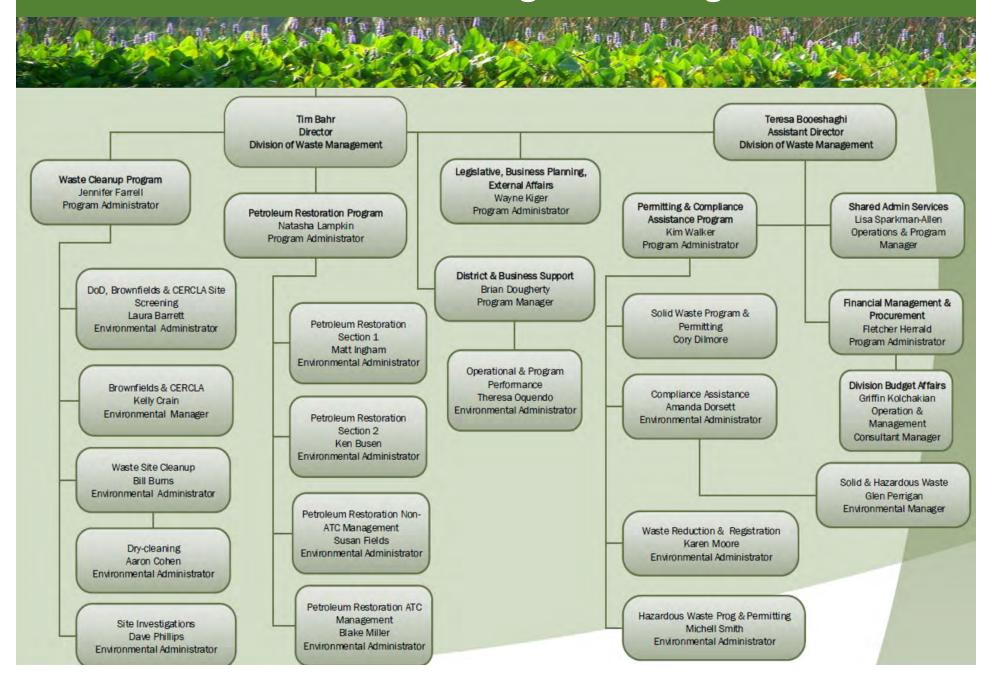


### Division of Waste Management Organization



### Division of Waste Management PFAS Efforts

- Development of Provisional Cleanup Target and Screening Levels
- Unregulated Contaminant Monitoring Rule 3 (UCMR3)
- Certified Fire Training Facilities
- Drycleaning Solvent Cleanup Program Sites
- State Cleanup Program Sites
- Department Of Defense Sites

# Provisional Cleanup Target Levels

### **Provisional Groundwater Cleanup Target Levels (PGCTL)**

- PFOA: 70 ppt (0.07 ug/L)
- PFOS: 70 ppt (0.07 ug/L)
- PFOA + PFOS: 70 ppt (0.07 ug/L)

Developed using non-cancer GCTL equation in 62-777, F.A.C.. Assumptions consistent with EPA calculation of Health Advisory Level (HAL).

# Provisional Cleanup Target Levels

### **Provisional Soil Cleanup Target Levels (PSCTL)**

- PFOA: 1.3 mg/kg residential, 25 mg/kg commercial/industrial, 0.002 mg/kg leachability
- PFOS: 1.3 mg/kg residential, 25 mg/kg commercial/industrial, 0.007 mg/kg leachability

Developed using non-cancer GCTL equation in 62-777, F.A.C., chemical specific properties and reference dose developed by EPA in their 2016 HAL calculation.



### **Irrigation Well Screening Levels (IWSL)**

Chemical	Residential (ug/L)	Industrial (ug/L)
PFOA	6.7	750
PFOS	72	370

Derived using the irrigation water equations developed by the University of Florida in the January 14, 2009 IWSL letter. Uses updated assumptions from the 2011 Exposure Factors Handbook and an oral RfD of 2E-05mg/kg-d.



