PFAS DATA ANALYSIS, INTERPRETATION & CAVEATS

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Thank You

Environmental Federation of Oklahoma

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

Thank You

- Oklahoma State University-Tulsa
- Dr. Sheryl Tucker, Vice Provost, Graduate Dean, OSU-Tulsa; OSU-Stillwater

INSTRUCTIONS FOR SUBMITTING A PROPOSAL

- **When I received the "Instructions for Submitting a Proposal" I speaking with Bob Joyce**
- **I got stuck on this question**
- **<u>Subject Area</u>: Select the most appropriate subject area(s) of the presentation:**
- **Air, Water, Solid Waste, Hazardous Waste, Health & Safety, Wildlife, etc.**

SUBJECT AREA

Select the most appropriate subject area(s) of the presentation.

☐ Air	☐ Water	☐ Solid Waste	☐ Hazardous Waste
☐ Corporation Commission		☐ Wildlife	
☐ Health & Safety	☐ Other (describe):		

AGENDA: PFAS

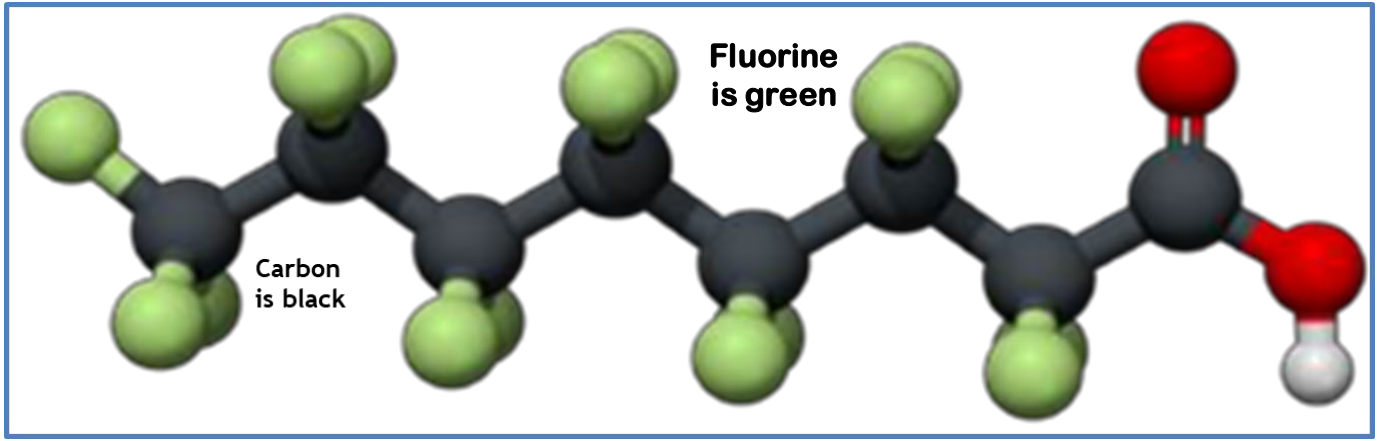
- Will be using a fictitious example today of Cowboy Bicycles

1. How big is this problem?
2. Chemical Analysis & Laboratory Accreditation
3. How to Triage Your Samples
4. Blanks
5. Admissibility of Evidence in Courts of Law

PFAS

Per- & Polyfluoroalkyl Substances (PFAS)

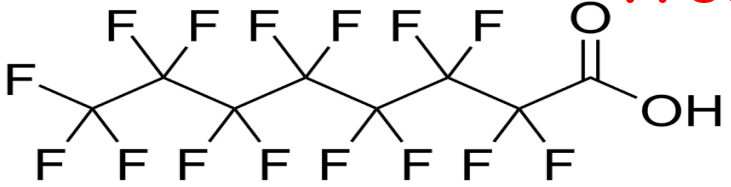
- **Per- or Poly: more than one**
- **Fluoro: contain fluorine**
- **Alkly: Hydrocarbon**



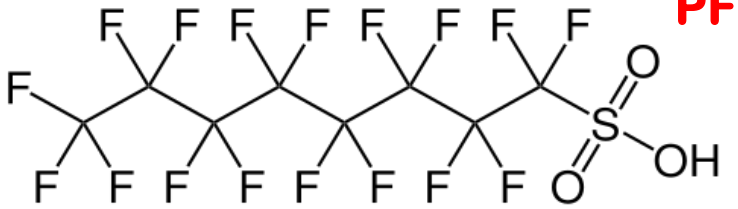
PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS)

- **PFAS: Umbrella term**
- **PFAS are family of 6,000 —› 10,000 manmade chemicals**
- **PFOS, PFOA, etc….**
- **Most common names: Teflon, Gore-Tex, Scotchgard, AFFF**

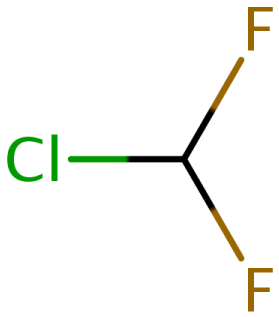
PFOS



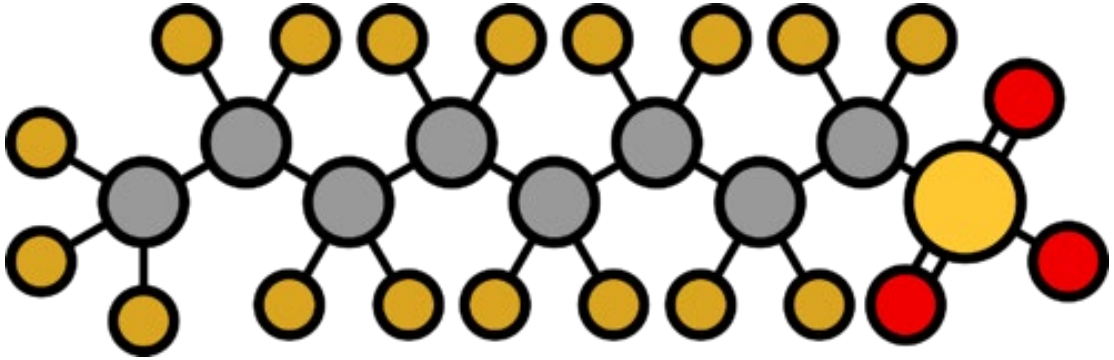
PFOA



PFAS



Difluoromonochloromethane
(R-22)



Perfluorooctanesulfonic acid (PFOS)

