The History, Euphemisms & Caveats of PFAS Analysis



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Thank You

Environmental Federation of Oklahoma > Howard (Bud) Ground

- >Jody Reinhart
- > Paula Hofford



Environmental Federation of Oklahoma

Working for Oklahoma's Economic and Environmental Future

Thank You

- > Oklahoma State University-Tulsa
- > Dr. Sheryl Tucker
- > Vice Provost
- Dean of the Graduate College



MY LENS: A CHEMIST

- ≻I am not a lawyer
- > Or politician!
- ≻I am a Chemist
- > These are just my views, my opinions....
- I have studied Chemistry for the past five decades
- >PFAS is the most complex chemical issue I have ever studied!!

Regs. per Ken Ede"

"Regs. per Ken Ede"

- > These are <u>my</u> recommendations!
- > These are <u>not</u> law nor regulations!!
- But they are just my recommendations to you.....

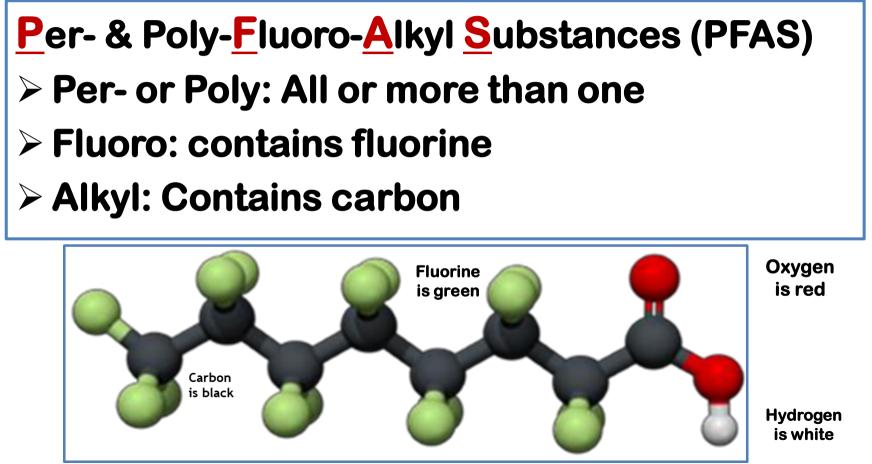
AGENDA: PFAS

- Studied Chemistry on the east coast
- Had two Chemistry professors who worked on the Manhattan Project during World War II (1943)
- > My introduction to PFAS was in 1970
- > 27 years after WWII, these Professors still talking about fluorocarbon chemistry (PFAS)





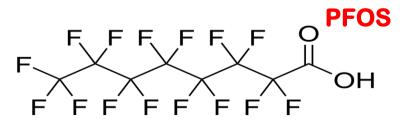
PFAS

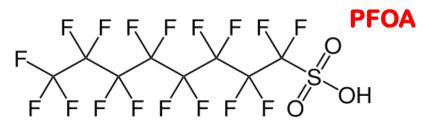


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PER-AND POLYFLUOROALKYL SUBSTANCES (PFAS)

- >PFAS: Umbrella term
- >PFAS are family of > 10 000 manmade chemicals
- > PFOS, PFOA, etc..... X 10 000
- Most common names: Teflon (PTFE), Kynar, Gore-Tex, Scotchgard, AFFF, etc.





How did we get here?

- > PFAS is found in every blood bank
- > Almost every human on this planet
- Polar bears
- > North Pole
- > South Pole
- Eagles
- > Most aquatic life

'Forever Chemicals' Are Building Up in the Arctic—and Likely Worldwide • June 12, 2020



PFAS found on Mt. Everest



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.

Why Are There Harmful Chemicals on Mount Everest?

The \$60,000 Question





\$60,000 Corvette

\$60,000 Lab Report

The \$60,000 Question

- >Lab Report: Paper and numbers
- Today, electronic reports, just numbers
- > If the numbers are not correct or
- >Not admissible in a court of law
- >You have just wasted \$60,000

My Goal

- To ensure you receive good, reliable data,
- >You must understand how to both:
- 1. How to <u>sample</u> for PFAS
- 2. Interpret the laboratory analysis

"\$10,000 per Mass Spec"

- The cost of the instrumentation to analyze
 PFAS substances is extremely expensive
- > \$400K to \$600K per mass spec
- Due to this expense, lab directors are placing more and more pressure on their Chemists to generate revenue
- > One lab director specifically stated that he expects \$10,000 per day per mass spec

\$10,000 per Mass Spec

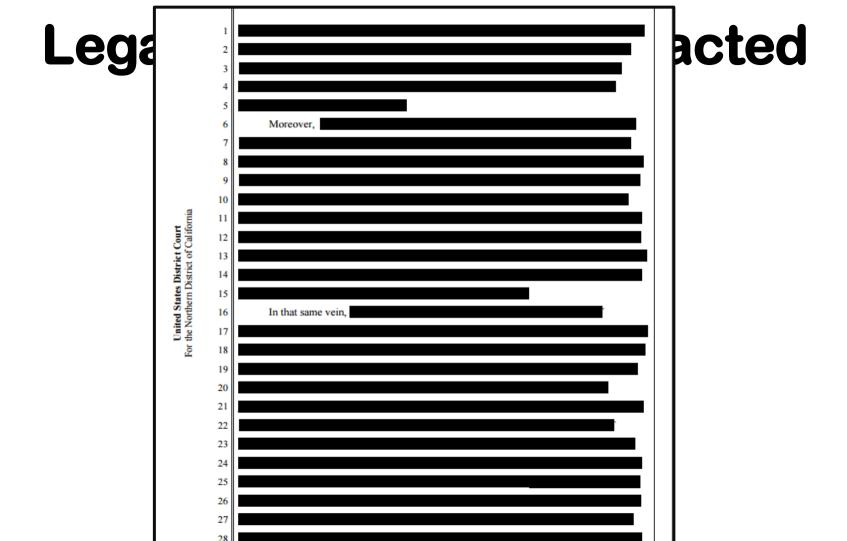
- Most laboratory errors today are caused by the very fast pace of PFAS analysis
- Many consulting companies have QA/QC software that are <u>not</u> written by Chemists
- Their software fails to catch many of these problems





Chemistry Euphemisms for PFAS

- Euphemisms: The substitution of an agreeable expression for one that may be unpleasant
- Euphemism derives from the Greek word euphemos, which means "sounding good"
- > Every occupation has their own euphemisms
- Instead of the word "Died"
- "Passed on" or "passed away"



Chemical Euphemisms

- **1. Unexpected Results**
- 2. Recalcitrant
- 3. Treatment of PFAS

Historical Perspective: 1938

- > Yesteryear: Failed Experiment
- >1938: "Two Failed Experiments"
- Today: "Two Experiments with <u>Unexpected Results</u>"
- >1938: Both experiments changed the world forever!

History of PFAS

- > 1938: Dr. Roy J. Plunkett with DuPont was trying to develop a gaseous refrigerator coolant
- > The experiment failed!
- Instead, he accidently developed the first solid fluorinated-hydrocarbon
- The waxy solid (not gas or liquid) that proved to be the most slippery, <u>inert material in existence</u>
- > Polytetrafluoroethylene (PTFE Teflon)

History of PFAS Reenactment of the 1938 discovery of Teflon

However, Dupont could not find a use for a substance that would not stick to anything.....

It was shelved!

This should have been a gas!



Note: This is a white powder!

1938: 2nd Unexpected Results

 \succ Two German scientists, **Otto Hahn & Fritz** Strassmann, successfully split the uranium atom into two or more parts (fission) "Über das Zerplatzen des Urankernes durch langsame Neutronen"

Abhandlungen der Preußischen Akademie der Wissenschaften

Jahrgang 1039 Mathematisch-naturwissenschaftliche Klasse

Nr. 12

Über das Zerplatzen des Urankernes durch langsame Neutronen

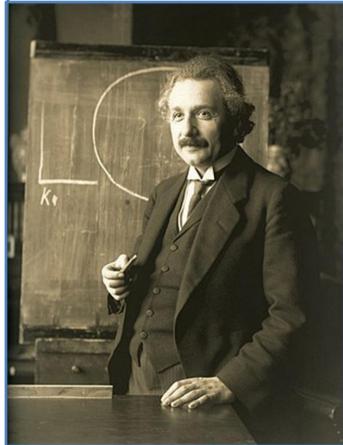
VDI

Otto Hahn und Fritz Strassmann

Berlin 1939 Verlag der Akademie der Wissenschaften is Komstnike bei Walter de Greștern, Co.

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- January 1933: Hitler becomes Chancellor of Germany
- May 1933: Albert Einstein escapes Germany to USA
- > 1938: Albert Einstein is made aware of discovery of fission
- Einstein writes a warning letter to President Roosevelt regarding Germany developing the atomic bomb



Albert Einstein Old Grove Rd. Nassau Point Peconic, Long Island

August 2nd, 1939

F.D. Roosevelt, President of the United States, White House Washington, D.C.

