PFAS (SYNTHETIC FLUORINATED CHEMICALS) OVERVIEW

August 2017

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WHEN YOU NEED TO BE SURE

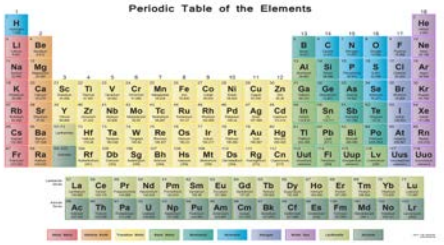
SGS

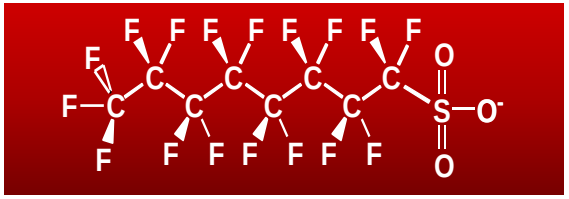
EMERGING CONTAMINANT

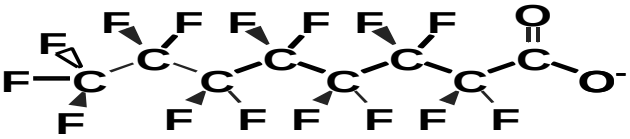
- Can be broadly defined as any synthetic or naturally occurring chemical or any microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and(or) human health effects.
- The United States Environmental 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.

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), also referred to Perfluorinated Chemicals (PFCs)
- 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 in the synthetic or extraction of another compound.

WHERE ARE THEY USED?

- 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 of microwave popcorn bags)
- AFFF – fighting fires
- Wiring and semi-conductors in electronic and aerospace industry
- Chrome plating (acid mist suppression)
- Personal Care Products

AFFF FOAMS

- Aqueous Film Forming Foams used in fire suppression contained PFOS and FTS based AFFF – Sites with years of use, e.g. military and airports affected.
- Also contain non fluorinated hydrocarbon surfactants 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

WHY ARE THEY A CONCERN?

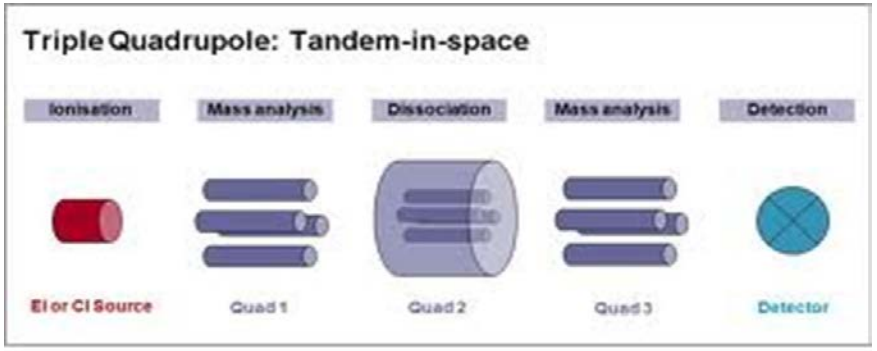
- PFOA and PFOS were produced in the largest amounts in the United States
- They are persistent and resistant to typical environmental degradation processes. As a result they are found in soil, air, groundwater and human blood samples world wide.
- Human Health Effects associated with PFAS in general 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)

POTENTIAL PFOS MARKET SITES

- Former Fluorochemical manufacturing facilities
- Water quality facilities – including desalination and water reuse
- U.S. Department of Defense installations
- AFFF training facilities
- Consumer product testing
- Wastewater treatment
- Sediment dredging
- Municipal airports
- Refineries and Petroleum Storage facilities

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.



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.

CHANGING REGULATORY LIMITS

- Health-based advisories for PFOA and PFOS have been developed by EPA and several state agencies
- 2013-2015 EPA conducts the third Unregulated Contaminants Monitoring Rule (UCMR3) study. Six analytes were monitored at the lists Reporting Limits.
  - PFBS 90 ng/L, PFHxS 40 ng/L, PFOS 30 ng/L
  - PFHpA 40 ng/L, PFOA 20 ng/L, PFNA 20 ng/L
- State reporting levels for drinking water to 1-20 ng/L dependant on state.
  - RLs 1-5 ng/l applied “across the board” to all PFCAs and PFSAs (NH, VT, MN)
  - RLs 2 ng/l for PFOA/PFOS in DW for NY
  - Soil Criteria, existing in AK, TX, MN, by QAPP in other states.