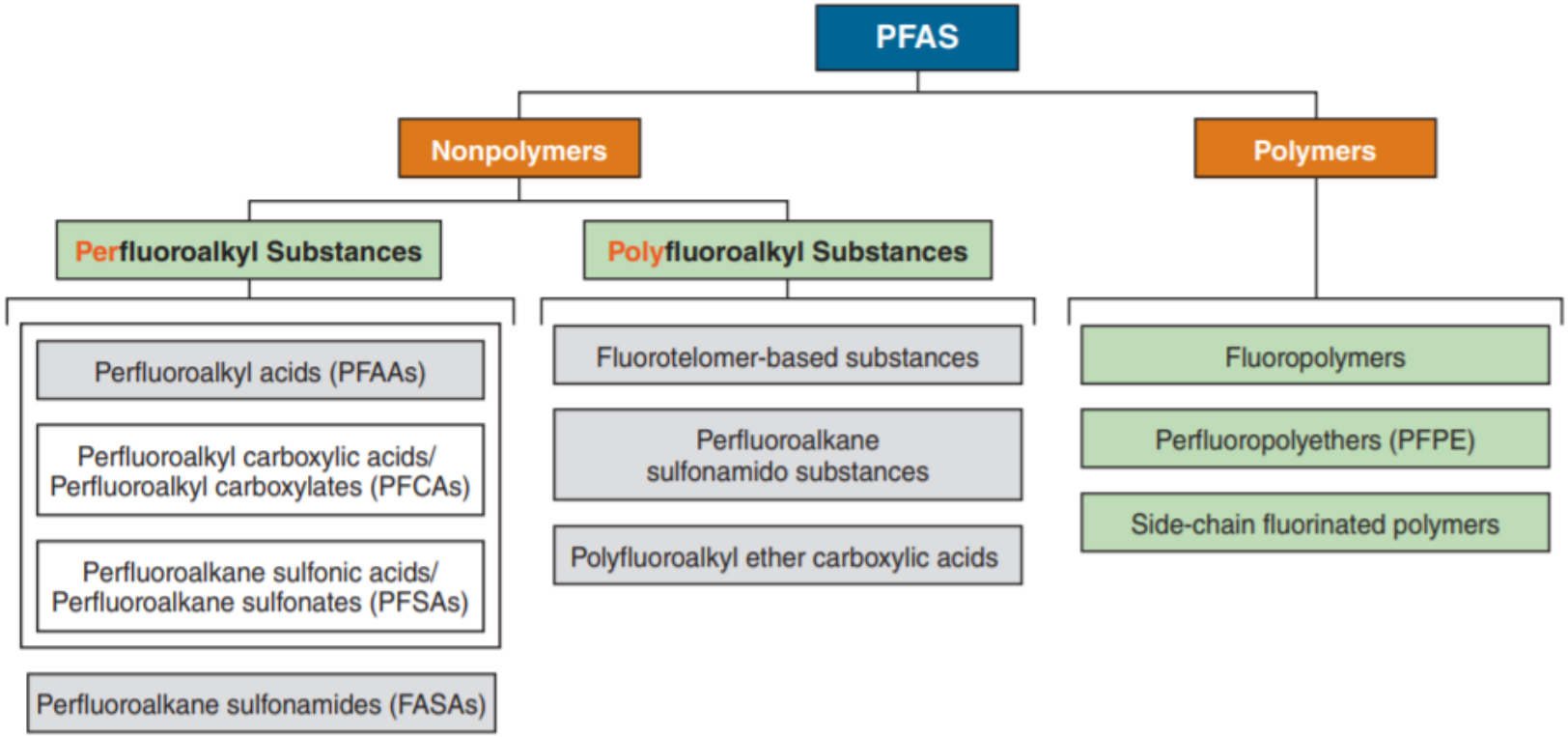


Figure 2-1. Summary of PFAS families

Source: Adapted with permission from Buck, R.C., J. Franklin, U. Berger, J. M. Conder, I. T. Cousins, P. de Voogt, A. A. Jensen, K. Kannan, S. A. Mabury, and S. P. van Leeuwenet. 2011. "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins." Integrated Environmental Assessment and Management, 7:513-541. Open access. Copyright 2011 SETAC. http://dx.doi.org/10.1002/ieam.258

Commercial and Consumer Products Containing PFAS

- Paper and packaging
- Clothing and carpets
- Outdoor textiles and sporting equipment
- Ski and snowboard waxes
- Cookware
- Cleaning agents and fabric softeners
- Polishes and waxes
- Latex paints
- Pesticides and herbicides
- Hydraulic fluids
- Windshield wipers
- Paints, varnishes, dyes & inks
- Adhesives
- Medical products
- Shampoo
- Hair conditioners
- Sunscreen
- Cosmetics
- Toothpaste
- Dental floss

Cosmetics with PFAS

- Eyeshadow
- Bronzer/highlighter
- Facial powder
- Foundation
- Sunscreen/makeup
- Mascara
- Anti-aging
- Moisturizer
- Eye cream
- Blush
- Shaving cream
- Facial moisturizer
- Brow liner
- Hair Spray

Fictitious Scenario

- Cowboy Bicycles manufactures bicycles
- Cowboy Bicycles has outgrown their current facility and wants to purchase a large parcel of land from a bank to expand their operations
- Cowboy Bicycles contracts with you to conduct a Phase I and II Real Estate Assessment on a vacant parcel of land

Cowboy Bicycles

- During the Phase I Real Estate Assessment (ASTM E1527-13), you interview some of the neighbors regarding this vacant land
- One of the neighbors tells you that many years ago the fire department used this piece of land to conduct training

Cowboy Bicycles

- The neighbor remembers that some type of white foam was used
- You contact your client (buyer) and they want both the soil and groundwater tested for PFAS

Your Goals

#1 Goal to analyze for PFAS in non-potable water (soils & groundwater)

#2 Assume litigation: you need ensure that this analysis will be admissible in a court of law

Admissibility of evidence in courts of law

- Most chemical analysis of samples (other than criminal or environmental) have a very small chance of litigation
- For example, you submit a soil sample from your garden or farm to determine the Phosphorus (P) or Cation Exchange Capacity (CEC)
- Just like a criminal forensic laboratory, we must assume all samples submitted to a lab will be followed by litigation

Old Professor's Adage: Environmental Report

- ***"Write like you are talking to a Judge"***
- ***"Sample like the Judge is watching you"***
- ***"Complete your Chain of Custody (COC) like a Judge will be reading it"***
- ***"Every time you submit a sample to a laboratory assume you will be explaining <u>your rationale</u> to a Judge"***

Admissibility of evidence

- Each Federal & State Permit requires you to use **their** chemical analytical procedures.
- In addition, most States requires "state approval labs"
- Therefore, before submitting a sample to a lab, you must ensure that lab is "certified" to analyze the chemical parameter per Federal Act or permit
- Example: Pre-treatment Permit, Clean Water Act

CITY OF TULSA WATER AND SEWER DEPARTMENT

INDUSTRIAL PRETREATMENT
4818 SOUTH ELWOOD
TULSA, OK 74107

CITY OF Tulsa
A New Kind of *Energy*.