Sir:

Some recent work by E.Fermi and L. Szilard, which has been communicated to me in manuscript, leads me to expect that the element uranium may be turned into a new and important source of energy in the immediate future. Certain aspects of the situation which has arisen seem to call for watchfulness and, if necessary, quick action on the part of the Administration. I believe therefore that it is my duty to bring to your attention the following facts and recommendations:

In the course of the last four months it has been made probable through the work of Joliot in France as well as Fermi and Szilard in America - that it may become possible to set up a nuclear chain reaction in a large mass of uranium, by which wast amounts of power and large quantities of new radium-like elements would be generated. Now it appears almost certain that this could be achieved in the immediate future.

This new phenomenon would also lead to the construction of bombs, and it is conceivable - though much less certain - that extremely powerful bombs of a new type may thus be constructed. A single bomb of this type, carried by boat and exploded in a port, might very well destroy the whole port together with some of the surrounding territory. However, such bombs might very well prove to be too heavy for transportation by air. -2-

The United States has only very poor ores of uranium in moderate ... quantities. There is some good ore in Canada and the former Czechoslovakia, while the most important source of uranium is Belgian Congo.

In view of this situation you may think it desirable to have some permanent contact maintained between the Administration and the group of physicists working on chain reactions in America. One possible way of achieving this might be for you to entrust with this task a person who has your confidence and who could perhaps serve in an inofficial capacity. His task might comprise the following:

a) to approach Government Departments, keep them informed of the further development, and put forward recommendations for Government action, giving particular attention to the problem of securing a supply of uranium ore for the United States;

b) to speed up the experimental work, which is at present being carried on within the limits of the budgets of University laboratories, by providing funds, if such funds be required, through his contacts with private persons who are willing to make contributions for this cause, and perhaps also by obtaining the co-operation of industrial laboratories which have the necessary equipment.

I understand that Germany has actually stopped the sale of uranium from the Czechoslovakian mines which she has taken over. That she should have taken such early action might perhaps be understood on the ground that the son of the German Under-Secretary of State, von Weizsücker, is attached to the Kaiser-Wilhelm-Institut in Berlin where some of the American work on uranium is now being repeated.

> Yours very truly. *M. Constein* (Albert Einstein)

Einstein was correct

April 1939, Hitler starts the *"Uranverein"*

April 1939, Hitler under "Wehrmacht" "recruits" all of the top theoretical physicists in Germany for one task.....

Goal: Build the first atomic bomb!

German Physicists: Uranverein



Horst Korsching



Walther Gerlach



Karl Wirtz



Werner Heisenberg



Walther Gerlach



Paul Harteck



Erich Bagge



Otto Hahn



Kurt Diebner



Abraham Esau

German Physicists: Uranverein





Siegfried Flügge

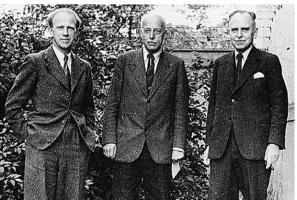
Hans Wilhelm Geiger



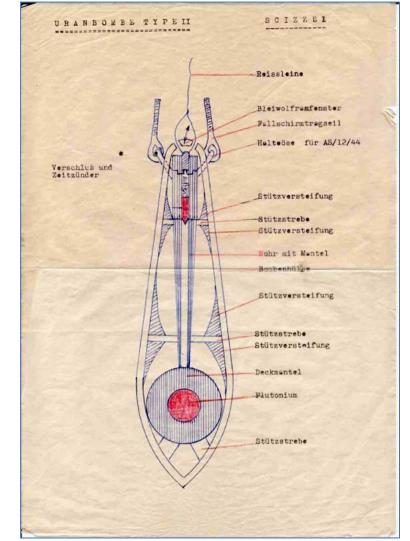
Max von Laue



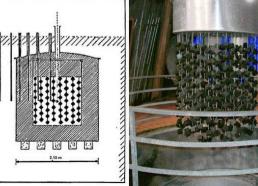
Carl von Weizsäcker













History of PFAS

- December 7, 1941: Japanese attack Pearl Harbor
- December 8, 1941: US enters World War II
- December 28, 1942: President Roosevelt authorized the formation of the Manhattan Project under Dr. Oppenheimer
- Germany had a three-year head start!



Dr. J. Robert Oppenheimer₃₁

Manhattan Project: August 13, 1942

- > Again, three years later
- Finally, America starts the Manhattan project in 1942



- > Germany, Japan & America had the same problem:
- > When uranium is mined, it consists of approximately
- > 99.3% Uranium-238 (U²³⁸): 92 protons + 146 neutrons
- U²³⁸ Cannot support a chain reaction (non-fissile)
- > 0.7% Uranium-235 (U²³⁵): 92 protons + 143 neutrons
- > U²³⁵ Can support a chain reaction (fissile)
- Needed: 64 kilograms (141 lbs) of highly-enriched uranium (U²³⁵)
- > Just 141 lbs of U²³⁵ you get this....

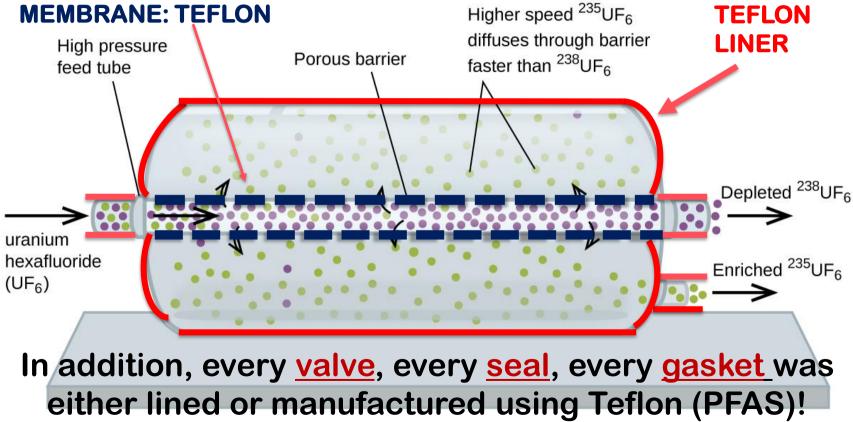


- Both Germany, Japan & USA needed a needed a way to separate U²³⁵ from U²³⁸ (Enrichment)
- > They needed a substance that could withstand:
- 1. Gaseous uranium hexafluoride UF₆ (extremely corrosive)
- 2. HF gas (extremely corrosive) H
- 3. High pressures
- 4. High temperatures &
- 5. Alpha radiation!

- All three countries used Gaseous Diffusion Stage to enrich uranium with a <u>Semi-permeable membrane</u>
- Manhattan Project: One former DuPont Chemist recalled Teflon (PFAS) properties
- > USA: Teflon (PFAS) was used for the first time
- > They applied a Teflon coating to:
- > The <u>lining</u> of each Gaseous Diffusion Stage
- Every <u>valve</u>, every <u>seal</u>, every <u>gasket</u> was either lined or manufactured using Teflon (PFAS)
- Semi-permeable membrane made from Teflon

Gaseous Diffusion Stage

SEMI-PERMEABLE **MEMBRANE: TEFLON**



PFAS

History of PFAS

- > Three years later
- August 06, 1945: The United States drops the Atomic Bomb on Hiroshima, Japan
- August 09, 1945: Another atomic bomb is dropped on Nagasaki, Japan
- September 02, 1945 Japan surrenders



History of the Atomic Bomb

- Historians (especially German) will give you 100 reasons why Germany did not develop the first atomic bomb, save one!
- > PFAS!
- Remember, Germany developed the first uranium fusion reaction
- Germany had a three-year head start
- Germany had the most brilliant theoretical physicists

"Recalcitrant"

- **TEACHING MOMENT: WORLD WAR II**
- The PFAS Carbon Fluorine bond is very resistant (recalcitrant) to:
- > Any biological attack (micro-organism)
- > Any chemical attack (strong acids or bases)
- > Any thermal attack
- Unaffected by convention wastewater treatment system

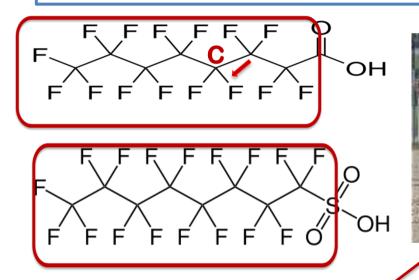
Recalcitrant PFAS

- > Simultaneously, Teflon (PFAS) was exposed to:
- 1. Gaseous URANIUM HEXAFLUORIDE (UF₆) (extremely corrosive)
- 2. HF gas (extremely corrosive) H-
- 3. High pressures
- 4. High temperatures &
- 5. Alpha radiation!

> Without breaking down!

2018: PFAS: Why so stable?

