7968-17a
FDA CAM Method: C-010.01, Version 2019
CDC: 6304.09

Which PFAS Analysis should I use?

Media	Method
Drinking water	USEPA 533
Drinking water	USEPA 537.1
Surface water, groundwater, wastewater, landfill leachate, soil, sediment, biosolid, and tissue	USEPA Method 1633
Surface water, groundwater, and wastewater	USEPA SW-846 Method 3512
Surface water, groundwater, and wastewater	USEPA SW-846 Method 8327
AFFF Concentrates	DoD AFFF01
Unfiltered drinking water, groundwater, and surface water	ISO 21675:2019
Unfiltered drinking water, groundwater, surface water, and wastewaters containing less than 2 g/L solid particulate material	ISO 25101:2009
Water sludge, influent, effluent, and wastewater	ASTM D7979-20
Soil	ASTM D7968-17a
Food (Bread, Lettuce, Milk, and Fish)	FDA CAM Method: C-010.01, Version 2019
Blood Serum	CDC: 6304.09

Which PFAS Analysis should I use?

Media	Method
Drinking water	USEPA 533 25 molecules
Drinking water	USEPA 537.1 18 molecules
Surface water, groundwater, wastewater, landfill leachate, soil, sediment, biosolid, and tissue	USEPA 1633 40 molecules
Everything	Total Organic Fluorine $\Sigma > 12\ 000$ molecules

What is the “Dark Matter” of PFAS?

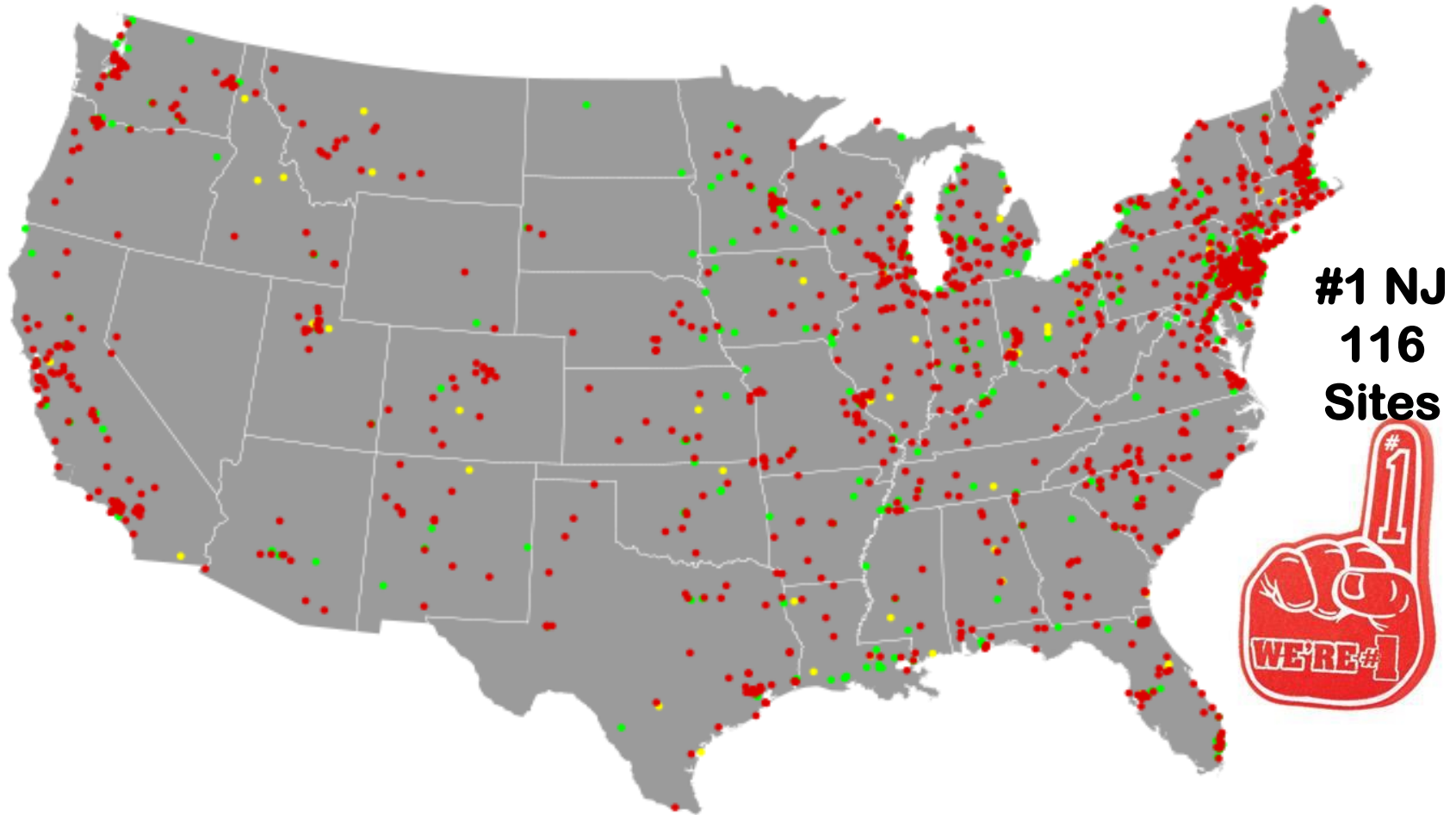
- **USEPA 1633 can analyze for 40 unique PFAS molecules**
- **TOF can analysis for > 12 000 PFAS molecules**
- **The “Dark Matter” is the difference between 12 000 and 40 =**
- **11 960 molecule we cannot test for today!**

What if PFOA/PFOS becomes a CERCLA hazardous substance?