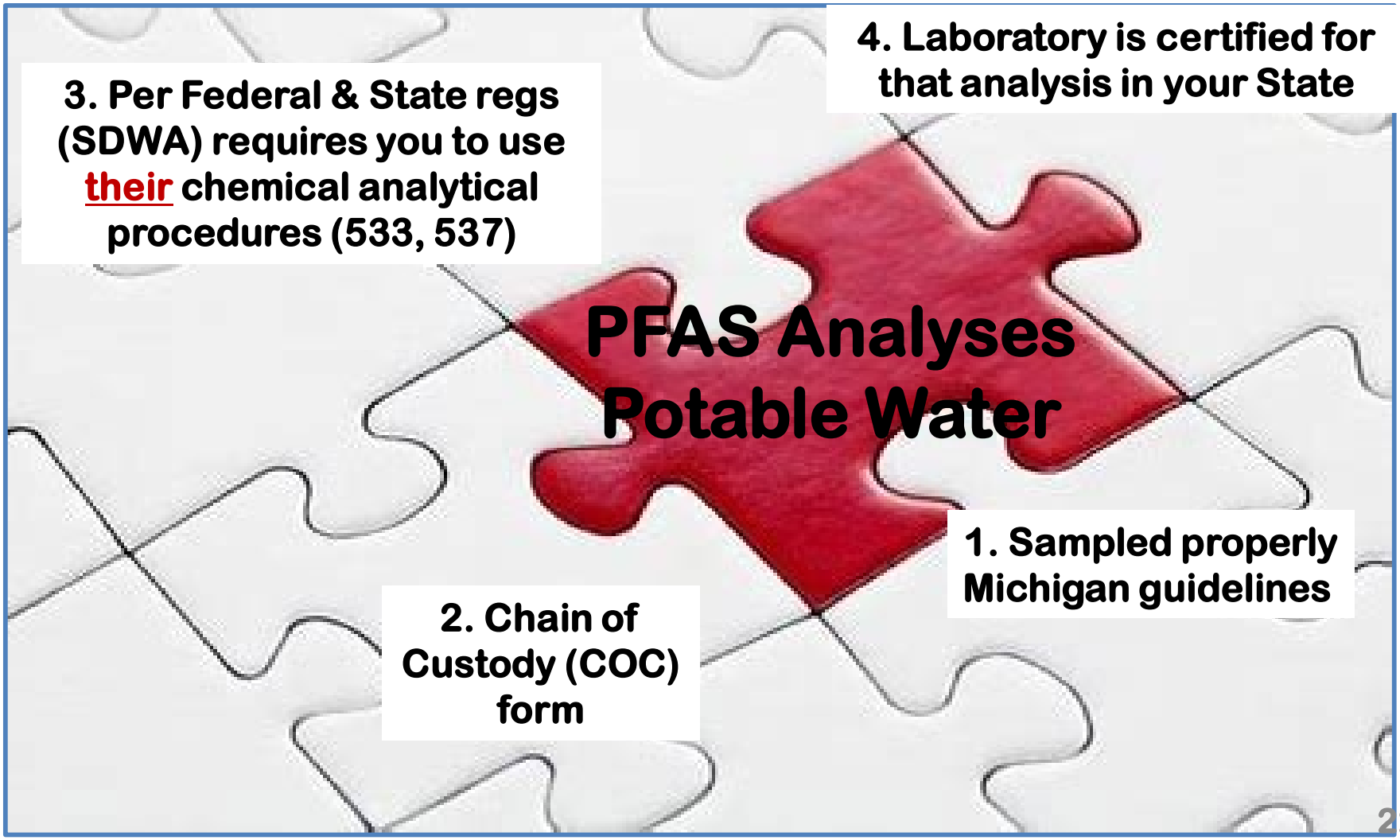
INDUSTRIAL WASTEWATER DISCHARGE PERMIT FOR:

II.B *Analytical Requirements:* All self-monitoring samples, required to be obtained by this permit, are to be analyzed utilizing methods found in 40 CFR Part 136 and amendments. With the exception of pH, all pollutant analyses are to be conducted by a laboratory certified by the Oklahoma Department of Environmental Quality to perform such analysis. The Permittee may perform pH analyses at the time of sampling, provided the Permittee has submitted an approved pH monitoring protocol to the Permitting Authority.

Admissibility of evidence

Therefore, all environmental samples must have five conditions:

1. **Sampled properly (field blank, preservatives, proper sample containers, etc.)**
2. **Chain of Custody (COC) form**
3. **On the COC, you must state the analyses you want**
4. **You must ensure that the analyses is consistent with the Federal Act that has jurisdiction on the sample (aliquot)**
5. **Laboratory is certified for that analyses**

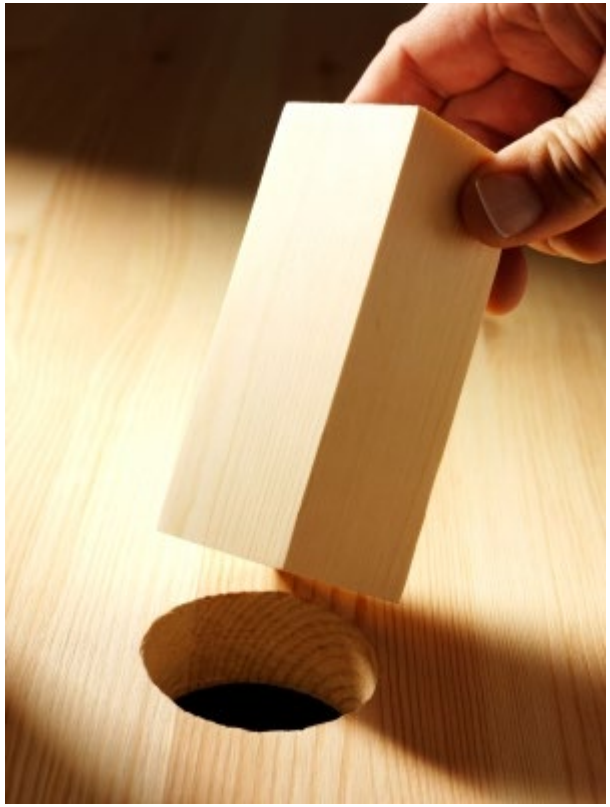

4. Laboratory is certified for that analysis in your State
3. Per Federal & State regs (SDWA) requires you to use their chemical analytical procedures (533, 537)
PFAS Analyses Potable Water
1. Sampled properly Michigan guidelines
2. Chain of Custody (COC) form