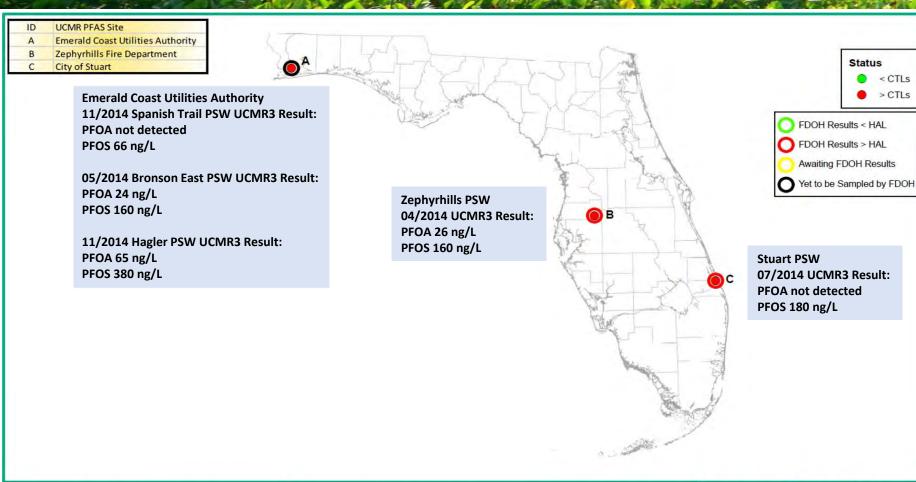
### **DRAFT** Surface Water Screening Levels

- For the protection of human health, surface water screening levels for the consumption of freshwater and estuarine finfish and shellfish include:
  - 0.150 ug/L for PFOA
  - 0.004 ug/L for PFOS

Developed in consultation with the Division of Environmental Assessment and Restoration.

### **UCMR3**





Florida UCMR 3 PFAS Sites Assessment Results With Associated Florida Department of Health Community Well Survey Sample Results As of August 29, 2019 UCMR: Third Unregulated Contaminant Monitoring Rule (2012)

PFAS: Per- and polyfluoroalkyl substances

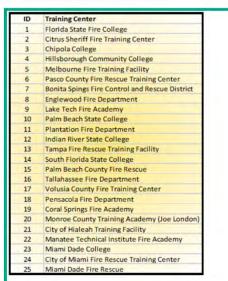
CTL: Cleanup Target Level HAL: Health Advisory Level FDOH: Florida Department of Health

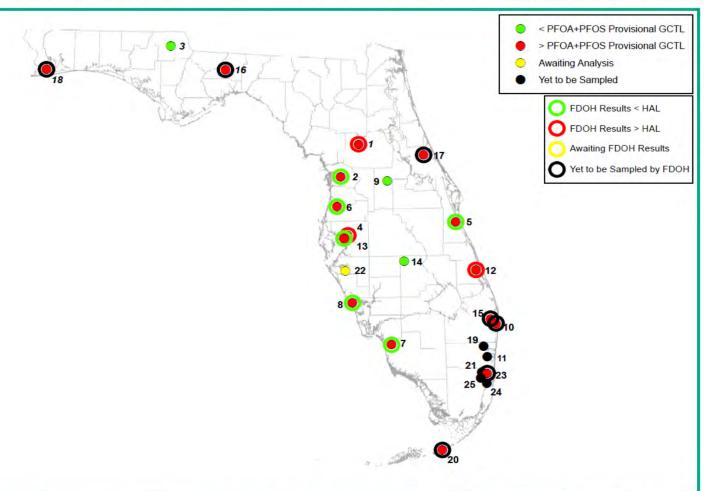




### Certified Fire Training Facilities







Florida Fire Training Facilities PFAS Assessment Results With Associated Florida Department of Health Community Well Survey Sample Results As of October 23, 2019 Facilities are listed in order of priority to be addressed