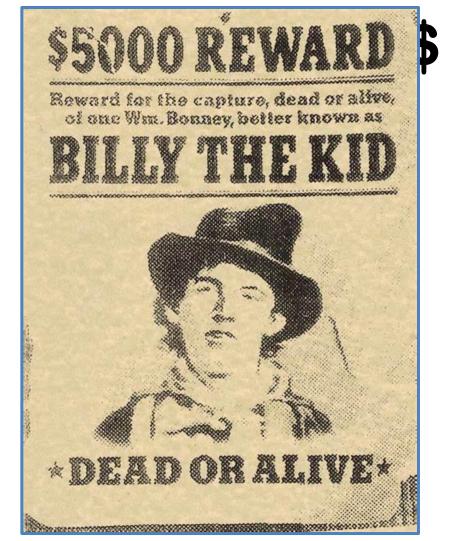
> Like an armored vehicle, no place to react





Melting Point of Carbon Steel: 1425°C (2600°F) Destruction temperature: 1000°C (1832°F)





\$50,000 Reward: Non-Incineration Methods

News Releases from Headquarters > Office of the Administrator (AO)

EPA, U.S. Department of Defense, and State Partners Launch Technical Challenge Seeking Innovative Ways to Destroy PFAS in Firefighting Foam

Trump Administration continues its commitment to support state, tribal, and local communities in addressing PFAS

08/25/2020

Contact Information: EPA Press Office (<u>press@epa.gov</u>)

Fayetteville, N.C. (August 25, 2020) — At a per- and polyfluoroalkyl substances (PFAS) roundtable hosted by U.S. Congressman Richard Hudson (NC-08) today in Fayetteville, N.C., U.S. Environmental Protection Agency (EPA) Administrator Andrew Wheeler launched an innovation challenge to identify solutions to destroy PFAS. The *Innovative Ways to Destroy PFAS Challenge* is a partnership between federal and states agencies seeking detailed plans for a non-thermal technologies to destroy PFAS in concentrated aqueous film forming foam (AFFF), a type of firefighting foam. This challenge is part of the significant progress the Trump EPA has made in implementing the <u>PFAS</u> <u>Action Plan</u>—the most comprehensive cross-agency plan ever to address an emerging chemical of concern.

"EPA researchers and staff are harnessing the power of crowdsourcing to identify ways to destroy PFAS through non-incineration methods," said EPA Administrator Andrew Wheeler. "The Trump Administration has offered major assistance to more than 30 states across the U.S. to protect human health regarding PFAS, and the agency is offering up to \$50,000 for the best design concept to safely destroy the chemical."



Prize

EPA is awarding \$60,000 in prize money to the winning concepts. Challenge winners also will have the opportunity to submit their winning design concepts to DoD's SERDP/ESTCP programs for further testing.

Top of page	Clean Air Excellence Awards	Background
	Green Power Leadership Awards	Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals that have been widely used for more than 60 years to make plastics, firefighting foams, and lubricants, and to help make products stain-resistant, waterproof, and nonstick. Newer forms of PFAS have been adopted over the past few years to replace older forms of PFAS compounds that were discontinued. Addressing and managing PFAS in the environment is one of the most pressing issues facing EPA, states and regions. This issue is particularly challenging because PFAS chemicals have a very strong carbon-fluorine chemical bond that leads to persistence in the environment and makes their complete destruction difficult. PFAS can be found at different concentrations in various waste streams including
	National Award for Smart Growth Achievement	
	President's Environmental Youth Award	
	Presidential Green Chemistry Challenge	
	Presidential Innovation	

Question...

>How recalcitrant is PFAS to microbial breakdown?

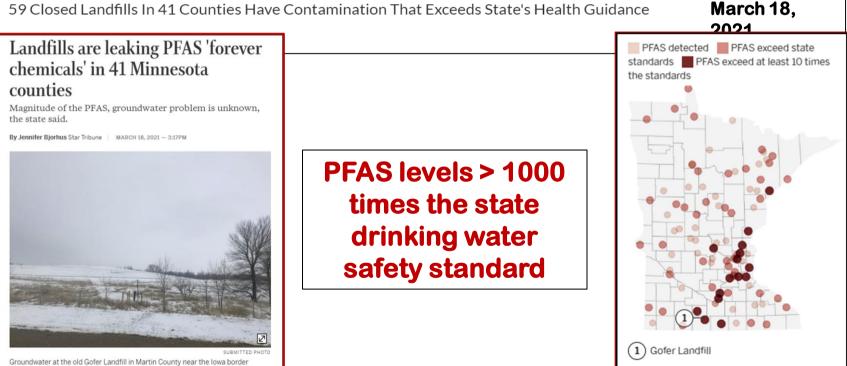
1335 Superfunds Sites in USA



To date, EPA has found <u>180 Superfund</u> Sites with PFAS contamination



Minnesota Pollution Control Agency MPCA: 'Almost Every Closed Landfill It Oversees' Has PFAS Groundwater Contamination



contains PFAS levels more than 1,000 times the state drinking water safety standard. No nearby drinking water wells have been contaminated, the MPCA said

Landfills are leaking PFAS 'forever chemicals' in 41 Minnesota counties

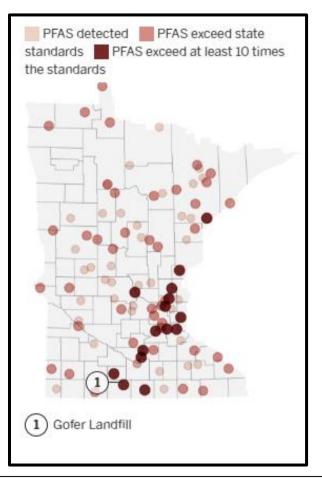
Magnitude of the PFAS, groundwater problem is unknown, the state said.

By Jennifer Bjorhus Star Tribune MARCH 18, 2021 - 3:17PM



SUBMITTED PHOTO

Groundwater at the old Gofer Landfill in Martin County near the lowa border contains PFAS levels more than 1,000 times the state drinking water safety standard. No nearby drinking water wells have been contaminated, the MPCA said.

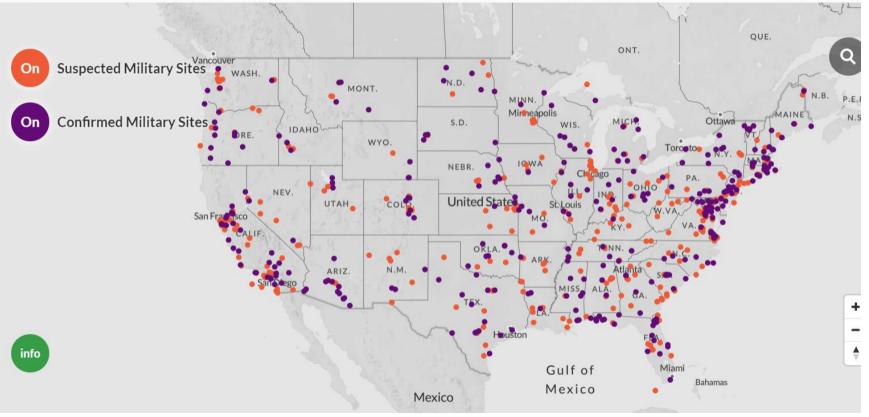


PFAS levels > 1000 times the state drinking water safety standard

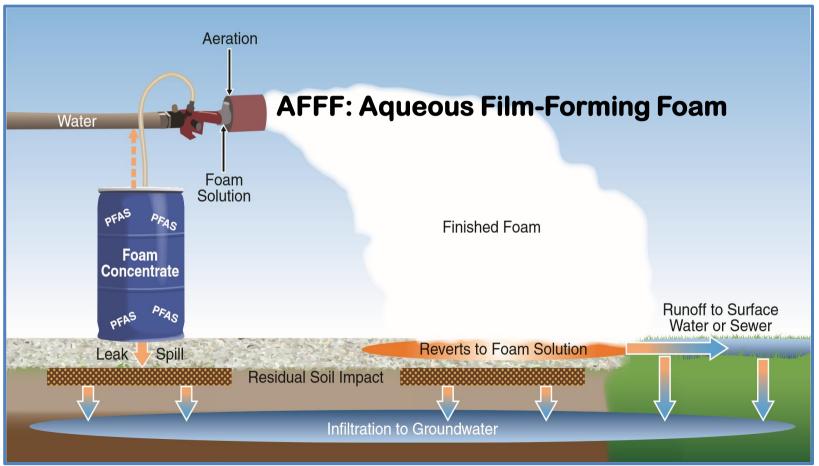


704 Military Sites With Known and Suspected Discharges of PFAS





Fire Fighting Foam with Deluge System



AFFF: Foam Concentrate

- EPA has established a lifetime <u>health advisory level</u> for PFOA & PFOS 70 parts per trillion
- If just one drop of a <u>1% solution</u> of PFAS was spilled into <u>1 liter</u> of water, the concentration of PFAS would be about
- > 500 000 000 parts per trillion!