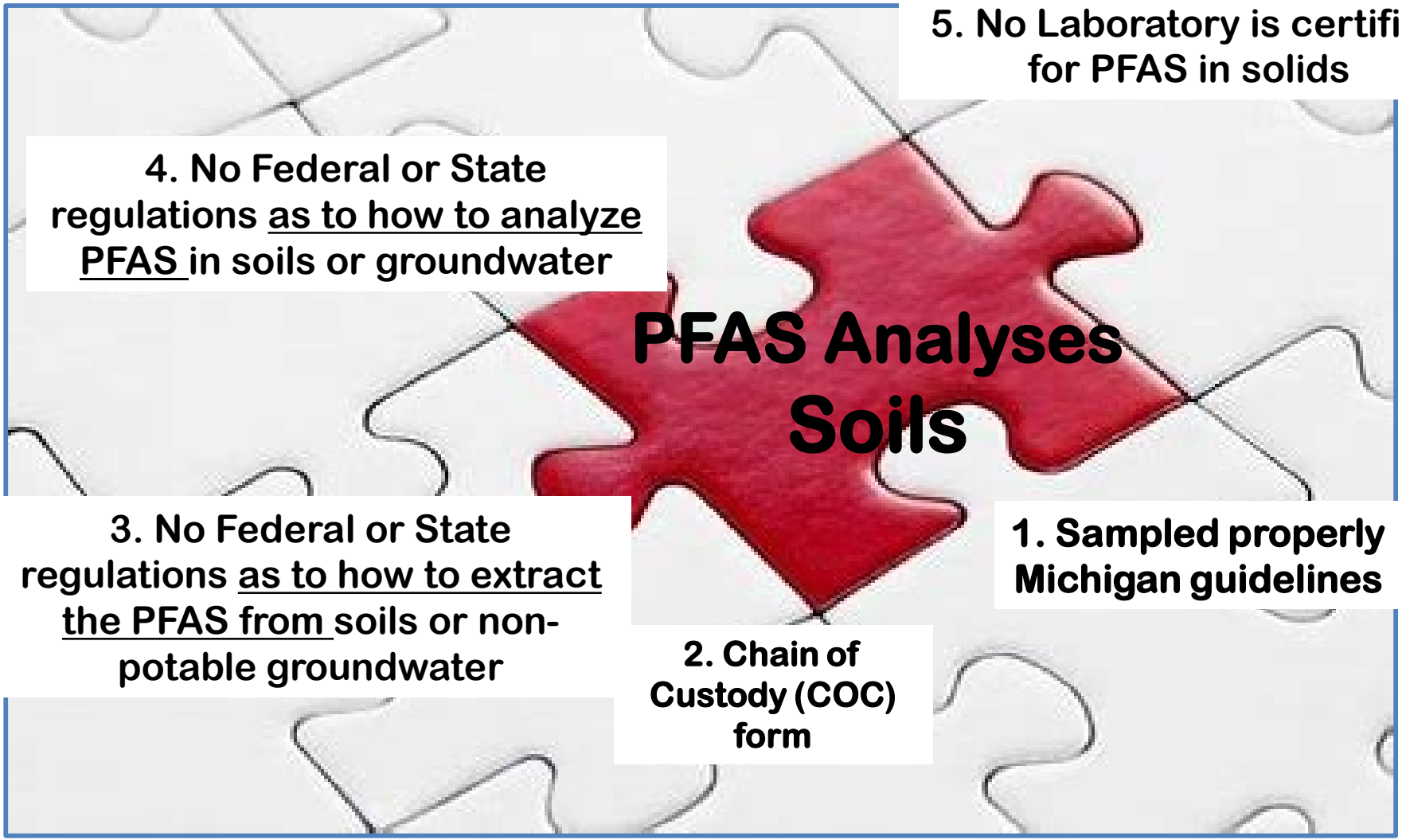
PFAS Analysis

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

PFAS Analysis

- In addition, presently under the Safe Drinking Water Act there are currently no Maximum Contaminant Level (MCL) established for PFAS chemicals
- EPA has established the health advisory levels at 70 parts per trillion




5. No Laboratory is certified for PFAS in solids
4. No Federal or State regulations as to how to analyze PFAS in soils or groundwater
PFAS Analyses Soils
3. No Federal or State regulations as to how to extract the PFAS from soils or non-potable groundwater
1. Sampled properly Michigan guidelines
2. Chain of Custody (COC) form

PFAS Analysis of non-potable water

1. Triage your samples
2. Run the blanks first
3. Lab blanks should be at least 250 mL
4. Analysis brackish water using serial dilution
5. Analysis soils, sludges, etc. via a standard extraction procedure
6. Understand the limitations of this analyses
7. Use a laboratory that is already certified for PFAS potable water

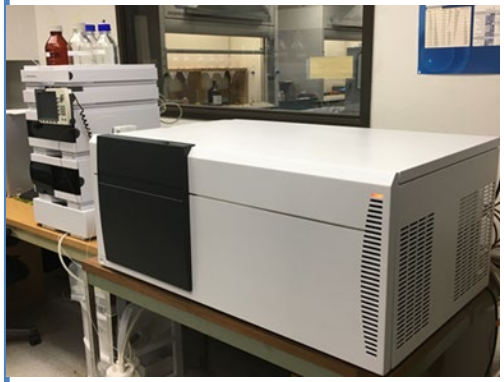
How to Triage Your Samples

- Presently, most laboratories are using liquid chromatography with a tandem mass spectrometry (LC/MS/MS) to analyze for the PFAS molecules
- The cost of a new LC/MS/MS is about $350,000
- Each day the LC/MS/MS is not operating could cost the laboratory $10,000 per day profit.
- These instruments were designed to analyze finished potable (drinking water) with very low TDS (total dissolved solids) and very low TSS (total suspended solids)

LC/MS/MS

How to Triage Your Samples

- This is why we need to work closely with your environmental laboratories to ensure you are not creating damage to their instruments
- Just one sample with a very high PFAS concentration can contaminate the LC/MS/MS for several days.



How to Triage Your Samples

- The easiest and most cost-effective method to protect their instruments is to triage your samples before they are received into the laboratory.
- The word “triage” comes from the French verb *trier* meaning to sort
- Triage: Sort by both matrix (drinking water, brackish water, solids) & PFAS concentration

Triage Your Samples

Key	MEANING
D	Drinking water (TDS < 500 PPM)
B	Brackish water (TDS > 500 PPM)
S	Solids (soils, sludges, products)
L	LOW PFAS < 100 PPT
H	HIGH PFAS > 100 PPT

Triage Your Samples

Groups	SAMPLES CONCENTRATIONS
D-L	Drinking water with LOW PFAS < 100 PPT
D-H	Drinking water with HIGH PFAS > 100 PPT
B-L	Brackish water with LOW PFAS < 100 PPT
B-H	Brackish water with High PFAS > 100 PPT
S-L	Solids, soils, products with LOW PFAS < 100 PPT
S-H	Solids, soils, products (e.g., boots, AFFF) with HIGH PFAS > 100 PPT

Group D: Drinking Water

- The first group, “Group D” is normal drinking water (potable water)
- EPA Test Methods 533 & 537 were designed for this matrix
- This matrix has low TSS (total suspended solids) and low TDS (total dissolved solids)
- In addition, these potable water samples will not harm any of instruments in the laboratory

Group D: Potable Water

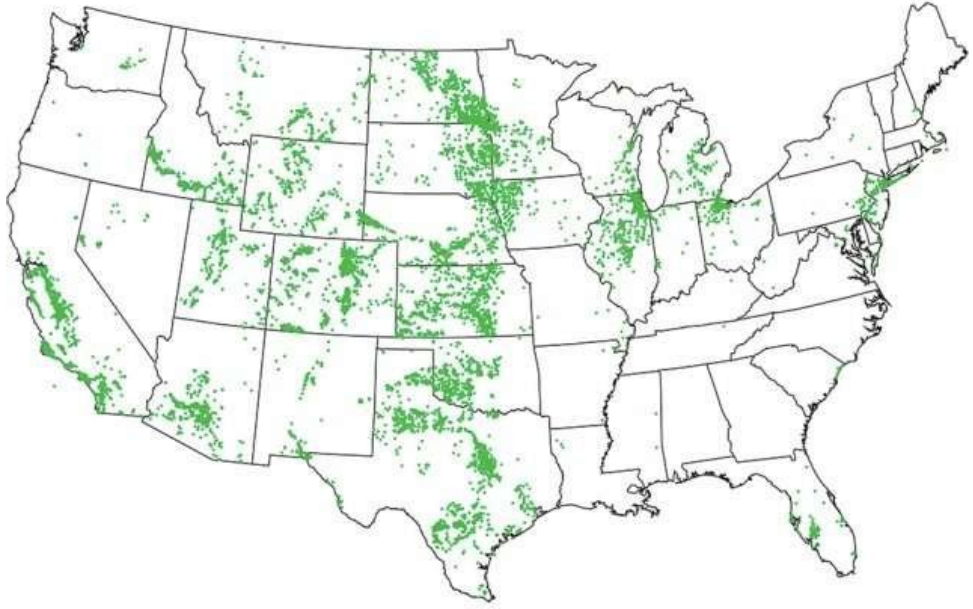
- These types of potable water are the easiest samples to analyze for PFAS in part per trillion range
- As a recommendation, I would purchase a portable TDS meter (< $50), if your sample is truly potable water, the TDS value should be less than 500 mg/L (groundwater)
- If the sample's TDS is much higher than 500 mg/L, that sample should be placed into the Group B samples