PFAS: Per- and polyfluoroalkyl substances

PFOA: Perfluorooctanoic acid PFOS: Perfluorooctanesulfonic acid

ng/L: nanograms per Liter

GCTL: Provisional Groundwater Cleanup Target Level

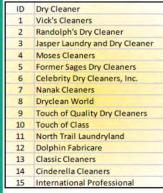
HAL: Health Advisory Level FDOH: Florida Department of Health

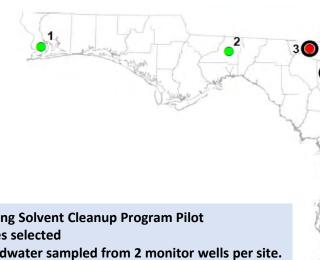




### Drycleaning Solvent Cleanup Program Pilot









Yet to be Sampled by FDOH

#### **Drycleaning Solvent Cleanup Program Pilot**

- 15 sites selected
- Groundwater sampled from 2 monitor wells per site.
  - source area location
  - · long history of monitoring
- 9 sites > Provisional GCTL
- DOH assisting with private well surveys.



Florida Drycleaning Solvent Cleanup Program PFAS Sample Results With Associated Florida Department of Health Community Well Survey Sample Results As of October 17, 2019 Florida Department of Environmental Protection PFAS: Per- and polyfluoroalkyl substances

PFOA: Perfluorooctanoic acid PFOS: Perfluorooctanesulfonic acid CTL: Provisional Cleanup Target Level HAL: Health Advisory Level FDOH: Florida Department of Health

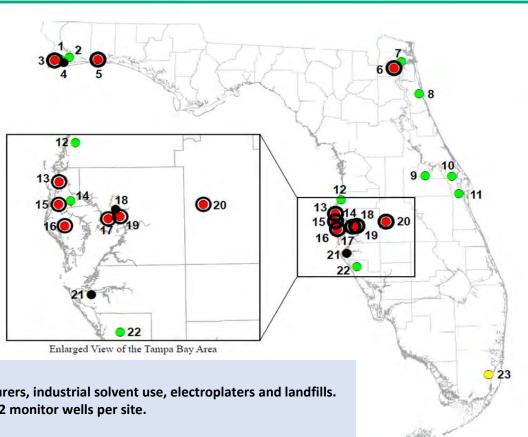




### State Lead Cleanup Sites



Lakeland Tanning Site Tortuga, Inc. 22 Spindrift Whogas, Inc. 23 Upsilon Davis



#### 23 State Lead Sites

- · Includes chemical manufacturers, industrial solvent use, electroplaters and landfills.
- Groundwater sampled from 2 monitor wells per site.
- 10 sites > Provisional GCTL
- · DOH assisting with private well surveys.

Florida State Lead Sites PFAS Sample Results With Associated Florida Department of Health Community Well Survey Sample Results As of August 29, 2019

PFAS: Per- and polyfluoroalkyl substances PFOA: Perfluorooctanoic acid PFOS: Perfluorooctanesulfonic acid CTL: Cleanup Target Level HAL: Health Advisory Level FDOH: Florida Department of Health