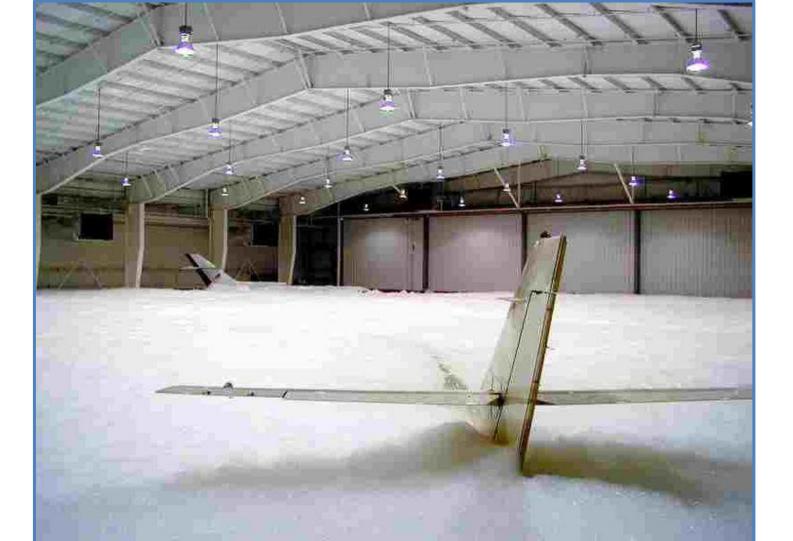


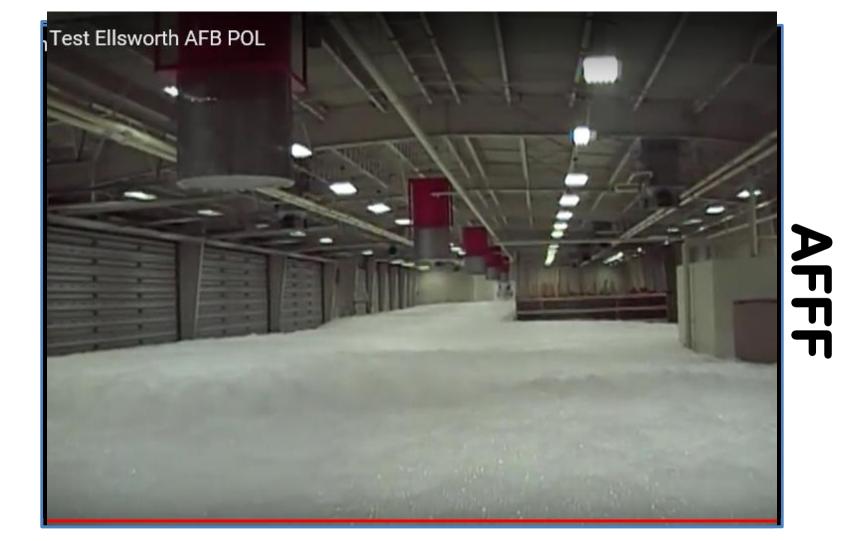






























Euphemism "Treatment" of PFAS

- > Chemistry perspective
- Treatment of PFAS equates to breaking the bond



- During incineration or using GAC or ion exchange or reverse osmosis, if you are not breaking this bond
- > You are <u>removing</u> PFAS, not treating the PFAS

Clean Harbors incineration facility cited in lawsuit against DOD

by Caitlan Butler | February 22, 2020 at 8:01 p.m.



Incinerator: In this December 2016 file photo, an employee walks across the Clean Harbors' complex in El Dorado with the new technologically advanced incinerator shown in the background. The company unveiled the new incinerator four years ago. Clean Harbors was recently named in a lawsuit against the U.S. Department of Defense.

Clean Harbors' El Dorado Incineration Facility has been named in a lawsuit against the United States Department of Defense, which alleges that the DoD has approved the incineration of toxic chemicals in violation of several federal laws.

Hearing set in East Liverpool incinerator lawsuit

BUSINESS

AUG 29, 2020

STEPHANIE UJHELYI Staff writer







HEADING TO COURT — Heritage Thermal Services, which operates this incinerator in East Liverpool, is a co-defendant in a hearing that will be held Sept. 9 in federal court in California. (File photo)

PFAS test at Covanta-operated incinerator scrapped following public outcry

The New Jersey DEP expressed disappointment, while the U.S. EPA said it will continue partnering with states and local governments as it seeks ways to destroy the toxic chemicals.

BRIEF

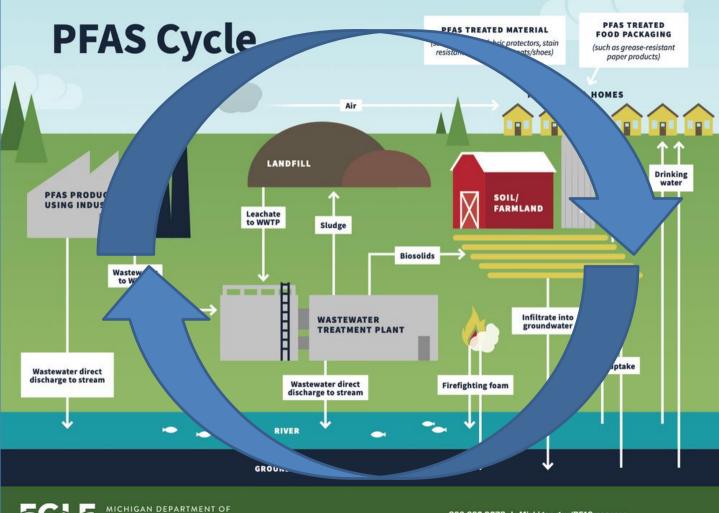
PFAS incineration in New York spurs legislation, loss of federal contracts



The image by Яіскў Sнояє is licensed under CC BY 2.0

Euphemism "Treatment" of PFAS

- > As of today.....
- > There is <u>NO</u> treatment of PFAS!
- > Regs. Per Ken Ede
- Solid PFAS waste: "Store" your PFAS waste in a hazardous waste landfill (Subtitle C)
- Liquid PFAS wastes: "Store" your PFAS waste in a hazardous waste injection well (Subtitle C)



ENVIRONMENT, GREAT LAKES, AND ENERGY

800-662-9278 | Michigan.gov/PFASresponse

Sampling Protocols for PFAS

- Oklahoma State University is writing the first sampling protocols for the State of Oklahoma
- Should be completed by Thanksgiving, 2021
- We have spent months reviewing the other 49 states PFAS protocols
- In addition, we have reviewed many other countries sampling PFAS protocols
- > We have found a common tread!



Per- and Polyfluoroalkyl Substances (PFAS) Sample Collection Guidance

The purpose of this document is to provide guidance on groundwater sampling protocols when collecting sample(s) for analysis for FAAS. Detection of these compounds at very low levels can be influenced by materials that are present at the sampling site, materials used by the sampling agent, or sample container handling practices. For more detailed information, please refer to Standard Operating Procedure (SOP) No. HVRBS-11 in the NVBCB HVRB. Master Quality Assurance Project Plan, prepared for sites investigated through contracts administered by the HVRB.

Because of the potential presence of PFAS in common consumer products and in equipment often used to collect groundwater samples, special handling and care must be taken when collecting FFAS samples. Accordingly, NNEDS strongly recommends that protocols specific to sampling groundwater for the presence of PFAS be used for all well purging and groundwater sampling collection and handling methods, and that the sampling be performed by a consultant familiar with these protocols.

NHDES recognizes that studies are orgoing to identify the potential for cross-contamination from PFAS-containing items during sampling, and that some studies have found that the referenced guidance may be conservative. NHDES recognizes that studies are anoging to lidentify the potential for cross-contamination from PFAS-containing items during sampling, and that some studies have found that the referenced guidance may be conservative. NHDES recommends appropriate quality assurance and quality control sampling be implemented if sampling protocols are modified. Please contact your progress manages for further information.

Other information is available from:

- ITRC Fact Sheet "Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for PFAS" (<u>https://pfas1.itrcweb.org/wp-</u> content/uploads/2018/03/pfas fact sheet site characterization 3 15 18.pdf)
- Michigan PFAS Sampling Guidance (<u>https://www.michigan.gov/ofarresponse/0.9038,7-365.66510 87154-649822--.0.html), with a quick reference guide available at: https://www.inchigan.gov/documents/ofarresponse/PFAS_Sampling_Ouick_Reference Field_Guide_634603_7.pdf
 </u>

Page 1 of 3

Revised May 2019

Per- and Polyfluoroalkyl Substances (PFAS) Sampling Guidelines for Non-Drinking Water **GENERAL PFAS** Michigan SAMPLING Department of Environmental CALIFORNIA STATE WATER OUALITY CONTROL BOARD Quality **GUIDANCE** This document contains an introduction to PFAS, biosecurity recommendations, and general recommendations to decrease the possibility of cross-contamination. SWRCB PFAS Website: https://www.waterboards.ca.gov/pfas/ DOW PLAS Website: https://www.waterboards.ca.gov/drinking_water/certiic/drinkingwater/PEOA_PEOS.html Water Boar September 2020

New Hampshire

Michigan

California

MassDEP Drinking Water Program One Winter Street, Boston, MA 02108

June 2021

Field Sampling Guidelines for PFAS

Using EPA Method 537 or 537.1

Please read entire instruction sheet prior to sampling.

Also, view the MassDEP video on how to conduct PFAS sampling at: https://youtu.be/zrwhwSI-R9M

Sampling for ger- and polylluorality's ubstances (PKA) using EPA method 532 or 5312, can be challenging due to the prevalence of PFAS compounds in consumer products. Many materials normally used in field and laboratory operations contain PFAS and cannot be used in sampling for PFAS-eg., tubing, sample containers, and sampling tools, in addition, many consumer goods, such as water-resistant jackets or fast food wrappers brought to a sampling is then ay contain PFAS that can also contaminate samples.

Field Clothing and Personal Protective Equipment

- . Do not wear clothing or boots containing Gore-Tex*.
- · Wear new nitrile gloves.
- · Wet weather gear should be made of polyurethane and polyvinylchloride (PVC) only.

· Wear safety boots made from polyurethane and PVC.