Group A: Drinking Water

- Generally, drinking water will have the lowest Practical Quantitation Level (PQL) for PFAS
- Minimum aliquot size for LC/MS/MS = 250 ml
- Do not allow the lab to use a sample size less than 250 mL

Group B: Brackish Waters

- **The second group, "Group B" are water samples with high TDS (>500 mg/L) and/or high TSS**

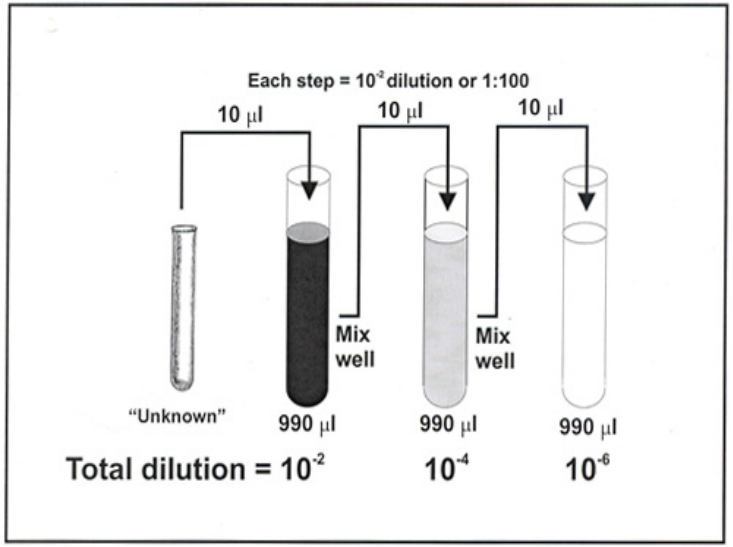


Brackish Groundwaters

Ahdab, Y., Thiel, G., Böhlke, J., Stanton, J., & Lienhard, J. (2018). Minimum energy requirements for desalination of brackish groundwater in the United States with comparison to international datasets. Water Research, 141, 387-404.

Group B: Brackish Waters

- Once the laboratory is notified that these samples are not drinking water, their test protocol changes
- Instead of analyzing the samples "as-is," the laboratory will make serial dilutions to ensure they do not ruin their instruments



Group B: Brackish Waters

- After the serial dilutions have been made, the laboratory can then run the samples for PFAS
- Two drawbacks to serial dilution:

1. Increases probability of error
2. Increases Practical Quantitation Level (PQL)

- If you believe that the brackish groundwater is high in PFAS (>100 PPT), please notify the laboratory
- This will prevent the contamination of their equipment

Group S: Solids and Sludges

- The last group (Group S) are also non-potable waters
- These could include soils, sludges or boots
- Samples are **not** tested "as-is"
- Rather these samples are **extracted**, then the **extract** is analyzed
- Unfortunately, there are no USEPA approved extraction procedures

Group S: Solids and Sludges

- Each lab has their own procedure, therefore there is little consistency between labs
- Recommendation: Use a standard extraction protocol for solids, soils, etc.
- Do not allow the lab to dictate this protocol
- Advantage: When you split samples, each lab will use the same procedure (yours)
- Contact me if you want a copy (Ken.Ede@Okstate.edu)

Triage

Matrix	Triage Group < 100 PPT	Triage Group > 100 PPT
Drinking Water	D-L	D-H
Brackish Water	B-L	B-H
Solids, sludge, soils, etc.	S-L	S-H

Triage Groups

Sample #	Matrix:	Est. PFAS concentration	Triage Group
1	Drinking Water	Low	D-L
2	Groundwater	< 100 PPT	D-L
3	Brackish Water	< 100 PPT	B-L
4	Brackish Water	> 100 PPT	B-H
5	Soil: AFFF	> 100 PPT	S-H
6	Soil: background	< 100 PPT	S-L

* Complete Entire COC to be in Compliance*

RUSH Due Date

Chain of Custody

Accurate Environmental Labs

Client Name-

Project Name-

Accurate Work Order #	Date Sample Taken	Time Sample Taken	Matrix or Source (Refer below)	Grab (G) or Comp (C)	Client I.D. / Sample Location or DEQ / EPA Location Code	Field Results (pH, Temp, Chlorine, …) (note analysis & units)			Sample Preserv. & Container →	Analysis Requested →							
									# of Container ↓								

On-Site Info — Raw Alkalinity (TOC Raw)= _____ mg/L — Turbidity (E.Coli)= _____ ntu

Matrix Codes — DW = Drinking Water WW = Wastewater SL = Sludge O = Other_____

E.Coli Source- GWUDI-FS= Groundwater under direct influence of Flowing Stream GWUDI-RL= Groundwater under direct influence of Reservoir/Lake

Field Instrument Calibration -				
Meter Type	Standards	Final Read.	Date , Time	Initials

Comments

-- All samples are scheduled to be disposed of in 4 weeks of receipt at Accurate.--

Certification by Company Official: I hereby certify that the above sampling occurred during a period such that the sample(s) is/are representative of a typical operating day discharge for the above facility. Signature : Date/Time

Sampled By: Company: Sample Method:

Relinquished By: Date/Time Received By: Date/Time

☐ Relinquished to Lab By: Date/Time Received at Lab By: Rec'd °C Date/Time

☐ Relq'd to Log-In Fridge By:

Reporting Requirements (standard 10-15 working days) | Compliance Reporting? | Yes or No (DMR, PWS,) | Oklahoma PWS ID # | RUSH Request (if available) _____ (Working Days)

Mail Report:

Address

Phone #: Fax #:

Email:

Mail Invoice:

Address:

Bid # -

PO # -

Phone #: Fax #:

www.accuratelabs.com (800) 516-5227

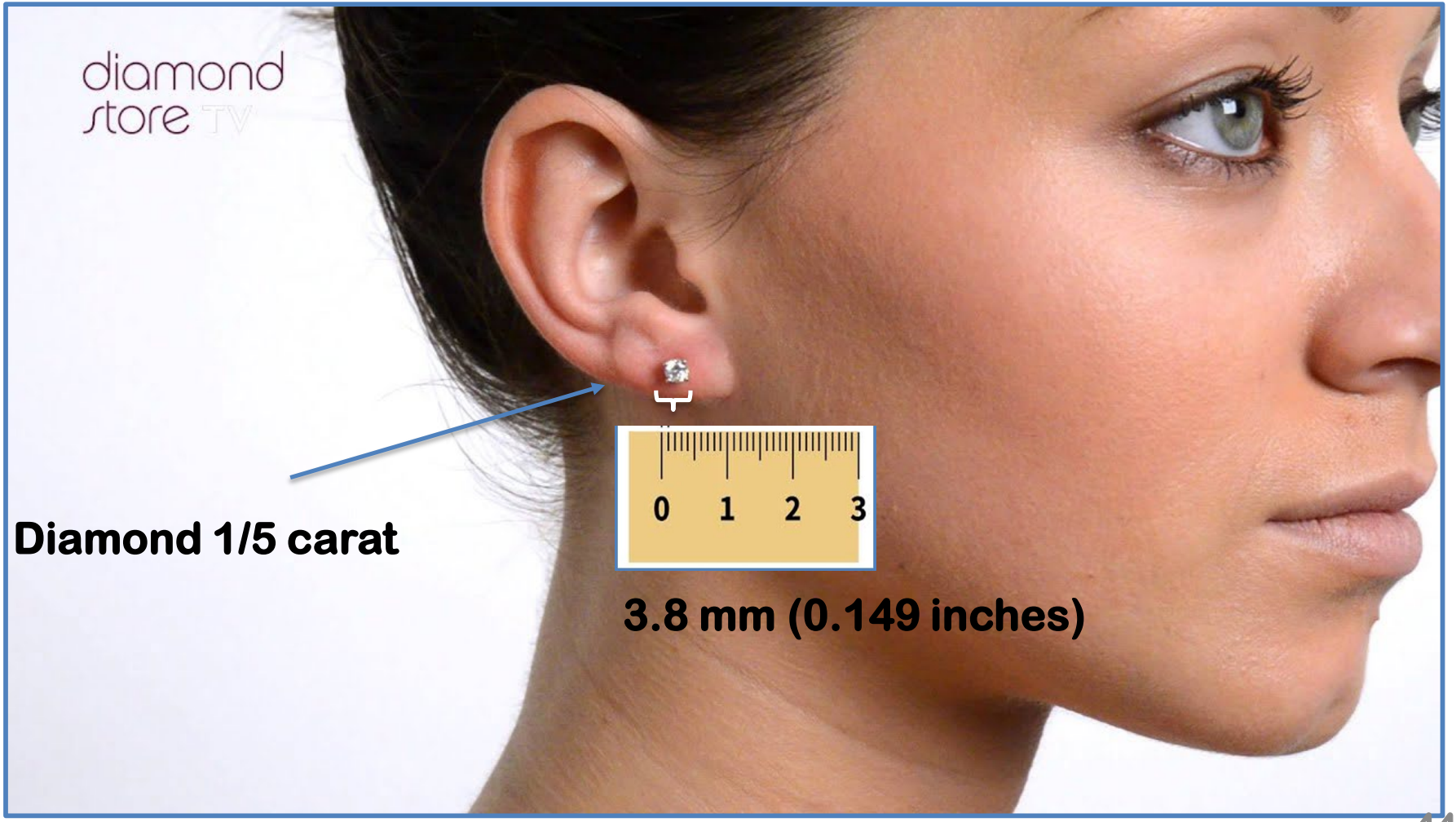
505 South Lowry Street Stillwater, OK 74074 Phone: (405) 372-5300 Fax: (405) 372-5396

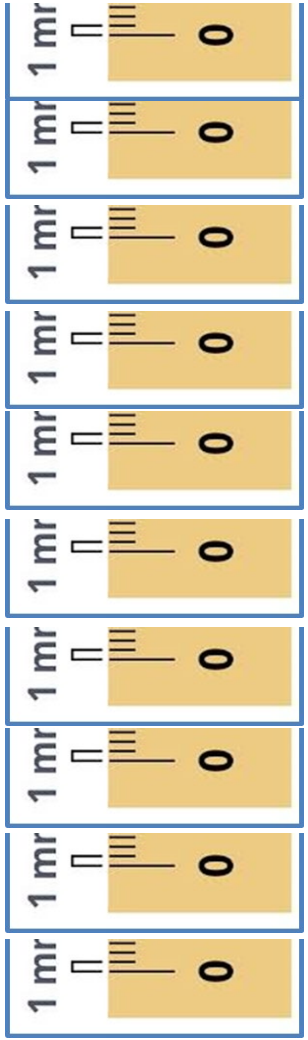
3910 E. 51st Street Tulsa, OK 74135 Phone: (918) 663-5400 Fax: (918) 663-6300

12036 N. Pennsylvania Oklahoma City, OK 73120 Phone: (405) 751-3132 Fax: (405) 751-3108

Lack of range of linearity

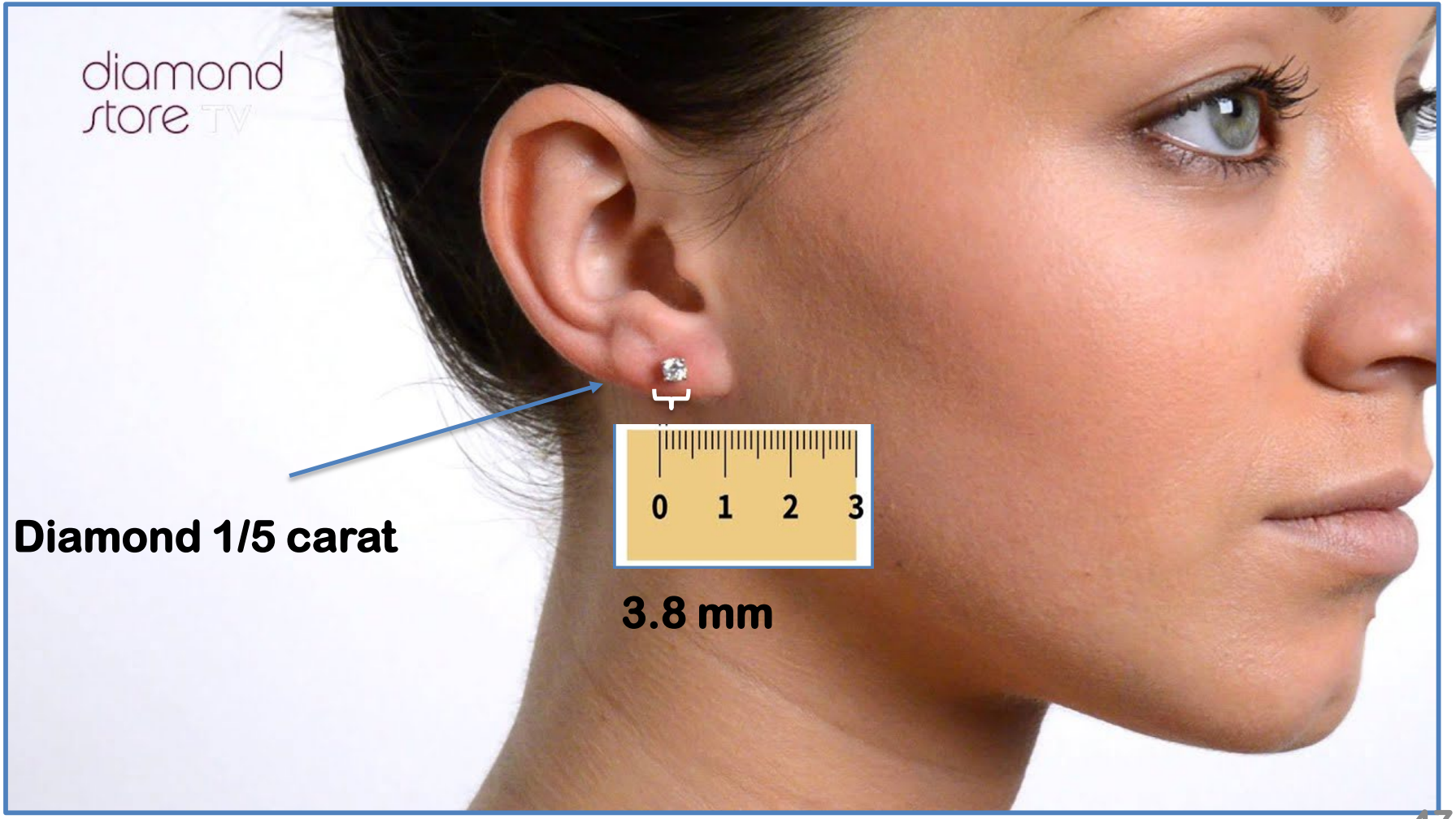
- At the present time, all analytical procedures for PFAS were designed for finished drinking water
- Goal: Report very low Parts per Trillion (1 to 5 PPT)
- However, most soils (and some groundwater) that was contaminated with fire fighting foam (AFFF), you will detect Parts per Million
- The difference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