< PFOA+PFOS CTL

> PFOA+PFOS CTL

**Awaiting Analysis** 

Not Sampled

FDOH Results < HAL

Awaiting FDOH Results

Yet to be Sampled by FDOH

FDOH Results > HAL

### PFAS at Federal Facilities

**Air Force:** 9 bases with PFAS onsite above HAL/PGCTL and/or PSCTL. No Off-Base sampling performed.

**Air Force BRAC:** 1 former base with PFAS in onsite soil.

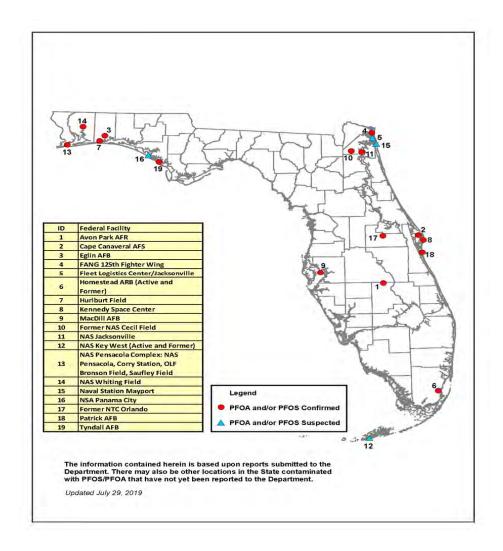
**Navy:** 5 bases/outlying Fields with PFAS onsite above HAL/PGCTL and/or PSCTL. 2 bases have offsite private well impacts above HAL/PGCTL.

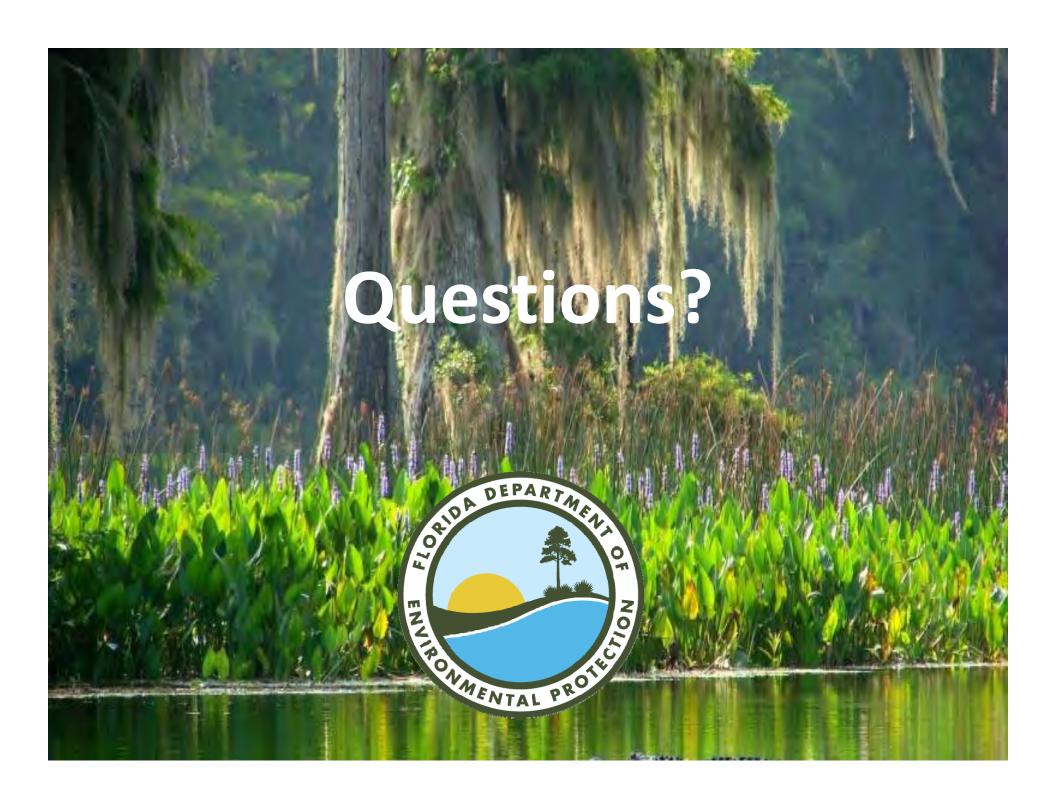
**Navy BRAC:** 2 former bases with PFAS in onsite groundwater above HAL/PGCTL. No offsite samples above HAL/PGCTLs to date.

NASA: Confirmed PFAS onsite above HAL/PGCTL. Investigations ongoing. National Guard: Investigations ongoing.

No information provided to the

Department yet.