- Do not use materials containing Tyvek* or polytetrafluoroethylene (PTFE), also known as Teffon*.
- . Do not use fabric softener on clothing to be worn in field.
- . Do not use cosmetics, moisturizers, hand cream, or other related products the morning of sampling.
- . Do not use prohibited sunscreen or insect repellant. See Do's and Don'ts table below for more information.

Food Considerations

No food or drink allowed on-site with exception of bottled water.

Field Equipment

- Must not contain Teflon* (aka PTFE) or low-density polyethylene (LDPE) materials.
- All sampling materials must be made from stainless steel, high-density polyethylene (HDPE), acetate, silicone, or polypropylene.

No waterproof field books can be used.

- No plastic clipboards, binders, or spiral hard cover notebooks can be used.
- Sharpies® and permanent markers not allowed; regular ball point pens are acceptable.
- . Keep PFAS samples in separate cooler, away from sampling containers that may contain PFAS.

Coolers filled with regular ice only - Do not use chemical (blue) ice packs.

Massachusetts

1

PFNA/PFAS Sampling Information For Water Systems Performing Sample Collection

1. Choosing a Laboratory

The analytical laboratory selected for perflurozonomoic acid (PFNA) analysis must be certified by the New Jerusy Department of Environmental Protection (NJDEP) Office of Quality Assumance (QQA). The methods allowed for the analysis of PFNA and other selected per- and polyfluorinated alkyl substances (PFAS) in dinaking water are EPA 537 Revision 1.1 and EPA 537. The list of laboratories certified for EPA 537 or 637.1 in a dinaking water matrix can be found by gioup to the NJDEP webgage at <u>www.ni.gov/dep.</u> Go to **Data Miser** found under **Information Tools** and choose the Category **Certified Laboratories**.

Ensure that the laboratory:

- has a detection limit (DL) less than or equal to 2 ng/L and a minimum reporting level (MRL) less
 than or equal to 5 ng/L for PFNA,
- · can electronically submit the results to the NJDEP through E2,
- will provide a laboratory report that includes at a minimum:
- qualified results (J-flagged) if PFNA is detected between the DL and the MRL;
 - a sample results report listing both the DL and MRL;
 - o Field Reagent Blank (FRB) results if analyzed; and
- documentation of any analytical issues that did not meet the method specifications.
- if requested, can provide quality control (QC) information that includes calibration check recoveries, surrogate recoveries, laboratory fortified blank (LFB) recoveries, internal standard responses and matrix spike information (Level 2 data package).
- can meet the required timeframe of submitting the data using E2 to the NJDEP within 10 days of the following quarter,
- for every quarter, can accommodate the analysis of your treatment plant samples and any possible FRB analyses.

2. Planning for the sampling

Minimize potential of background contamination:

Due to the ubiquitous nature of these PFAS, there is a higher than usual potential for sample contamination. To minimize this potential, careful preparation for this sampling event is strongly recommended. The clothing worn, personal care products used, and objects brought to the sampling site should be considered.

Clothing NOT to be worn includes:

Tyvek suits

¹ Or follow this link:

https://www13.state.nj.us/DataMiner/Search/SearchByCategory/isExternal=y&getCategory=y&catName=Certific d+Laboratories

New Jersey

NEW YORK STATE OF Conservation Conservation

SAMPLING, ANALYSIS, AND ASSESSMENT OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

Under NYSDEC's Part 375 Remedial Programs

January 2021



www.dec.ny.gov

New York

Per- und polyfluorierte Alkylverbindungen (PFAS)

Organische Verbindungen, die vollständig (per-) oder teilweise (poly-) fluoriert sind

Verwendung

Schon seit siebzig Jahren produzieren Unternehmen per- und polyfluorierte Alkylverbindungen (PFAS) in großen Mengen, um ganz unterschiedliche Materialien hitze-, wasser- und fettabweisend zu machen. Meist steht die Oberflächenbehandlung im Vordergrund, beispielsweise von Textilien, Haushaltsgegenständen und Baustoffen, in de Papierveredelung und in chemischen Spezialitäten. PFAS finden sich aber auch in Reinigungsmitteln, Löschschäumer Kabelummantelungen, hydraulischen Flüssigkeiten und werden auch in der Metallurgie, Elektronik und Medizintechni verwendet. Dabei können sie sowohl bei der Herstellung als auch bei der Verwendung und der Entsorgung in die Umwelt gelangen und den Menschen belasten.

Nach OECD Schätzungen gibt es über 4000 PFAS, die teilweise oder vollständig fluoriert sind. Grundsätzlich wird zwischen Polymeren und Nicht-Polymeren unterschieden. Alle PFAS sind menschengemacht, sie kommen nicht natürlich in der Umwelt vor. Zu den Polymeren gehören Perfluorpolyether, Polymere mit fluorierten Seitenketten sowie Fluorpolymere wie das Polytetrafluorethylen (PTFE), das in unterschiedlichen Produkten unter den Handelsnamen Teflon[®], Scotchgard™ und Goretex[®] bekannt ist.

Nicht-Polymere können sowohl perfluorierte als auch polyfluorierte Alkylverbindungen sein. Aus den polyfluorierten Stoffen können perfluorierte Verbindungen entstehen, beispielsweise durch Stoffwechselprozesse im Menschen, Tieren, Pflanzen und Mikroorganismen oder durch nicht-biologische Abbauprozesse in der Umwelt.

Daten der Umweltprobenbank

PFAS Untersuchungen sind einer der Schwerpunkte in der Umweltprobenbank. Es gibt viele Daten für perfluorierte sowie für einige polyfluorierte Alkylsubstanzen, die von jungen Erwachsenen sowie Pflanzen, Tieren und nichtbiologischen Proben der Binnengewässer, Küsten und terrestrischen Ökosysteme stammen. Für die meisten Probenarten gibt es auch Zeitreihen. Hierbei wurden sowohl regulierte als auch nicht regulierte PFAS untersucht.

Gefahren für Mensch und Umwelt

Perfluorierte Verbindungen sind in der Umwelt und im Menschen sehr langlebig. Je nach Stoffeigenschaft verteilen sie sich in den Umweltmedien, einige Verbindungen reichern sich auch in den Nahrungsnetzen an. Mit den Weltmeeren und über den Luftpfad können sie sich über die Erde verteilen und so auch die entlegenen Polarregionen erreichen. Einige der perfluorierten Verbindungen sind als toxisch bekannt.

Germany



PFAS National Environmental Management Plan

Version 2.0 – January 2020

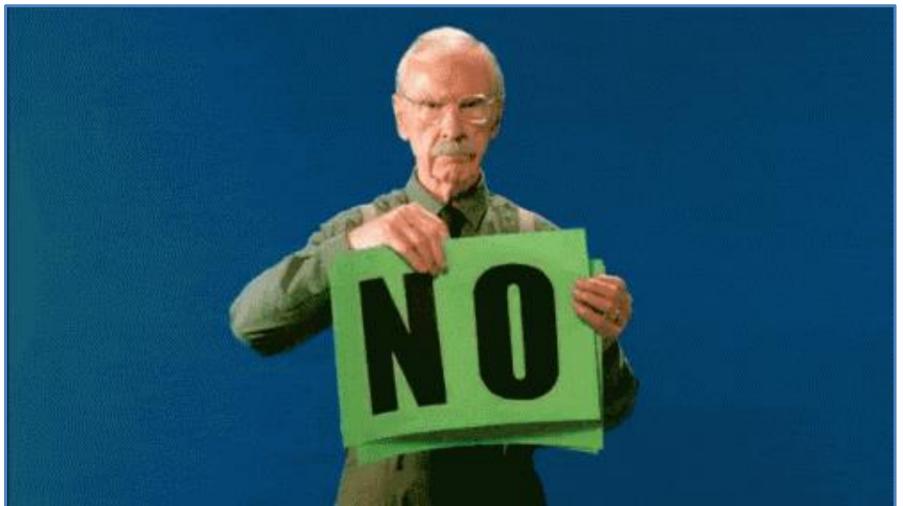
National Chemicals Working Group of the Heads of EPAs Australia and New Zealand



Australia & New Zealand

Sampling Protocols

- Regs. Per Ken Ede
- Assume that every site you visit will be investigated one day for PFAS
- Use your PFAS sampling plan for every site you visit
- > Why, because all PFAS protocols are based on the "land of NOs"



Land of NOs

NO Gore-Tex clothing nylon clothing or
 NO Gore-Tex boots hats

- NO Gore-Tex hats, gloves, etc.
- > NO Tyvek
- NO new clothing
- > 100% Cotton only
- > NO Polyester or

 All clothing must be washed at least 7 times without fabric softener

Land of NOs

- NO clothing chemically treated for <u>insect</u> <u>repellence</u>
- NO clothing that has been treated for <u>ultraviolet protection</u>
- NO clothing that has been treated for <u>stain</u>

<u>resistance</u>

> NO clothing that has ever been washed with clothing that contains any treated for insect resistance, ultraviolet protection water, dirt, and/or stain resistant chemicals

NO Post-It or any other adhesive paper products

Personal Care Products: Land of NOs

- NO Eyeshadow
- NO Bronzer or highlighter
- NO Facial powder
- **NO** Foundation
- NO Sunscreen
- ≻ NO Mascara
- NO Eye cream