diamond
store TV
Diamond 1/5 carat
0 1 2 3
3.8 mm (0.149 inches)



3.8 mm x 1 000 000 = 3800 meters


Elevation 3800 m


diamond
store TV
Diamond 1/5 carat
0 1 2 3
3.8 mm


Elevation 3800 m

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 → 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	3600
2	Liquid	996	3992
3	Solid	37 000 000	18 900 000
4	Solid	99 000 000	112 000 000
5	Solid	16 000 000	1 900 000

PFAS range of accurate reliability between:

5 PPT → 1000 PPT

Blanks

- Because PFAS is ubiquitous, blanks must be used to determine the background concentrations

1. Trip Blanks
2. Field Blanks
3. Equipment Blanks

Blanks

- **Trip Blank**: Also known as transport or travel blanks.
- A sample container filled with deionized water and any applicable preservatives in the laboratory.
- It is then sealed and marked "return unopened".
- The trip blank accompanies the sample containers to the field and back to the laboratory where it is analyzed for the same parameters as the collected samples

Trip Blanks: PFAS

- Positive results indicate contamination of samples during:

1. Transport (unlikely)
2. Preservative (from the lab)
3. Container (from the lab)
4. Labs DI water system is not working
5. Sample prior to yours was high in PFAS (memory)

- Analyze Blanks first! If any parameter is above BDL (Below Detection Limit), the Lab must call you!
- You may want to resample
- (EPA) You cannot subtract the blank values from the sample values

Field Blanks: PFAS

- A sample container is filled with deionized water during sample collection in the field.
- In the field, the water is transferred from one container to another (exposing it to the sampling environment, usually air).
- A field blank measures the incidental or accidental sample contamination during the sampling

Field Blanks: PFAS

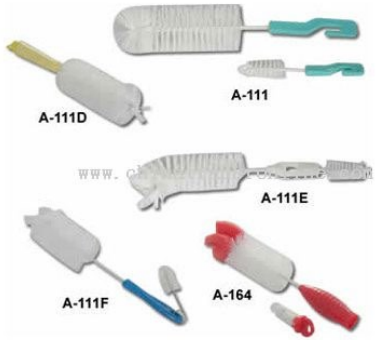
- Most PFAS molecules are non-volatile, therefore,
- Positive results indicate <u>contamination</u> of samples during:

1. From the ambient air (unlikely)
2. Transport (unlikely)
3. Preservative (from the lab)
4. Container (from the lab)
5. Labs DI water system is not working
6. Sample prior to yours is high in PFAS (memory)

- Analyze first! If any parameter is above BDL (Below Detection Limit), the Lab must call you!
- You may want to resample
- (EPA) You cannot subtract the blank values from the sample values

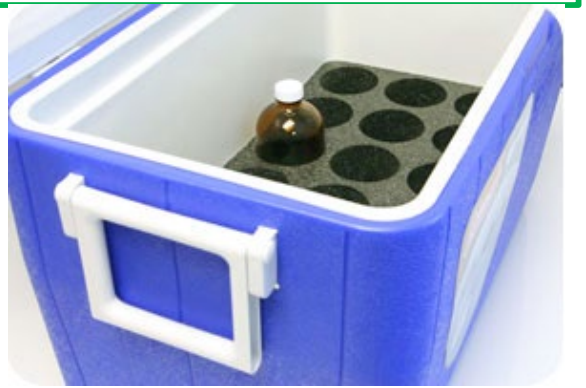
Equipment Blank: PFAS

- A sample container is brought to field empty and labeled **"Equipment Blank."**
- A bottle of deionized water (DI water) and detergent is also brought to clean the sampling equipment.



Equipment Blank

- During the decontamination of the equipment used in the field (such as a bailer, auger, collection spoon, containers), the final rinsate is collected in the Equipment Blank container.
- This rinsate is analyzed for the same parameters as the field samples.



Equipment Blank

- An equipment blank measures the incidental or accidental sample contamination during the decontamination of sampling equipment.

Ways to avoid using Equipment Blanks:

1. Use only disposal bailers.
2. Use bailers or sampling pumps dedicated to a well.
3. Use disposal sampling spoons, etc., if you cannot, then