### Perfluoroalkyl Substances (PFAS) Human Health Considerations



Dr. Christopher M. Teaf

Center for Biomedical & Toxicological Research
Florida State University

Hazardous Substance & Waste Management Research
Tallahassee, FL



Air & Waste Management Association Tallahassee, FL October 2019



### Reported Health Effects

### Noncancer

- Increased serum cholesterol, liver enzymes/weight, uric acid
- Delayed mammary gland development; decreased immune response, delayed skeletal ossification (*used for proposed RfD*); potential reduced fetal growth from prenatal exposure
- Potential immune hazard to humans
- Effects often extrapolated from high dose animal studies

### > Cancer

- Not genotoxic
- Animals liver, testes, mammary glands, pancreas
- Humans suggested links to testicular, kidney, thyroid
- IARC Group 2B; possibly carcinogenic
- EPA not classified as to carcinogenicity; "suggestive"
- USEPA SAB (2006) "likely", not updated

### **C8 Panel Studies**

- Exposure, health studies 2005-2013 Ohio Valley communities
- Concluded "probable link" to C8 exposure
  - √ high cholesterol
  - √ ulcerative colitis
  - √ thyroid disease
  - ✓ cancer (testicular, kidney)
  - ✓ pregnancy-induced hypertension
- Inconsistencies in the studies and newer epidemiology

### ... PFAS Criteria Chaos Ensues

- > Several states have developed their own drinking water criteria for PFOA and PFOS, and some have developed criteria for other PFAS as well.
- > Resultant numbers reflect different conclusions:
  - ✓ critical effect upon which to derive a safe dose
  - √ how study data should be interpreted
  - ✓ how animal data should be extrapolated to humans
  - ✓ what drinking water ingestion rate to use
  - ✓ what relative source contribution value to use, etc.
- > As a result, little consistency for state drinking water limits

### Florida DEP Health-based Criteria

#### Provisional GCTL

- 70 parts per trillion (0.070 ppb), equal to EPA Health Advisory
- evaluated as individual or sum of PFOA + PFOS
- basis developmental (RfD of 0.00002 mg/kg•day)

#### Alternate SCTL

- PFOA 1.3 mg/kg Res; 25 mg/kg Comm/Ind; 0.002 mg/kg Leach
- PFOS 1.3 mg/kg Res; 25 mg/kg Comm/Ind; 0.007 mg/kg Leach

### Provisional Irrigation Screening Levels

- PFOA 6.7 ug/L Res; 750 ug/L Comm/Ind
- PFOS 72 ug/L Res; 370 ug/L Comm/Ind

### Draft Surface Water Screening Levels

PFOA 0.150 ug/L; PFOS 0.0004 ug/L (fish/shellfish)

### **Examples of Other State PFOA Levels**

Alaska	400 ppt
Maine	70 ppt
Minnesota	35 ppt
New Hampshire	38 ppt
New Jersey	14 ppt
Texas	290 ppt
Vermont	20 ppt

Thanks to Dr. Leah Stuchal, UF

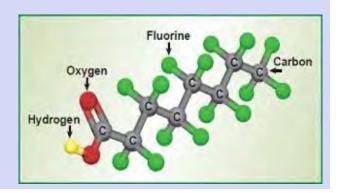
### **PFAS Exposure Assessment Issues**

- Exposure found in blood of nearly all people tested
- Bioaccumulative but levels of blood PFOA decreasing
- Drinking water exposure often localized
- PFOA in water often linked to industrial sites, fire training areas, landfills, WTPs, home septic systems
- Attention will need to be paid to association vs causation as the toxicology moves forward



### **PFAS Summary**

- Persistent; exposure not uncommon
- Diverse pharmacodynamic, toxicity profiles in animals
- Human epidemiology studies inconclusive
- Risk assessment uncertain, reflected in agency guidance
- Multidisciplinary efforts evaluate new evidence
- Additional questions remain with shorter chain PFAS



# Per- and Polyfluoroalkyl Substances (PFAS) Site Investigations and Lessons Learned

Eric Sager, P.G. Clearwater, Florida Geosyntec consultants







Florida Chapter AWMA Conference FDEP Division of Waste Management Updates and Emerging Contaminants October 30, 2019

