# DO'S AND DON'TS OF PFAS SAMPLING

Guide to PFAS Free Sampling

Beth Proffitt

SGS North America Inc.

Business Development Manager

WHEN YOU NEED TO BE SURE

SGS

I apologize, I am NOT Harry Behzadi!

# EMERGING CONTAMINANT

- Can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects.
- The United States Environmental Protection Agency (EPA) has identified Perfluorinated chemicals (PFCs) as an emerging contaminant group. PFCs are man-made compounds that are highly soluble in water and are chemically and thermally resistive. Their resistance to degradation causes PFCs to be detected at low concentrations throughout the environment, including the Arctic.

# STANDARDS AND GUIDELINES

- On May 19, 2016, EPA released Drinking Water Health Advisory (HA) of 70 parts per trillion (ppt) applicable to both the individual PFOA and PFOS chemical concentrations and when both PFOA and PFOS are found in drinking water, the 70 ppt HA level is applicable to the combined concentrations of PFOA and PFOS. This HA level offers a margin of protection for all Americans from adverse health effects resulting from a lifetime exposure to PFOA and PFOS in drinking water.

- No federal drinking water standards have been established for PFOS and PFOA. The EPA is currently collecting drinking water data to determine if establishing a Maximum Contaminant Level (MCL) is warranted under the Safe Drinking Water Act based on PFOS and PFOA occurrence in drinking water, the number of people potentially being exposed, observed exposure levels, and costs for treatment to reduce levels.

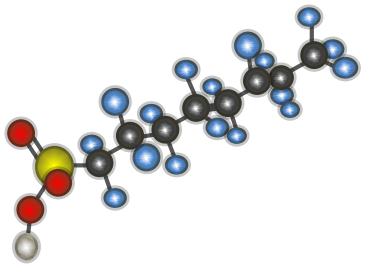
# REGULATIONS

- The U.S. EPA initiated a program in 2006 to phase out emissions and in 2015, the use long-chain PFAS
- Health-based advisories for PFOA and PFOS have been developed by EPA and several state agencies
- PFOA and PFOS were included in UCMR3
- State reporting levels for drinking water to 1-20 ng/L dependant on state.
  - PFNA (NJ) @ 13 ng/L (lower RL required)
  - MN (PFBS, PFHxS)
  - RLs 1-5 ng applied “across the board” to all PFCAs and PFSAs (NH, VT, NY, MN etc.)
  - Soil Criteria, existing in AK, TX, MN, by QAPP in other states. Others in development
  - Fish advisories calculated by old HALs are site specific risk assessments that produce very low allowable levels in water to avoid fish advisories

# WHY ARE THEY A CONCERN?

- PFOA and PFOS were produced in the largest amounts in the United States
- They are persistent and resistant to typical environmental degradation processes. As a result they are found in soil, air, groundwater and human blood samples world wide.
- Human Health Effects associated with PFAS in general population and DW contaminated sites (Cholesterol increase, Uric Acid increase, Thyroid disease, Testicular and Kidney cancer, Pregnancy induced hypertension, Diabetes, Birth weight decrease, and more)