- > NO Hand cream
- **NO** Blush
- NO Shaving cream
- NO Facial moisturizer
- > NO Brow liner
- > NO Hair Spray
- > NO Fragrances (perfume or aftershave)

Land of NOs

- NO Pre-wrapped food or snacks (such as candy bars, energy bars)
- > NO Popcorn made in a microwave
- > NO: Low-density **Polyethylene (LDPE) in** containers and bottles, > NO waterproof plastic bags, and

tubing

- NO Blue Ice
- NO Waterproof field books
- > **NO** Treated paper
- NO plastic clipboards
- > NO plastic binders
 - markers (Sharpie)

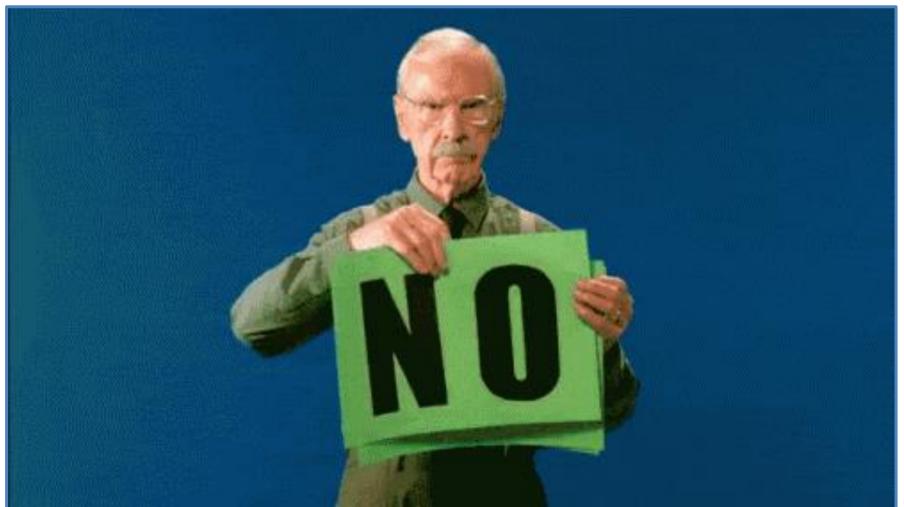
The Sampling Land of "NOs"

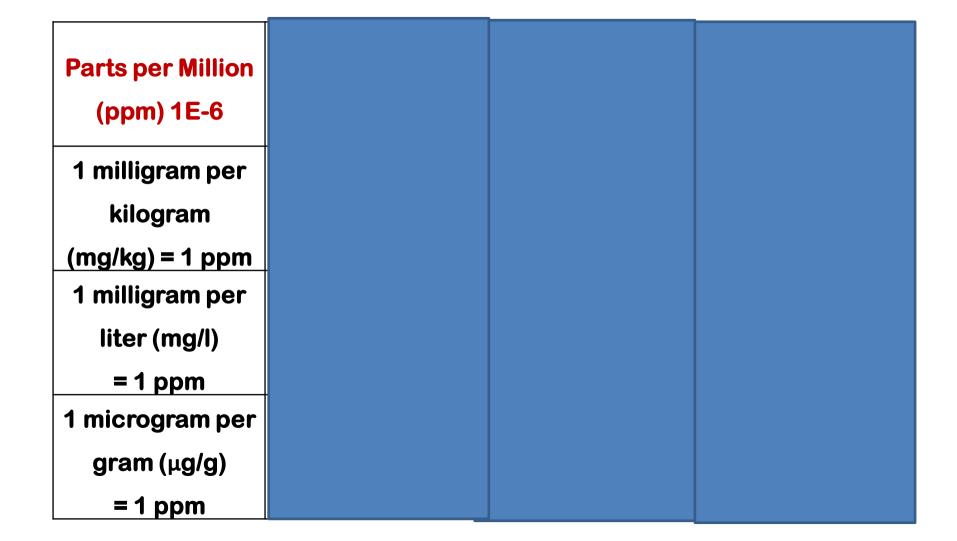
- NO TEFLON (PTFE): Hoses, tubing, wiring, gears, valves, etc.
- <u>NO Kynar (PVDF:</u>
 - Tubing, films/coatings on aluminum,
 - galvanized, aluminized steel, wire insulators, and lithium-ion batteries

- <u>NO Neoflon (PCTFE):</u>
 Valves, seals, gaskets &
 - food packaging
- NO Tefzel (ETFE):
 - Wire and cable insulation and covers, films for roofing and siding, liners in pipes, cable tie wraps

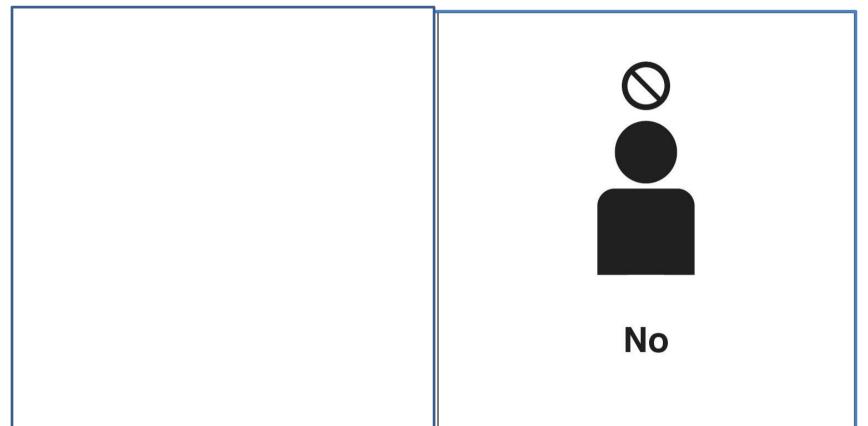
Only Two Exceptions

>When you compile all of these documents into one document there are only two exceptions!





OUR GOAL.....



Our Goal

Our goal is to write the most "sampler-friendly" document in the United States

- >One example: No Gore-Tex
- Problem: Gore-Tex is found everywhere you see the words "waterproof or water-resistant"

One Solution

>Go old school

Before WWII clothing was "waterproofed" with beeswax and other natural products

Advantage: NO PFAS and do not cause health issues to your workers

>Examples:



QUICK VIEW

Men's Double L Waxed-Cotton Upland Coat \$249-\$269 28



Men's L.L.Bean Upcountry Waxed-Cotton Down Jacket \$199-\$209 **** 81



QUICK VIEW

Women's L.L.Bean Upcountry Waxed-Cotton Down Jacket \$199 **** 47

Viewing 1 - 3 of 3

Waxed-Cotton











Non-PFAS Substitutes

Purchased leather gloves and then applied bee's wax



REVLON 1875W Lightweight + Compact Travel Hair Drver, Black Visit the REVLON Store *** 29,271 ratings 1 195 answered questions REVION margent Choice for "heir draw" List Price: \$49.99 Details Price: \$9.34 (\$9.34 / Count) Vprime FREE One-Da & FREE Returns You Save: \$2.65 (22%) Get a \$100 Gift Card: Pay \$0.00 \$9-34 upon approval for Color: Black 9.34 (\$9.34 / Count) \$9.54 (\$9.54 / Count) 10.99 (\$10.99 / Count) Hair Type Wavy, Curly







SECTION 2 - COMPOSITON/INFORMATION ON INGREDIENTS



L.L.Bean > Footwear > Men's > Boots > Hunting > Black ③

Men's Arctic Sport Muck Boots, High-Cut Item #: TA260532 | ***** 83 Reviews | Write a Review

Table 6: Allowed/Approved Sunscreens

- Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30
- Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30
- Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
- Banana Boat® Sport Performance Sunscreen Stick SPF 50
- Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50
- Coppertone® Sport High Performance AccuSpray Sunscreen SPF 30
- Coppertone® Sunscreen Stick Kids SPF 55
- L'Oréal® Silky Sheer Face Lotion 50
- Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50
- Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30
- Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50
- Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70
- Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70
- Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30
- Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+
- Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30

Chemistry Euphemisms

- Matrix Interference
- > "qualifiers" on laboratory reports
- ≻J
- ≻B

> Memory

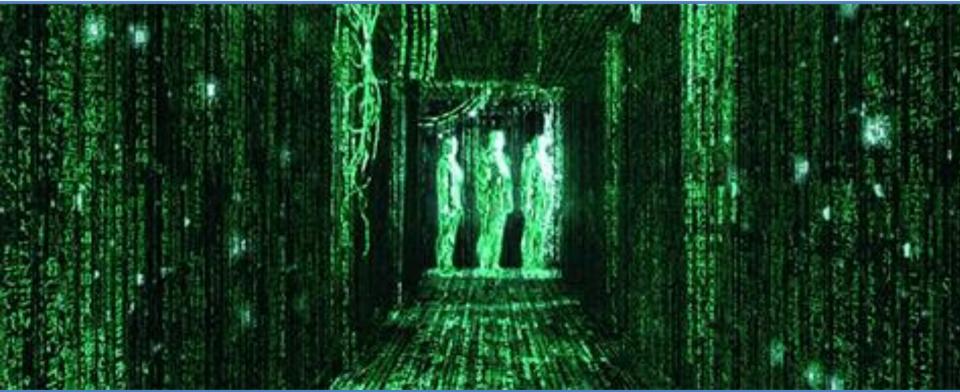
Lack of linearity

Matrix Interference



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PFAS Matrix Interference

- > The term "Matrix" includes water, soil, solids, sludges, boots, cake, etc.
- > However, water is rarely a problem
- > Therefore, generally matrix interference refers to everything other than water
- Problem: Matrix Interferences can cause either:
- False Positives or
- > False Negatives

Leaked FDA Documents Reveal Dangerous 'Forever Chemicals' in Meat, Poultry, Milk, and Chocolate Cake

The amount of PFAS found in chocolate cake was more than 250 times

higher than the federal guidelines for PFAS in drinking water.