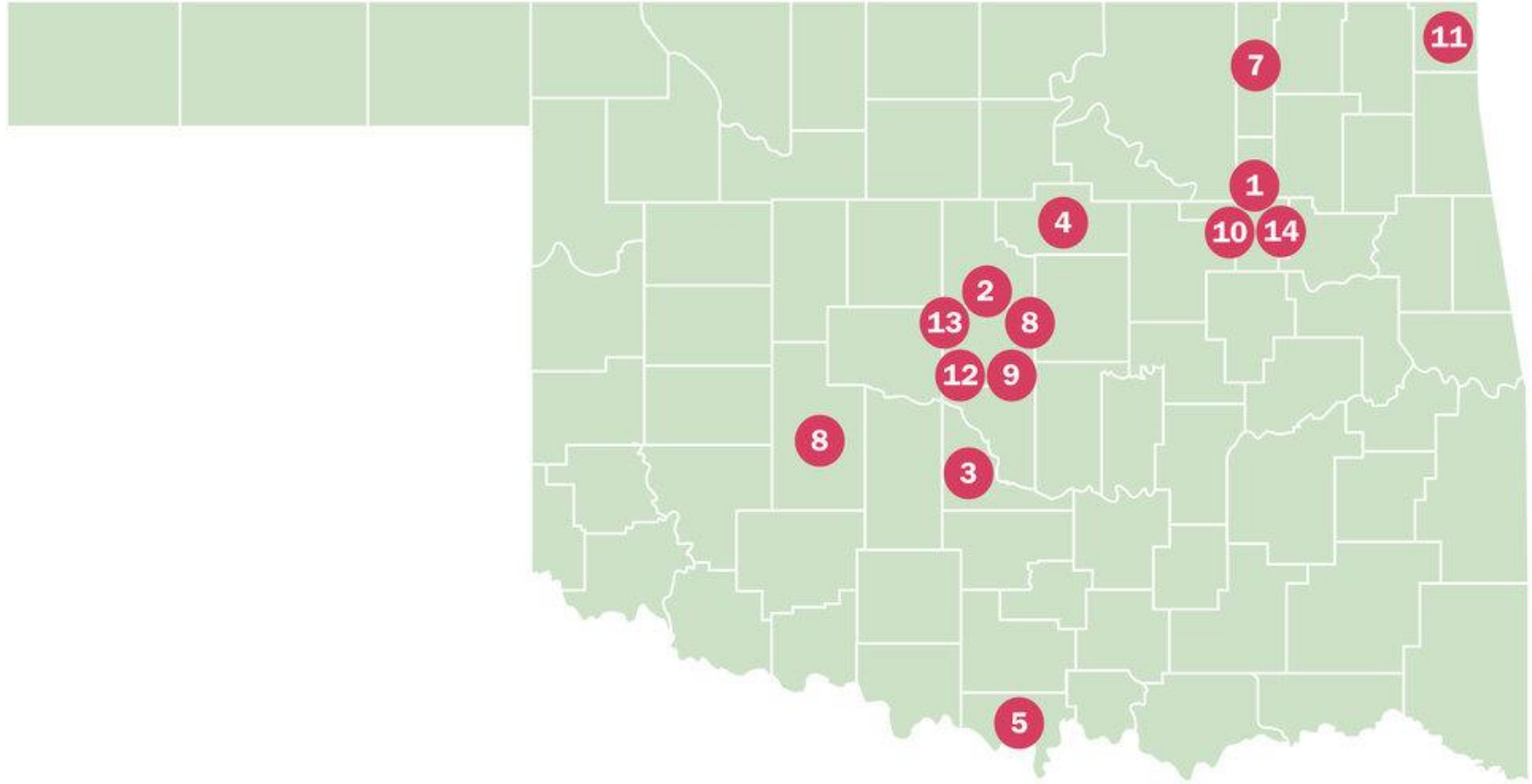
1. “Closed” Superfund sites may be reopened!