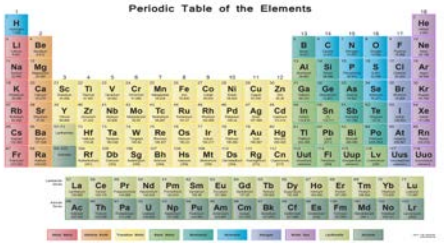

# WHAT ARE PFAS?

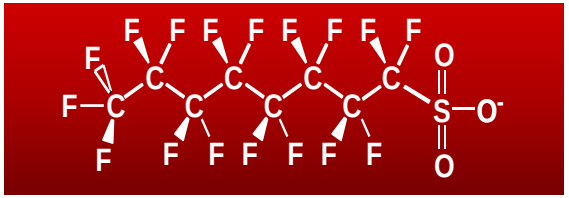


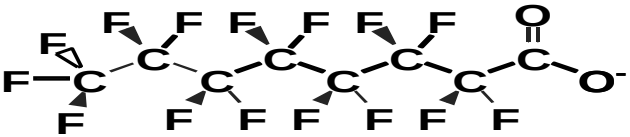
- PFAS are a large group of man-made fluorine-containing chemicals with unique properties to make materials to which they are applied stain and stick-resistant.
- PFAS are used to repel oil and water from clothing, carpeting, and furniture, in food packaging, and on non-stick surfaces on cookware.
- PFAS are very resistant to breakdown, migrate easily, and concentrate in the food chain. As a result, they may be found throughout the environment in groundwater, surface water, soil, and air, as well as in food.
- PFAS have been used for decades in many common products and are persistent in the environment.

# WHAT ARE PFAS COMPOUNDS?

- PFAS are a class of synthetic compounds containing thousands of chemicals formed from carbon chains with fluorine attached to these chains.
- The C-F bond is the shortest and the strongest bond in nature and is responsible for most of the unique and useful characteristics of these compounds
- PFAS are surfactants that repel oil and water, reduce wear or surface adhesion
- Introduced as early as 1948 (Teflon, or PTFE polymer) with a great increase in use in the late 1960s and 1970s.
- At low concentrations, many have significant water solubility





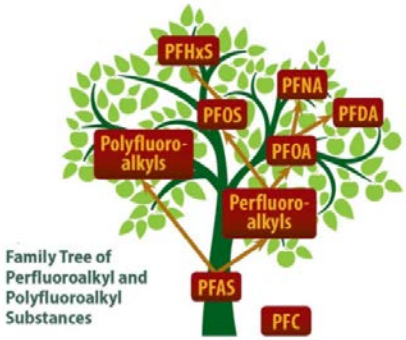
# TERMINOLOGY AND NAMING

- Per and polyfluoroalkyl substances (PFASs), have been referred to as Perfluorinated Chemicals (PFCs) in the past
- EPA more concerned with Long Chain PFAS
- Long chain PFASs comprise two sub categories
  - Long chain Perfluoroalkyl Carboxylic Acids (PFCAs) with eight or more carbons, including PFOA
  - Perfluoroalkyl Sulfonates (PFSAs) with six or more carbons including
    - Perfluorohexane Sulfonic acid (PFHxS) and
    - Perfluorooctane Sulfonic acid (PFOS)
  - Precursor: Compounds that are required for synthesis or extraction of another compound.

# AFFF FOAMS

- Aqueous Film Forming Foams used in fire suppression contain PFOS and FTS at Sites with years of use, e.g. military and airports affected.
- Also contain non fluorinated hydrocarbon compounds that enhance surfactant activity.
- 0.5-1.5% w/w PFOS & FTS. PFOS being replaced by other generally shorter chain PFAS products.
- PFOS is only part of the story for AFFF sites

# OTHER SOURCES OF PFAS




- PFAS have been used in many industries, including aerospace, automotive, construction, manufacturing, electronics, and textiles.
- PFAS have been used since the 1940s as manufacturer-applied oil and water repellants on products such as clothing, upholstery, paper, and carpets, and were also used in making fluoropolymers for non-stick cookware.
- PFAS surfactant qualities were also utilized in mist suppressants that can be added to metal plating baths to prevent air releases

*Image courtesy of https://**www.atsdr.cdc.gov**

# POTENTIAL PFAS MARKET SITES


- Former Fluorochemical manufacturing facilities including textile/carpet manufacturers
- Water & Wastewater treatment facilities – including desalination, water reuse, and receiving water bodies
- U.S. Department of Defense installations
- AFFF training facilities
- Landfills
- Sediment dredging

# MORE POTENTIAL SITES

- Airport hangars and other facilities storing firefighting foams.
- Crash sites, including aircraft and motor vehicle sites where AFFF may have been used
- Refineries and Petroleum Storage facilities
- Metal coating and plating facilities (mist suppressant)
- Wiring and semi-conductors in electronic and aerospace industry
- Large rail yards