The FDA report found much higher levels in the chocolate cake, the Associated Press reported, with PFAS levels

FDA: Total PFAS Chocolate Cake: 17,640 PPT Seafood 865 PPT Meat 765 PPT Leafy Greens 813 PPT

PFAS in food

FDA Makes Available Testing Method for PFAS in Foods and Final Results from Recent Surveys

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Constituent Update

October 31, 2019

PFAS Matrix Interference

- If you believe you have matrix interference, either change:
- 1. The analytical procedure
- 2. The solvent used for extraction

Mercury in Oklahoma Soil

- I have tested many Oklahoma soil samples
 <u>Mercury</u> using the cold vapor technique
- > Average concentration ≈ 0.02 \rightarrow 0.04 mg/kg
- Professor contacted me regarding a large grant he received for the sampling and testing for mercury in remote parts of Oklahoma
- > He found very high concentrations of Hg?

Mercury in Soil

Location	Mercury Concentration (mg/kg)
Surface	0.2

Remember: Average Hg conc. in OK is about 0.03 mg/kg

Mercury in Oklahoma Soil



Matrix Intorforance

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to Method 7000 for a discussion of interferences.

4.2 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

4.3 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

4.4 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 254 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Alternatively, the sample may be allowed to stand for at least an hour under a hood (without active purging) to remove the chlorine.

Mercury Analysis

4.0 INTERFERENCES

4.1 Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds which have broad band UV absorbance (around 253.7 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures (Section 9.0) must be strictly followed.



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

PFAS Matrix Interference

- Again, other than water, the matrix may cause either false positives or false negatives for PFAS
- If your results do not seem correct, work with your lab to either:
- > Change the analytical procedure or
- > The extraction solvent

Qualifiers

A qualifier on a laboratory report tells the client additional information regarding the <u>integrity</u> of the data

Sample Location	Sample Description	Sample Date	Sample Method	Qualifiers	Total PFAS
MW-1 ng/L	Water	10/1/2021	537.1	J, B	4,500
MW-2 ng/L	Water	10/1/2021	537.1	В	550
Soil Sample #1 ng/kg	Soil	10/1/2021	537-m	J, M, B	600
Trip Blank ng/L	Water	10/1/2021	537.1	В	478
Field Blank ng/L	Water	10/1/2021	537.1	J & B	400
Equipment Blank ng/L	Water	10/1/2021	537.1	В	25

Laboratory Qualifiers

> M = modified

4. Laboratory is certified for that analysis in your State

3. Per Federal & State regs (SDWA) requires you to use <u>their</u> chemical analytical procedures (533, 537.1)

PFAS Analyses Potable Water

2. Chain of Custody (COC) form 1. Sampled properly ODEQ guidelines

PFAS Analysis

- At the present time, all PFAS analysis was <u>designed</u> for <u>finished potable water ONLY</u>
- There are no final regulations as to how to analyze for PFAS in soils, sludges, non-potable groundwater, finished products (boots)



5. NO Laboratory is certified for PFAS in solids

4. NO Federal or State regulations <u>as to how to analyze</u> <u>PFAS</u> in soils or groundwater

3. NO Federal or State regulations <u>as to how to extract</u> <u>the PFAS from</u> soils or nonpotable groundwater



PFAS Analyses

Soils

2. Chain of Custody (COC) form 1. Sampled properly ODEQ guidelines

M = modified

- Any time you see a "M" next to a test procedure, this means the laboratory has <u>modified</u> a drinking water analytical test protocol to test nondrinking water
- > 537-M or 533-M, etc.
- Remember M = modified or made-up
- > Why? Because at the present time



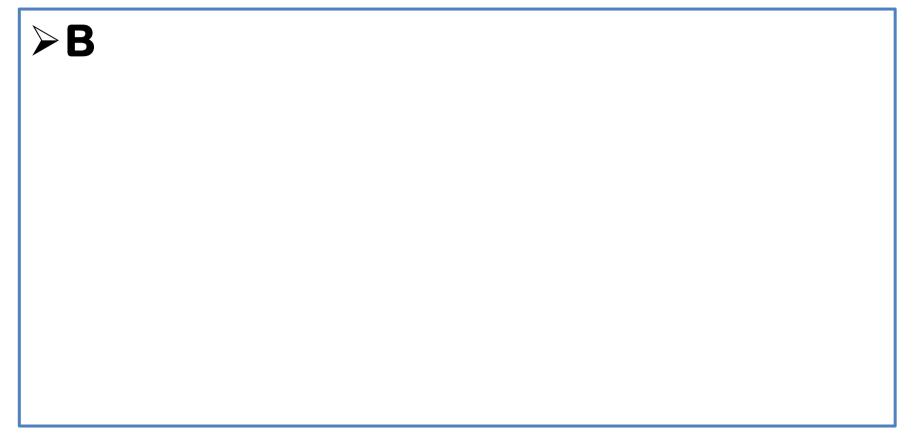
m = modified

- No Federal or State regulations <u>as to how to</u> <u>extract the PFAS from</u> soils or non-potable groundwater
- Shandy Extraction Protocol



- No Federal or State regulations <u>as to how to</u> <u>analyze PFAS</u> in soils or groundwater
- No Laboratory is certified for PFAS in solids, soils, groundwater only drinking water

"B" Laboratory Qualifiers



Laboratory Qualifiers

- B = Compound was found in the laboratory method <u>blank and</u> the <u>sample</u>
- How did PFAS contaminate both the method blank and the sample?
- > The answer: The labs water purification's system!

"B" Laboratory Qualifiers

- > Every laboratory has a water purification system
- However, the valves, tubing, gaskets are all made out of Teflon (PFAS)
- This Teflon leaches from the water purification system into your samples
- Before each shift, the Chemist should "waste" one to two gallons of purified water into the sink
- Next, the Chemist should run the equipment blanks

Sample Location	Sample Description	Sample Date	Sample Method	Qualifiers	Total PFAS
				· · · · · · · · · · · · · · · · · · ·	
Trip Blank ng/L	Water	10/1/2021	537.1	В	478
Field Blank ng/L	Water	10/1/2021	537.1	J & B	450
Equipment Blank ng/L	Water	10/1/2021	537.1	В	25



Massachusetts Department of Environmental Protection - Drinking Water Program

Per- and Polyfluoroalkyl Substances (PFAS) Report

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"B" qualifier — means the chemical was found in both the sample and a "blank".
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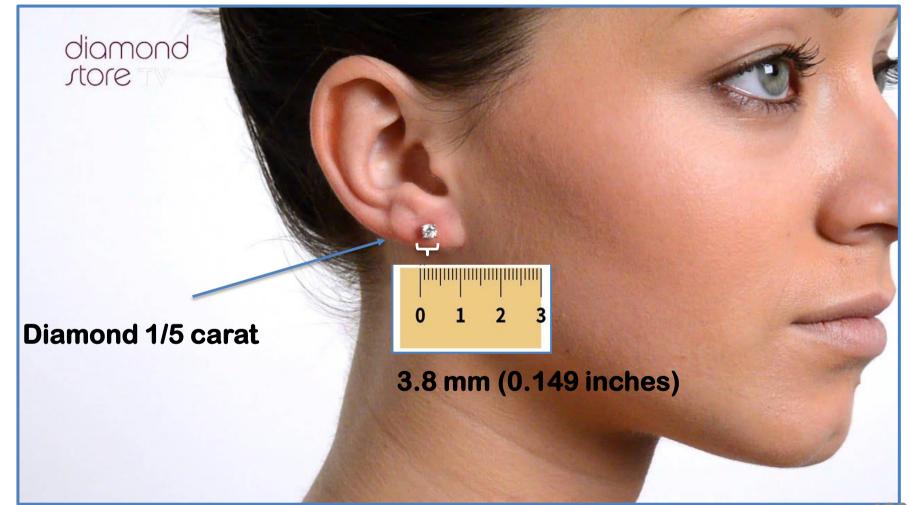
When chemicals are found in both the blank and the test sample, the reported value is qualified with a "B" to show the uncertainty in the source of the contamination. Such samples must be recollected and reanalyzed. In the example above,

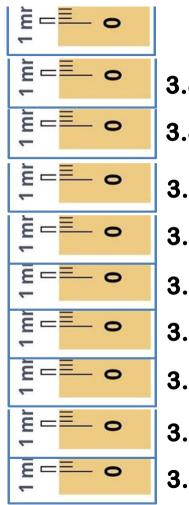
Chemistry Euphemisms

"Lack of linearity"

Lack of Range of Linearity

- > At the present time, all analytical procedures for PFAS were designed for finished drinking water
- Goal: Report very low Parts per Trillion (1 to 5 PPT)
- However, most soils (and some groundwater) that was contaminated with fire fighting foam (AFFF), you will detect Parts per Million
- The difference between a PPT (1E-12) and PPM (1E-6) = 1 million
- > To give a perspective