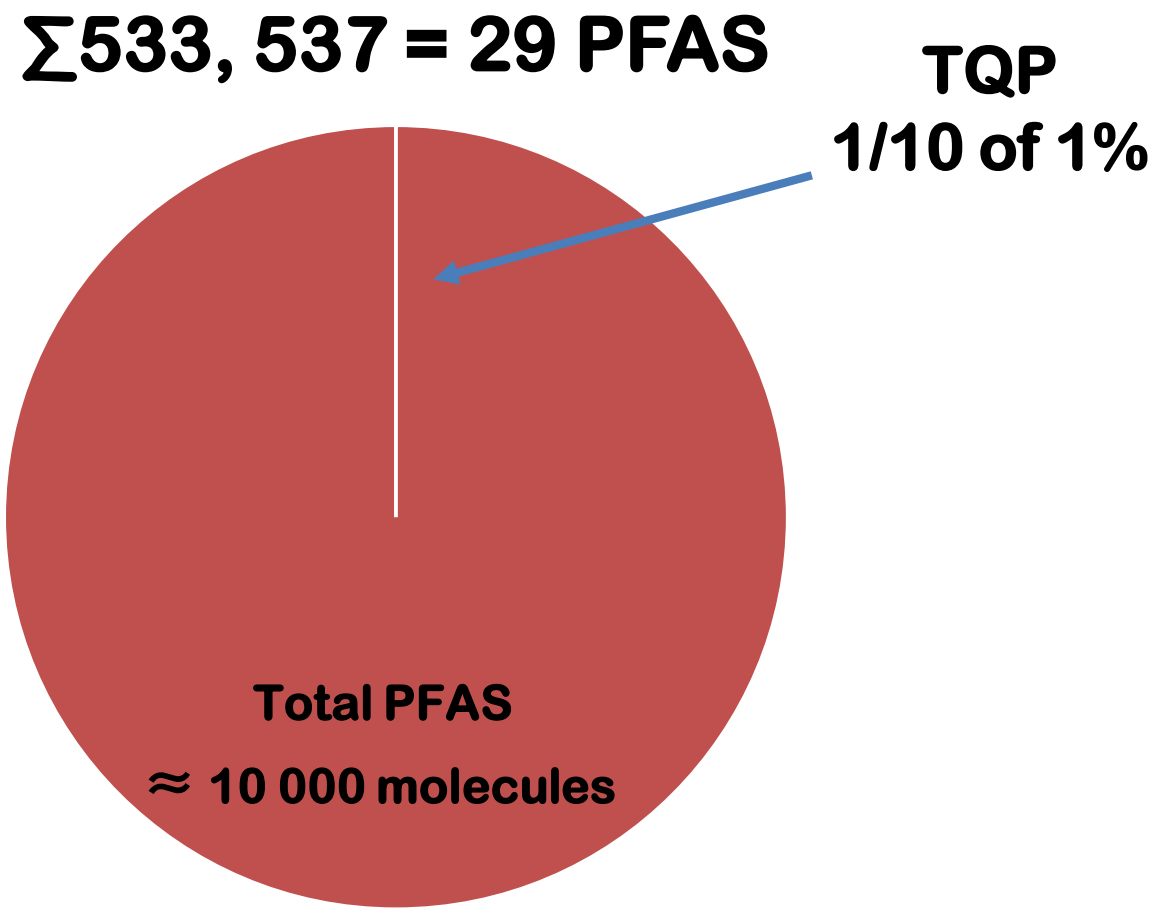
- Analyze equipment blank first! If any parameter is above BDL, the Lab must call you!

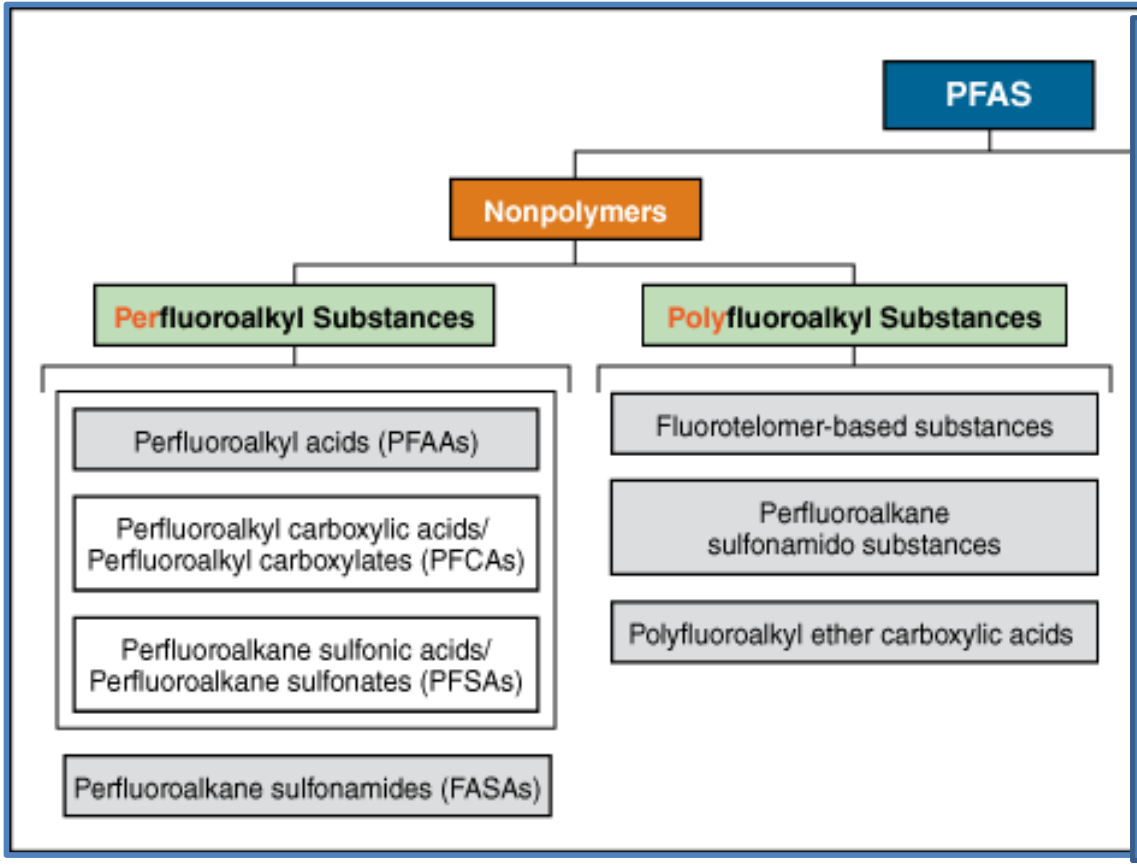
Consider resampling!

Chemical Analysis of PFAS

- 2018: EPA published Test Method 537.1
- Total 18 molecules
- 2019: EPA published Method 533
- Total 29 PFAS molecules
- **Total PFAS ≈ 10 000 molecules**

Total PFAS v. Total Quantifiable PFAS (TQP)




PFAS
Nonpolymers
Perfluoroalkyl Substances
Polyfluoroalkyl Substances
Perfluoroalkyl acids (PFAAs)
Perfluoroalkyl carboxylic acids/
Perfluoroalkyl carboxylates (PFCAs)
Perfluoroalkane sulfonic acids/
Perfluoroalkane sulfonates (PFSAs)
Perfluoroalkane sulfonamides (FASAs)
Fluorotelomer-based substances
Perfluoroalkane
sulfonamido substances
Polyfluoroalkyl ether carboxylic acids


NEW!
Breakthrough
PVDF Technology
Berkley
SUPER STRONG
Trilene
100% Fluorocarbon
PROFESSIONAL GRADE

AP (After Pandemic): PFAS

EPA developing analytical techniques

- **Total Organic Fluorine (TOF)**
- **Measure the total amount of organically-bound fluorine in PFAS molecules**
- **Yes, the total sum of all +10,000 PFAS molecules at one time!**
- **This will be an eye-opener for most of us!**

AP (After Pandemic) PFAS

EPA developing analytical techniques

- **SW-846 Method 8327 Direct Injection**
- **SW-846 Method 8328, Solid Phase Extraction**

Department of Defense (DoD)

- **Quality Systems Manual (QSM) for Environmental Laboratories (Version 5.2)**
- **ASTM D7979 – 19**
- **ISO 17025**
- **FDA 2019.1**

Professional Science Master's Degree

- If you have ever thought about your:
- **Master of Science Degree in Environmental Science from Oklahoma State University,**
- Please contact me!!
- Ken.Ede@okstate.edu


QUESTIONS?
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