# IT IS GETTING PERSONAL

- Water and soil repellants used in clothing and carpet
- PFOA is used to make Teflon ™ products including non-stick cookware
- Food packaging (in fast food wrappers or microwave popcorn bags)
- Consumer product testing
- Personal Care Products

# PROCESSES AND PRODUCT USES/SOURCES


| | |
|---|---|
| Fluoropolymer coatings | Some grease-resistant paper |
| Plastics/polymers | Fast food containers/wrappers |
| Surfactants used in fire fighting foams | Microwave popcorn bags, pizza boxes, candy wrappers |
| Mist suppressants for metal plating operations | Non-stick cookware such as Teflon™ coated pots/pans |
| Photomicrolithography process to produce semiconductors | Oil and water repellent (Teflon™, Stainmaster® carpets, Scotchgard™ and Gore-Tex®) |
| Photography and film products | Stain-resistant coatings such as Scotchgard™ used on carpets, upholstery and other fabrics |
| Adhesives, Aviation hydraulic fluids, cleaning products | Water-resistant clothing such as Gore-Tex® |
| Paints, varnishes and sealants | Personal care products such as shampoo, dental floss, and cosmetics (nail polish, eye makeup) |

# HOW TO SAMPLE FOR PFAS

- Because of the potential presence of PFAS in common consumer products and in equipment typically used to collect soil, groundwater, surface water, sediment, and drinking water samples as well as the need for very low reporting limits, special handling and care must be taken when collecting samples for PFAS analysis to avoid sample contamination.

# SAMPLING EQUIPMENT

- Pumps and Tubing: Don't use Teflon™ and other fluoropolymer-containing materials *(**Do use** high density polyethylene [HDPE] or silicone tubing materials)*
- Don't use Passive diffusion bags
- Don't use Low density polyethylene (LDPE) Hydrasleeves (**Do use** *HDPE Hydrasleeves)*

- Sample storage and preservation: Don't use LDPE or glass bottles, Teflon™-lined caps, chemical ice packs (i.e., Blue ice®) *( **Do use** HDPE or polypropylene containers with HDPE or polypropylene caps, regular ice and Zip-loc bags)*
- Decontamination: Don't use Decon 90 *(**Do use** Alconox® or Liquinox®, potable water followed by deionized PFAS-free water rinse)*

# CERTIFICATE


SGS Accutest certifies that the DI water shipped, Kit #:_____ is free of any PFAS compounds as per the attached report. Please see attached report for list of compounds.

_____

SGS Accutest Sample Management, Name and Date

WHEN YOU NEED TO BE SURE

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# SAMPLING EQUIPMENT CONTINUED

- Clothing: Don’t use, clothing or boots with Gore-Tex® or other synthetic water-resistant and/or stain-resistant materials, Tyvek material, fabric softener *(**Do use** clothing made of cotton preferred)*
- Field documentation: Don’t use waterproof/treated paper or field books, plastic clipboards, water proof markers, Post-its and other adhesive paper products *(**Do use** loose plain paper, metal clipboard, ballpoint pens)*
- Personal care products on day of sample collection: Don’t use cosmetics, moisturizers, hand cream, sunscreen, insect repellent
- Food and beverage: Don’t use Aluminum foil, pre-packaged food, fast food wrappers or containers

# FIELD/EQUIPMENT BLANKS

- When sampling for PFAS, it is recommended that additional and/or more frequent field/equipment blanks be collected prior to and during sampling to check for residual PFAS on sampling equipment due to the potential for cross-contamination issues and the need for very low reporting limits.
- SGS- PFAS free Blank water with certificate of analysis.
- Use Trip Blanks for PFAS as required by some states.