### PFAS Site Investigations

- Prepared Investigation Work Plans for airports in California
- Conducted site investigations at a large Federal facility (over 650 samples and 150 locations) and 14 other AFFF-use facilities in Florida
- Prepared PFAS-specific SOPS

















### Scopes of Work

- Reviewed aerial photos, site documents, and current/historical investigations, including NTSB's Aircraft Accident Reports
- Completed site visits and interviewed people with historical knowledge
- Prepared Work Plans with figures and tables summarizing areas of investigations, sample locations, depths and rationale
- Collected samples from multiple media
  - Supply wells (evaluate potential exposure and deconwater source)
  - Direct push technology and monitoring well groundwater sampling
  - Surface water sampling
  - Sediment sampling
  - Soil sampling









### Geosyntec D consultants

### Sources Investigated









### Geosyntec consultants

### Sources Investigated









### Field Planning/Readiness = Informed Staff

- Geosyntec and subcontractors
- Staff that can make real-time decision and ask informed questions
- Lead to identification of AFFF-use site









### Why PFAS-Specific SOP?

- Avoid cross-contamination, false positive results
  - PFAS potentially present in variety of commonly-used materials
  - Low method detection limits (low to sub ng/L)
- Current sampling guidance reflect abundance of precaution, rather than scientific findings
  - Guidance varies state by state, still in infancy
  - Rapid changes to state of knowledge, state and federal guidance and regulations







### Geosyntec consultants

### PFAS Considerations – Sampling Materials

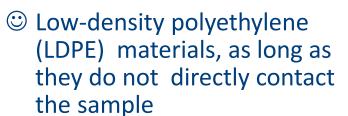
### Try to avoid

- ⇔ Polytetrafluoroethylene (PFTE)
- ⊗ Viton™ (i.e., fluoroelastomers)
- Stain- or water-resistant materials, as these are typically fluoropolymerbased
- (3) "Fluoro" materials
  - Fluorinated ethylene propylene (FEP)
  - Ethylene tetrafluoroethylene (ETFE)
  - Polyvinylidene fluoride (PVDF)
- DPE in direct contact with the sample



#### Safe to use

High-density polyethylene (HDPE), silicone, acetate, stainless steel



- For example, PFAS can sorb to porous LDPE tubing
- ❖ If an item cannot be easily avoided, use QA/QC samples to confirm no cross-contamination (e.g., field blanks)













### Geosyntec D

### PFAS Considerations - Sample Bottles, Packaging and Shipping

Safe to Use	Try to Avoid	Why?
HDPE containers and screw caps	Glass sample containers	PFAS adherence to glass surfaces
Sample preservative (e.g., Trizma®)		Used to remove free chlorine in drinking water method 537
Sample container labels, shipping and handling labels, chain of custody record		
LDPE (e.g., Ziploc®) bags	Aluminum foil (sometimes used for fish tissue samples)	PFAS can be used as a protective non-stick layer on aluminum foil
Regular (wet) ice	Chemical (e.g., blue) ice packs, unless it is in a sealed bag	Potential to be contaminated from previous field events
Hard-shell coolers, bubble wrap, duct tape, packing tape		







### Geosyntec<sup>D</sup>

### PFAS Considerations – Field Personnel

### **Try to Avoid**

- X Water or stain-resistant boots and clothing
- X Clothing recently laundered with a fabric softener
- X Coated HDPE suits
- X Latex gloves
- X Sunscreen and insect repellants containing fluorinated compounds as ingredients, such as polyfluoroalkyl phosphate esters
- X Cosmetics, moisturizers, hand cream, and other related products which may contain PFAS
- X Food wrapper and packaging









### Safe to Use

- ✓ Boots made of polyurethane, polyvinyl chloride (PVC), rubber, or untreated leather
- ✓ Other field boots covered by PFAS-free (e.g., polypropylene) over-boots
- ✓ Rain gear made of polyurethane, PVC, wax-coated, vinyl or rubber
- ✓ Clothing made of synthetic (e.g. polyester) or natural (e.g. cotton) fibers
- ✓ PPE (safety glasses, reflective vests, hardhats, disposable powder-free nitrile gloves
- ✓ Uncoated HDPE suits
- ✓ Sunscreen and insect repellant tested and found to be PFAS free
- ✓ Bottled water and hydration drinks