CHANGING REGULATORY LIMITS

- EPA HEALTH ADVISORY LIMITS

for PFOS 200 ng/l
for PFOA 400 ng/l

for PFOS 70 ng/l
for PFOA 70 ng/l
PFOA + PFOS 70 ng/l

vel for PFOA 40 ng/l

vel for PFOA 14 ng/l and PFNA
ng/l?

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.
- Sample for Drinking Water collected in 250ml wide-mouth HDPE bottles preserved with Trizma.
- Hold time is 14 days to extract and 28 days to analyze.
- All Teflon should be avoided – sampler must avoid aluminum foil, blue ice, pre-wrapped foods or snacks and no Post-It notes

CERTIFICATE OF ANALYSIS

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

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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*:**

- Don't use: Pumps and Tubing that contain 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 or Acetate Hydrasleeves)*
- Don't use: Detergents such as Decon 90 *(**Do Use:** Alconox® or Liquinox®, potable/bottled water followed by deionized PFAS-free water rinse)*
- Don't use: LDPE or glass bottles, Teflon™-lined caps, and chemical ice packs (i.e., Blue Ice®) for storage *(**Do Use:** HDPE or polypropylene containers with HDPE or polypropylene caps and regular ice in Zip-loc bags)*

SAMPLING EQUIPMENT:

- Don't use: Clothing or boots made with Gore-Tex® or other synthetic water-resistant and/or stain-resistant materials, Tyvek material, fabric softener. PPE may become and issue.
- *Do Use: Cotton Clothing and old style rubberized rain gear.*
- Don't use: Waterproof or treated paper and field books, plastic clipboards, Sharpie® markers, Post-its and other adhesive paper products
- *Do Use: Loose leaf paper, metal clipboard, ballpoint pens*
- Don't use: Personal care products on day of sample collection: cosmetics, moisturizers, hand cream, sunscreen, insect repellants and other related products
- *Do Use:* Natural products for sunscreen and insect repelants
- Don't use: Aluminum foil, pre-packaged food, or items in fast food wrappers or containers

MONITORING WELL SAMPLING

- When feasible, use single-use, disposable polyethylene or silicone materials (tubing, bailers, etc.) for monitoring well purging and sampling equipment.
- 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 pump sampling equipment, familiarize yourself with the sampling pump/accessory equipment specifications to confirm that device components are not made of Teflon® or PTFE.

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 any 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.

LAB CONCERNS

Minimizing Background

- Sample Prep
  - No Teflon components in SPE Extraction Manifold
  - HDPE Sample Reservoirs
  - New components leached and methanol rinsed
  - Separate prep equipment for suspected high concentration samples
  - DI water routinely tested
  - Change Gloves frequently

- Instrumentation
  - Teflon solvent lines replaced with PEEK tubing
  - Solvent frits replaced with glass
  - Vespel Components replaced with PEEK or other material
  - Agilent developed an HPLC kit designed to minimize PFAS background
  - Isolator Columns
  - Polypropylene vials and caps used
    - Can not re-inject
    - Do not reseal

STANDARDS

- Lack of certified reference material.
  - Sy
  - Im
  - Ma ailable for every analyte
  - So n one vendor
  - Br
    - linear isomers only
    - s in up to 30% branched isomer
- DoD b to develop custom mixes.
  - 24
  - 17 dilution mix
  - 2-5 ards

CHALLENGES

ıblished methods

ɔoratory background

ve and mass labeled

: analytes

ıvailable PT samples

· Regulatory oversite

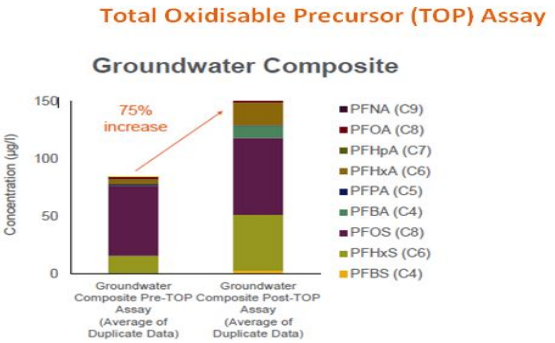
vels

PFAS – GENERAL MARKET TRENDS & DEMAND

- Large overall market increase
- Non-DW based methods
  - EPA, DoD, ISO 17025
  - All expected in next 12 months
  - Multi-matrix, isotope dilution, expansion of analyte lists
  - Lower RLs
- Regulatory Limits
  - Lower detection limits at state level (1-5 ng/L)
  - More compounds added
  - More matrices added
- Multiple Tier choice of products needed
  - Short list, fast and inexpensive (site assessment, DW)
  - Longer lists, low DLs/ blanks, high identification (risk assessment, damages, fish advisories)
  - Variation in client needs
- Screening Tools
  - TOP

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
- Delta is converted precursors



- 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).