# OTHER NOTES TO CONSIDER WHEN REQUESTING PFAS ANALYSIS

- DoD QSM 5.1 requires isotope dilution instead of internal standards.
- DoD does not recommend TRIZMA for GW samples.
- DoD samples require extra bottles for MS and MSD.
- DW method 537 requires internal standards.
- DW method 537 specifies that the SPE cartridge contains SDVB, some compounds do not extract efficiently such as PFPeA, so an alternate cartridge will be used which is a modification to the method. The State of NH list includes PFPeA.
- DW method 537 requires field reagent blanks. Some states recommend trip blanks. The client must predetermine their field QC requirements.

# SAMPLING MONITORING WELLS

- When feasible, use single-use, disposable polyethylene or silicone materials (tubing, bailers, etc.) for monitoring well purging and sampling.
- When reuse of materials or sampling equipment across multiple sampling locations is necessary, follow project decontamination protocols with allowed materials identified above, and incorporate collection of equipment rinsate blanks into sampling program, as appropriate.
- When using positive displacement/submersible pumps, familiarize yourself with the sampling pump/accessory equipment specifications to confirm that the device components do not contain Teflon® or PTFE.

# PRODUCTION WELL SAMPLING

- If feasible, do not use Teflon® tape or pipe thread paste on pipe fittings or sampling tap threads on the pump discharge pipe.
- As with all other sample parameters, the sample for PFAS should be collected at the last hour (or hours) of the pumping portion of the testing program.
- Discharge water should be purged through the sampling tap on the discharge pipe for a minimum of 20 minutes prior to collection of samples.

# ACTIVE PRODUCTION WELL SAMPLING

- If feasible, avoid contact with any Teflon® tape or pipe thread paste on pipe fittings or sampling tap threads on the water supply discharge pipe.
- The sample for PFAS should be collected while the production well pump is operating, and, preferably, has been operating for at least one hour.
- Discharge water should be purged through the sampling tap on the discharge pipe for a minimum of 20 minutes prior to collection of samples.

# SAMPLE COLLECTION METHOD/SEQUENCE

- Using new nitrile gloves collect the sample for PFAS **first - prior to collecting samples for** any other parameters into other containers; this avoids contact with any other type of sample container, bottles or package materials.
- As with all other samples, do not place the sample bottle cap on any surface when collecting the sample, and avoid all contact with the inside of the sample bottle or its cap.
- When sample is collected and capped, place the sample bottle(s) in an individual sealed plastic bag (e.g. Ziploc®) separate from all other sample parameter bottles, and place in shipping container packed only with ice.

**PFC-free**

# SAMPLE COLLECTION, CONTAINERS & HOLDING TIME


- Samples for soil and ground water collected in 4 oz or 125ml wide-mouth HDPE bottles fitted with unlined polyethylene screw caps.  Shipped on ice.
- Currently no prescribed holding times – default to EPA guidance of 14 days to extract and 40 days to analyze.

- Drinking Water samples collected in 250ml wide-mouth HDPE bottles preserved with Trizma.
- Hold time is 14 days to extract and 28 days to analyze.