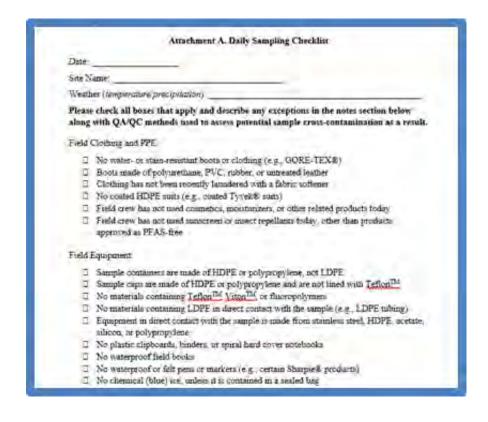


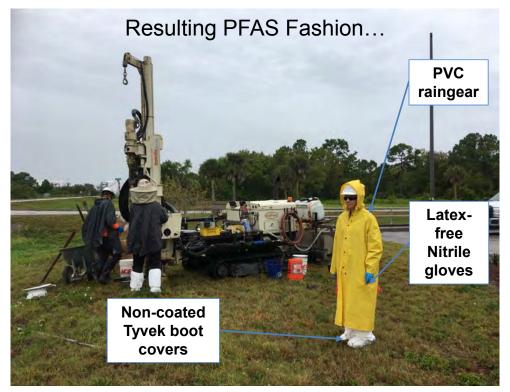




### Geosyntec D

### PFAS Considerations – Field Personnel











### Geosyntec consultants

### Importance of QA/QC Samples

	Sample Type	Purpose	Ratio
QA/QC	Field duplicates (water)	Assess field and analytical precision, sample heterogeneity	1:10
	Equipment blanks	Confirm decontaminated equipment is PFAS-free	1:10
	Field blanks	Assess ambient contamination within the field and laboratory	
	Matrix spike/matrix spike duplicates	Assess interferences caused by the sample matrix (DoD only)	1:20
	Temperature blanks	Cooler temperature	1 per cooler







### Other Considerations - Decon Water Sources: Pros and Cons

Geosyntec Consultants

- Laboratory-certified PFAS-free water
  - Known source
  - Small volume and expensive
- On-site water source
  - Large volumes and least expensive
  - Potential PFAS detections and client sensitivities
- Drilling subcontractor and/or Geosyntec office water source
  - Large volumes and less expensive
  - Potential PFAS detections















Bucket decon procedure



Centrally-located decon pit with

pressure washing



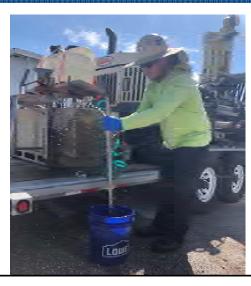








Sample	PFOA	PFOS	PFBS	PFHXS
Initial Sample	3500	2300	4100	33000
Before decontamination	13	1.4 U	59	4.1
After 1st rinse with pressure washer	1.3 U	1.3 U	2.6 U	1.3 U
After liquinox scrub and 2nd rinse	1.3 U	1.3 U	2.5 U	1.3 U
After final rinse	1.3 U	1.3 U	2.6 U	1.3 U



3. Final rinse through vertical screen







#### Other Considerations – Investigation Derived Waste

- Cradle-to-grave liabilities
  - Landfill leachate
  - "Treated" aqueous discharge
  - Biosolids
- Landfills and water treatment facilities beginning to refuse waste derived from PFAS/AFFF sources