- ❖ **1,303 Superfund sites in US**
- ❖ **Approximately a quarter of these sites have been fully remediated and officially closed**
- ❖ **For Superfund there are no time limits**
- ❖ **All sites are subject to “reopener” clauses**
- ❖ **This will enable EPA to reopen previously closed cleanup sites with new testing and remediation requirements**

SUPERFUND SITES



Superfund Sites in Oklahoma



Superfund Sites in Oklahoma

1. **Compass Industries, Tulsa County** : Landfill was contaminated with jet fuel, oily sludge, solvents, acids, caustics, bleaches and benzene. Cleanup was completed in 1991.
2. **Fourth Street** : abandoned refinery, Oklahoma County : Oil refinery was contaminated by solidified waste oils that contain lead and other metals. In the process of being removed from the hazardous site list.
3. **Hardage/Criner, McClain County** : Industrial waste site was contaminated by pesticides, solvents, arsenic, acids, oils, paint sludge, ink and heavy metals. Monitoring continues.
4. **Hudson Refinery, Payne County**: Oil refinery was contaminated by more than 70 chemicals, some carcinogenic. EPA outlined a cleanup plan in 2007.
5. **Imperial Refining, Carter County** : Oil refinery was contaminated by metals and refining wastes. EPA is transporting contaminated soil off site for disposal. So far, more than 43,000 tons have been removed.
6. **Mosley Road Sanitary Landfill, Oklahoma County**: Once accepted about 2 million gallons of hazardous waste, which was dumped into unlined pits. The site is being reviewed for early deletion from the hazardous waste list.
7. **National Zinc Co., Washington County** : Land was contaminated with lead, zinc and cadmium. Yards were dredged. Cleanup found to be complete in 2006.
8. **Oklahoma Refining, Caddo County** : Soil was contaminated with sludge and refining waste. About 153,000 cubic yards of soil have been cleaned.
9. **Sand Springs Petrochemical : Complex, Tulsa County**: Former Sinclair refinery left behind petroleum and acid sludge waste. The Arkansas River was made safer for recreational use. Contaminated soil cleaned up, according to most recent report.
10. **Tar Creek, Ottawa County**: Zinc and lead mining site contaminated land with heavy metals. Children tested high for lead. Rivers that connect to the area are being tested for contamination, and EPA will devise a multistate plan for cleanup.
11. **Tenth Street dump/junkyard, Oklahoma County**: Oklahoma City landfill was contaminated with polychlorinated biphenyls. Contaminated ground has been capped. Monitoring continues.
12. **Tinker Air Force Base, Oklahoma County** : Industrial hazardous wastes were disposed of at the base between the 1940s and 1970s. The EPA has removed contaminated storage tanks and soil, and plugged wells to reduce contamination of groundwater.
13. **Tulsa Fuel & Manufacturing, Tulsa County**: Contaminated with lead and zinc. The state has assessed health risks, and is testing water and soil. A cleanup plan is being drafted.

Source: U.S. Environmental Protection Agency

What if PFOA/PFOS becomes a CERCLA hazardous substance?

2. New cleanup sites may be identified and listed

- ❖ **A number of states have adopted testing requirements for PFAS in water and soil, with a focus on sites with special risks**
- ❖ **For example, California has been requiring testing at airports, wastewater treatment plants, and certain manufacturing facilities since 2019**
- ❖ **Under CERCLA, this testing could lead to the identification and prioritization of new PFAS “hotspots” that could meet the criteria for listing as Superfund sites**

What if PFOA/PFOS becomes a CERCLA hazardous substance?

3. New state action and litigation could follow

- ❖ **Public awareness of PFAS contamination is likely to increase as expanded federal testing and remediation requirements are implemented**
- ❖ **Federal listing will also bolster claims by plaintiffs and increase the likelihood that courts will grant claims for medical monitoring and other relief**

What if PFOA/PFOS becomes a CERCLA hazardous substance?

4. Diligence requirements will expand

- **Proposed industry standards for “all appropriate inquiry” (AAI) by prospective purchasers of property already recognize that PFAS is a concern**
- **Once listed, assessment of PFAS will become mandatory for fulfilling AAI requirements**
- **The identification of PFAS as a Recognized Environmental Condition in Phase I Environmental Site Assessment reports may impact many transactions**

IF PFOA/PFOS becomes a CERCLA hazardous substance? Will I need to test for PFAS for every Phase I Real Estate Assessment?

- **My recommendation: NO**
- **This is where a risk-based analysis is needed**
- **However, USEPA has given some guidelines:**
- **Federal Register Volume 87, Number 171
(Tuesday, September 6, 2022)**

Federal Register Volume 87, Number 171

- Aviation operations
- Carpet manufacturers
- **Car washes**
- Chemical manufacturing
- Chrome electroplating, anodizing, and etching services
- Coatings, paints &
- varnish manufacturers
- Firefighting foam manufacturers
- Landfills
- Medical Devices
- Any fire department or firefighting training centers
- Paper mills

Federal Register Volume 87, Number 171

- Pesticides and Insecticides
- **Petroleum & coal product manufacturing**
- **Petroleum refineries and terminals**
- Photographic film manufacturers
- Polish, wax, and cleaning product manufacturers
- Polymer manufacturers
- Printing facilities where inks are used in photolithography
- Textile mills (textiles and upholstery)
- Waste management and remediation services
- Wastewater treatment plants

Not mentioned in Federal Register
Volume 87, Number 171

- **Dry cleaners**
- **Commercial Laundry cleaners
(uniforms & red rags)**