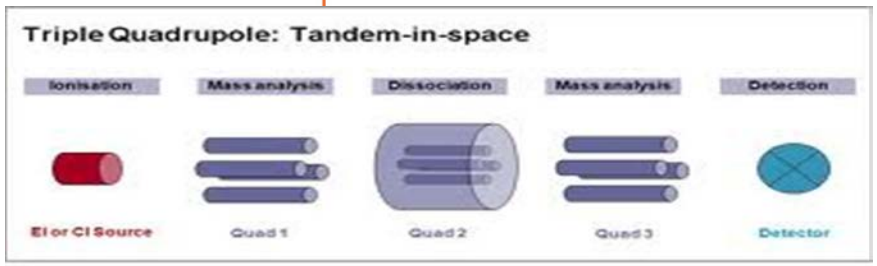
# CONTAINER & PRESERVATIVE REQUIREMENTS

| Sample Type | Container/Preservative | Matrix code on COC | Method | Comments |
|---|---|---|---|---|
| Soil, sediment | 1x 4oz HDPE/none | SO/SED | 537MOD | |
| Groundwater, surface water, water | 2x 125 ml HDPE/none | GW/SW/WW | 537MOD | |
| GW/SW/WW needing lower RLs | 2x 250 ml HDPE/none | GW/SW/WW | 537MOD | |
| Effluent | 2x 125 ml HDPE/TRIZMA | WW or EF | 537MOD | Finished samples may need TRIZMA. TRIZMA is a buffer and removes free chlorine. |
| DW | 2x 250 ml HDPE or PP/TRIZMA | DW | 537 | |
| DW - not for compliance | 2x 250 ml HDPE/TRIZMA | WW | 537MOD | Matrix code DW triggers the lab to use method 537 so samples need to be logged as WW. |

# ANALYSIS AND METHODS


- EPA 537 Drinking Water Method Released 2008
- Other matrices use EPA 537 method modified to include isotope dilution
- ASTM D7968-14 Standard Test Method for Determination of Perfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry
- ASTM D7979-15 Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Waste Water by Liquid Chromatography Tandem Mass Spectrometry
- Various research papers, vendor application notes, and DoD QSM 5.0.
- New methods under development by EPA and DoD for non-drinking water matrices. DoD QSM 5.1.

# ANALYSIS AND METHODS




- **LC/MS/MS** has allowed for more sensitive determination of individual PFASs in soil, water, tissue, and air.
- **LC**: Unlike gas chromatography, which is unsuitable for nonvolatile and thermally fragile molecules, liquid chromatography can separate a very wide range of organic compounds.
- **MS**: Mass spectrometers generate three dimensional data. In addition to signal strength, they generate MS data that can provide valuable information about the molecular weight, structure, identity, quantity, and purity of a sample.

# CHALLENGES

ıblished methods

ɔoratory background

ve and mass labeled

: analytes

ıvailable PT samples

· Regulatory oversite

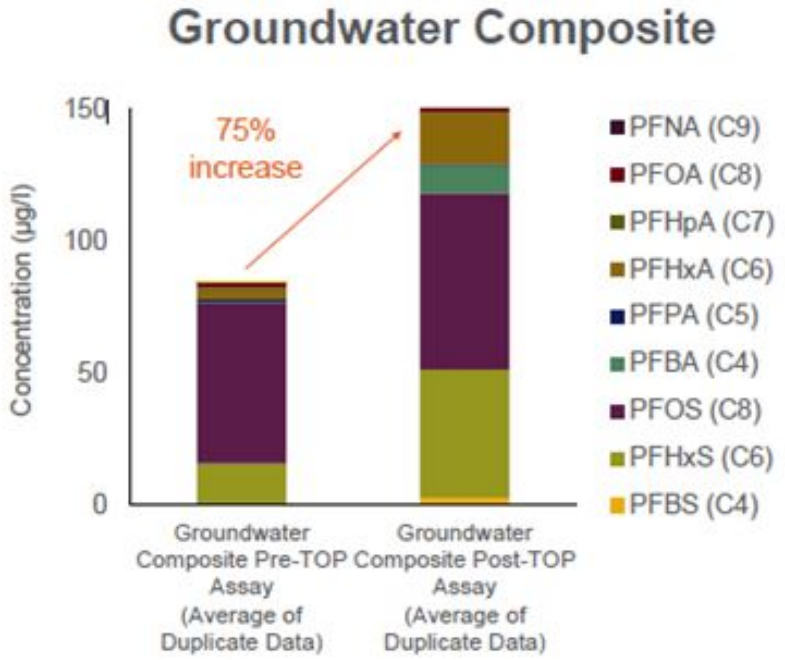
vels

# TOP (Total Oxidisable Precursors) Assay

- Process of transforming PFAS Precursors in a sample to measurable perfluorinated Carboxylic acid which can be measured.
- Sample + persulfate + heat converts precursors to terminal PFCAs and PFSAs
- LC MS/MS analysis without conversion (Before) + conversion (After) + LC MS/MS analysis
- The difference is the converted precursors