EXPANDING ANALYTE LIST

Analyte	Synonym	CAS #	Report Lists								Certs	
			PFOA PFOS	UCMR3 List	EPA 537 List	TEXAS TCEQ List	AFCEE PFAS23	HOOSICK PFAS24	AFCEE PFAS25	QSM 5.1 "List"	DOD ELAP	FL NELAC
PERFLUOROALKYLCARBOXYLIC ACIDS												
Perfluorobutanoic acid	PFBA	375-22-4				X	X	X	X	X	X	X
Perfluoropentanoic acid	PFPeA	2706-90-3				X	X	X	X	X	X	X
Perfluorohexanoic acid	PFHxA	307-24-4			X	X	X	X	X	X	X	X
Perfluoroheptanoic acid	PFHpA	375-85-9		X	X	X	X	X	X	X	X	X
Perfluorooctanoic acid	PFOA	335-67-1	X	X	X	X	X	X	X	X	X	X
Perfluorononanoic acid	PFNA	375-95-1		X	X	X	X	X	X	X	X	X
Perfluorodecanoic acid	PFDA	335-76-2			X	X	X	X	X	X	X	X
Perfluoroundecanoic acid	PFUnDA or PFUnA	2058-94-8			X	X	X	X	X	X	X	X
Perfluorododecanoic acid	PFDoDA or PFDoA	307-55-1			X	X	X	X	X	X	X	X
Perfluorotridecanoic acid	PFTrDA	72629-94-8			X	X	X	X	X	X	X	X
Perfluorotetradecanoic acid	PFTeDA	376-06-7			X	X	X	X	X	X	X	X
Perfluorohexadecanoic acid	PFHxDA	67905-19-5						X				
Perfluorooctadecanoic acid	PFOcDA	16517-11-6						X				
PERFLUOROALKYLSULFONATES												
Perfluorobutanesulfonic acid	PFBS	375-73-5		X	X	X	X	X	X	X	X	X
Perfluoropentanesulfonic acid	PFPeS	2706-91-4								X		
Perfluorohexanesulfonic acid	PFHxS	355-46-4		X	X	X	X	X	X	X	X	X
Perfluoroheptanesulfonic acid	PFHpS	375-92-8					X	X	X	X	X	X
Perfluorooctanesulfonic acid	PFOS	1763-23-1	X	X	X	X	X	X	X	X	X	X
Perfluorononanesulfonic acid	PFNS	474511-07-4								X		
Perfluorodecanesulfonic acid	PFDS	335-77-3				X	X	X	X	X	X	X
PERFLUOROOCTANESULFONAMIDES												
Perfluorooctane sulfonamide	FOSA or PFOSA	754-91-6				X	X		X	X	X	X
N-Methyl perfluorooctane sulfonamide	N-MeFOSA	31506-32-8					X	X	X		X	X
N-Ethyl perfluorooctane sulfonamide	N-EtFOSA	4151-50-2					X	X	X		X	X
PERFLUOROOCTANESULFONAMIDOACETIC ACIDS												
Perfluoro-1-octanesulfonamidoacetic acid	FOSAA	2806-24-8									X	
N-Methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9			X				X	X	X	X
N-Ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6			X				X	X	X	X
PERFLUOROOCTANESULFONAMIDOETHANOLS												
N-Methyl perfluorooctane sulfonamidoethanol	N-MeFOSE	24448-09-7					X	X	X		X	X
N-Ethyl perfluorooctane sulfonamidoethanol	N-EtFOSE	1691-99-2					X	X	X		X	X
FLOUROTELOMER SULFONATES												
4:2 Fluorotelomer sulfonate	4:2 FTS	757124-72-4								X		
6:2 Fluorotelomer sulfonate	6:2 FTS	27619-97-2					X	X	X	X	X	X
8:2 Fluorotelomer sulfonate	8:2 FTS	39108-34-4					X	X	X	X	X	X