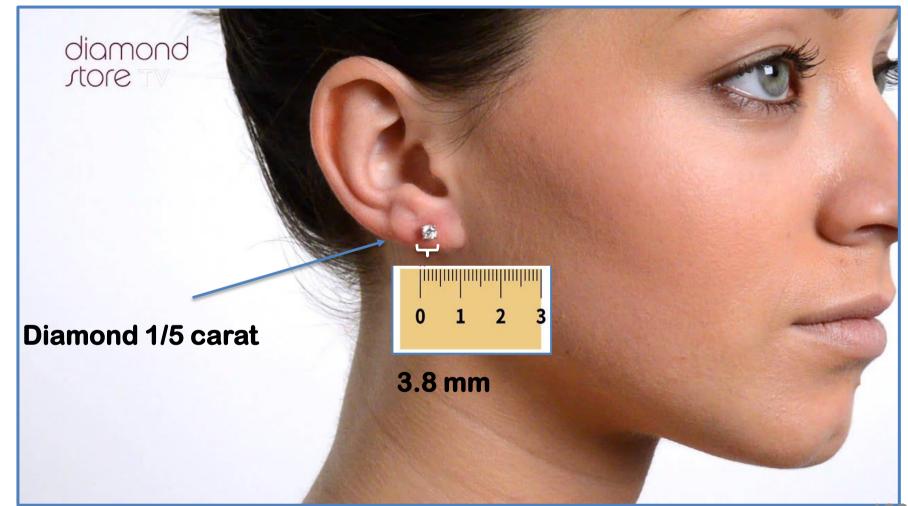




3.8 mm x 1 000 000 = 3800 meters

3.8 mm



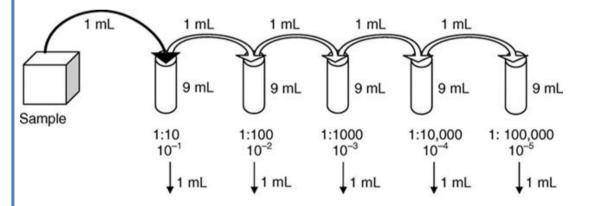


Elevation 3800 m

Serial Dilution

- Every time a Chemist pipettes one solution into another there are always small errors
- Every error is then multiplied by x100,000 or x1,000,000





Analytical Caveats of PFAS

- 1. Lack of range of linearity
- > Again, today's analytical techniques were designed for finished potable water
- LC/MS/MS only has a range of accurate reliability between:
- > 5 PPT \rightarrow 1000 PPT
- Any value below 5 PPT or above 1000 PPT is an estimate (J-flag)

Actual samples: Split Labs

SAMPLE ID	Matrix	Lab A PPT	Lab B PPT
1	Brackish Water	1035	
2	Liquid	996	
3	Solid	30 700 000	
4	Solid	90 900 000	
5	Solid	15 000 000	

PFAS range of accurate reliability between:

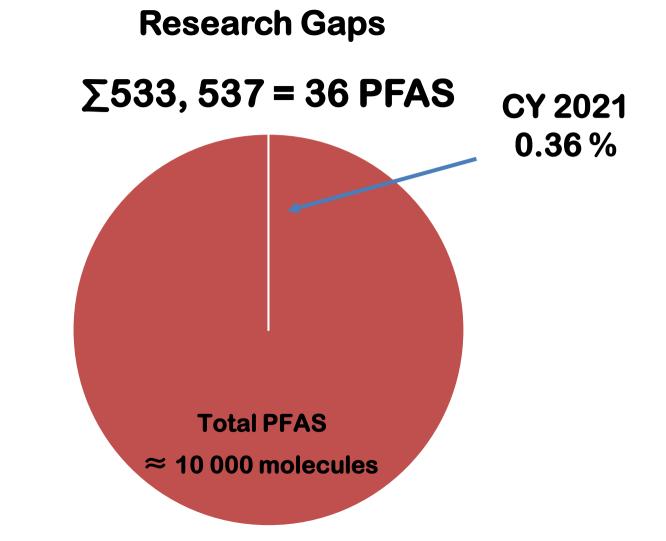
5 PPT \rightarrow 1000 PPT

PFAS Chemist's Euphemisms

"Research Gaps"

PFAS Chemist's Euphemisms

- The analytical results have "Research Gaps"
- Very polite expression to tell the reader that the PFAS family has about 10 000 different molecules
- > Presently we can detect about 36 molecules
- Therefore this "research gap" means the Chemist cannot identify 9964 of the 10 000 molecules!

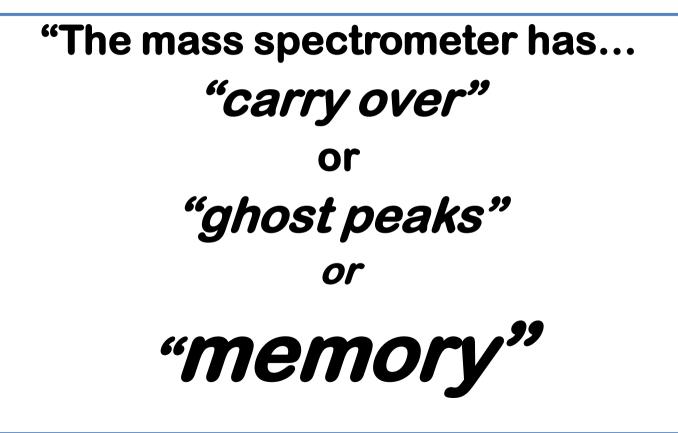




Chemistry Euphemisms

> Memory

Chemist's Euphemisms

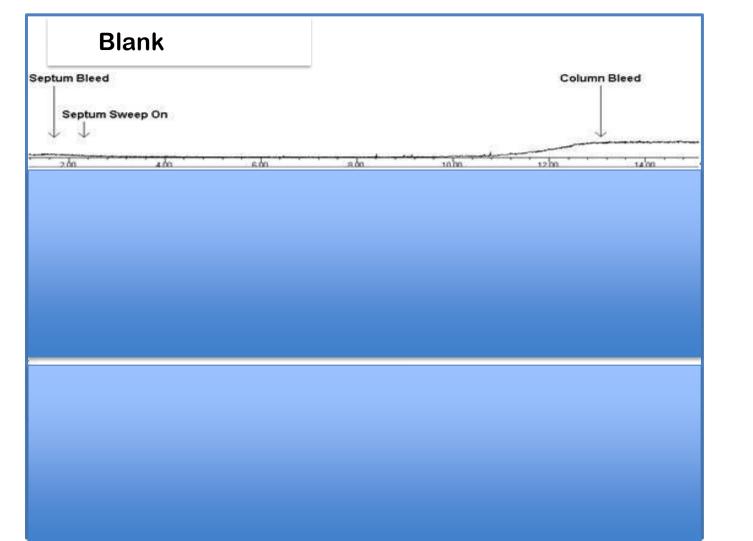


Chemist's Euphemisms

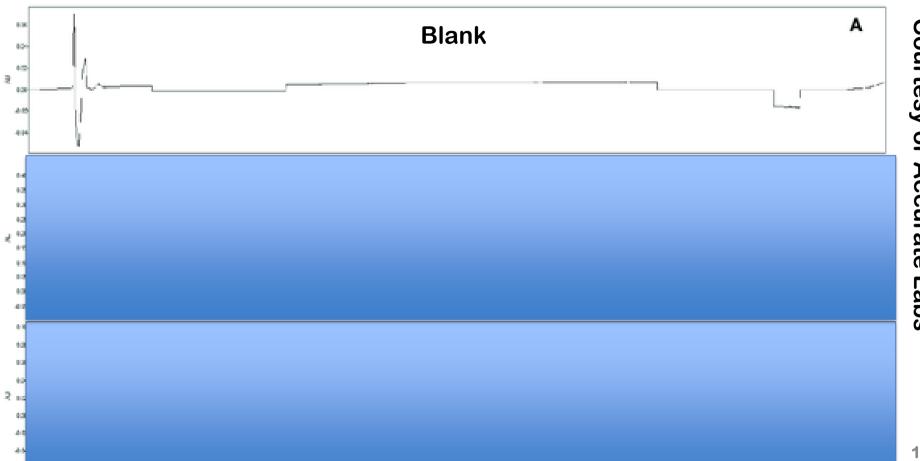
> Memory Euphemism:

Polite expression to tell the reader that the Chemist forgot to run a blank sample between your sample and the previous one

Therefore, if the previous sample is contaminated, your sample will also show contamination!



Courtesy of Accurate Labs



Courtesy of Accurate Labs

Memory

SAMPLE ID	Matrix	Lab A PPT
1	Brackish Water	
2	Groundwater	
3	Trip Blank	
4	Field Blank	
5	Equipment Blank	

Blanks

- Secause PFAS is ubiquitous and chemical instruments have "memory," blanks should be run first
- If any parameter is above BDL (Below Detection Limit), the Lab must call you!
- * You may want to resample
- * You cannot subtract the blank values from the sample values

Thank You



Contact information: Kenneth F. Ede, PhD, CHMM e-mail: Ken.Ede@okstate.edu