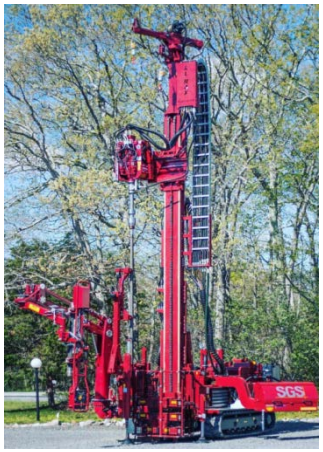
# PRECURSORS MAY CAUSE PROBLEMS LATER

## Total Oxidisable Precursor (TOP) Assay




- Significant increases in perfluorinated carboxylic acids and sulphonic acids (PFAAs) following TOP assay reveal the hidden mass of PFAA precursors present
  - An additional 240% of PFAS in soils and 75% in groundwater
- Demonstrates matrices impacted with AFFF contain a greater mass of PFAS than identified by conventional analysis with LC-MS/MS (EPA Method 537).

# FIELD TEAM EQUIPMENT CLEANLINESS




- If it supports your PFAS project, we've tested it.
  - Support Truck Water Tanks
  - Rig Tender Water Tanks
  - Consumables (Macroliners, PVC)
  - Thread Lubricant
  - Auger Flights
  - Drill Rod
  - Drill Bits & Hammers
  - Dual Rotary Casing

**PFC-free**

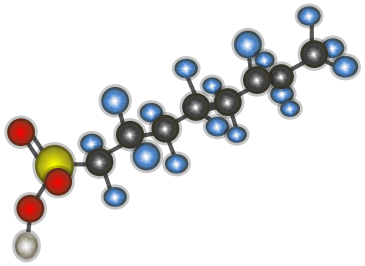
# WHERE - SGS PFAS BY FACILITY


- **SGS Orlando, FL**
  - Full Service Regulatory Analysis
  - PFAS in Drinking Water, Water and Solids by internal standard
  - PFAS in Water and Solids by isotope dilution (ID)D / NELAP / ISO 17025 accredited (add state accreditations for DW, NPW, Solids where available)
- **SGS Wilmington, NC**
  - HRMS Specialty (Dioxin/Furans, PCB Congeners, HRMS PAHs) + PFAS
  - Serve Source Evaluation, Con. Sites, NPDES
  - PFAS in Drinking Water, Water and Solids by internal standard (non-ID)
  - DoD / NELAP / ISO 17025 accredited

# WHERE - SGS PFAS BY FACILITY


- **SGS AXYS, Victoria, BC**
  - HRMS , LC/MS/MS, GC/MS ultra-trace only, all matrices excluding DW
  - PFAS in Water, Solids, Tissue, Serum, Method Development (multiple target analyte methods).
- **SGS West Creek, NJ**
  - North American Environmental Drilling Division
    - United States
    - Virgin Islands
  - Sampling for PFAS in Drinking Water, Water and Solids
  - PFC/PFAS Free

# CONTACT INFORMATION



**THANK YOU!**

Beth Proffitt

1741 W. University Dr., Suite 149

Tempe, AZ  85281

(480) 275-8931

**BETH PROFFITT**
Business Development Manager, Tempe Service Center
SGS North America Inc. – Tempe
1741 W. University Drive, Suite 149
Tempe, AZ 85281

Office: 480.275.8931
Mobile: 602.501.5673
Elizabeth.proffitt@sgs.com



- Beth Proffitt works for SGS North America Inc., in the Environmental Health and Safety Division (EHS).
- Within the EHS Department there are six environmental laboratories in the US.
- She graduated from Georgia State University with a BS in Biology and a minor in Chemistry.
- She has been working in environmental laboratories in Arizona since 1985, (a couple years).
- She has held every job in the business from Dishwasher to Project Manager, Lab Manager and now Business Development Manager.
- She opened the SGS service center in Tempe in 2011.
- Ms. Proffitt will be presenting: The Do's and Don'ts of PFAS Testing / Guide to PFAS-free sampling in the place of Dr. Harry Behzadi, so be gentle!