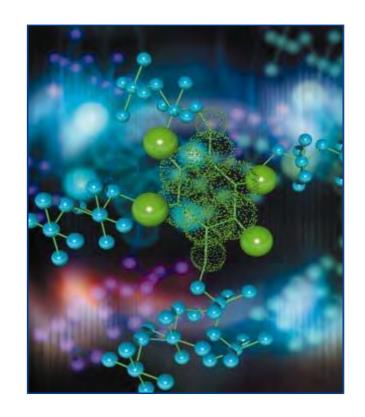




#### Geosyntec oconsultants

#### **Contact Information**

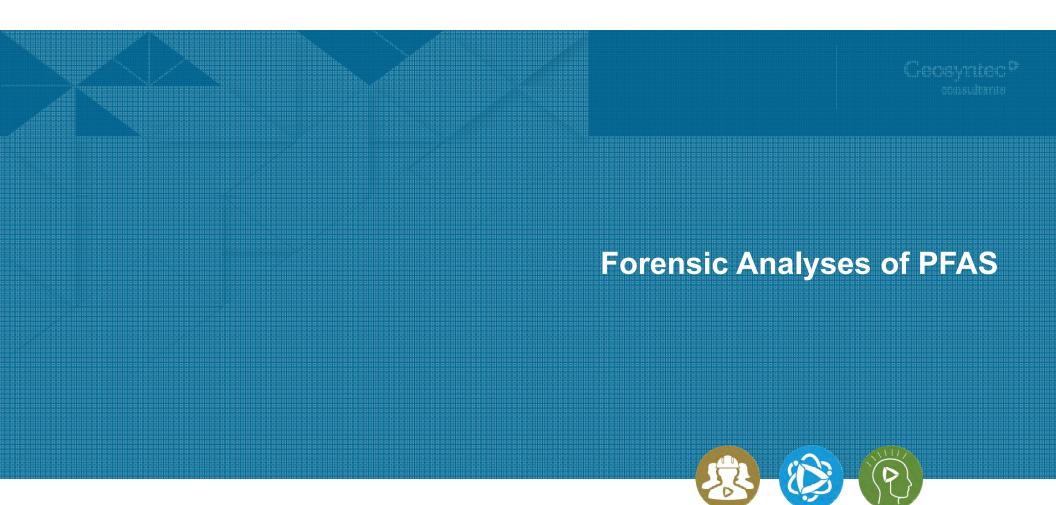
Eric Sager, P.G.
Principal Geologist
Phone: 727.330.9952
esager@geosyntec.com

















#### Who's PFAS Is It?

- Numerous potential PFAS sources
- Forensics is a means of limiting liability
- PFAS liabilities can be intimidatingly large
- Multiple forensic tools applicable









#### **PFAS Forensic Tools**

#### Multiple potential forensic tools available. The science is still emerging!

#### Forensic Tools for Multiple Compounds

- Chemical fingerprinting
- Ratio comparisons
- Multivariate analysis
- Fate and transport properties



- Isomer comparison
- Application of specialized analyses like TOP Assay









#### Geosyntec<sup>b</sup> consultants

#### PFAS Forensic Tools: AFFF

- Multiple AFFFs likely used at most sites (3M, National Foam, Ansul, Angus, Buckeye, Fire Service Plus)
- Two AFFF manufacturing methods
  - $3M \rightarrow PFOS$  and homologues (PFSAs), both branched and linear isomers
  - All others  $\rightarrow$  PFOA and homologues (PFCAs), fluorotelomer alcohols (e.g. 6:2 FTOH), polyfluorinated compounds, no PFOS, only linear PFAS
- Unique differences (chain lengths, abundance of surfactants, intermediates, side products)











# **Environment Testing TestAmerica**

# PFAS: An Introduction to the Chemistry and Analysis



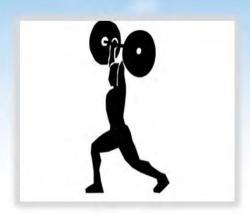
Presented by: Taryn McKnight, Product Manager Eurofins TestAmerica



### What are PFAS?

Synthetic compounds formed from carbon chains with fluorine atoms attached

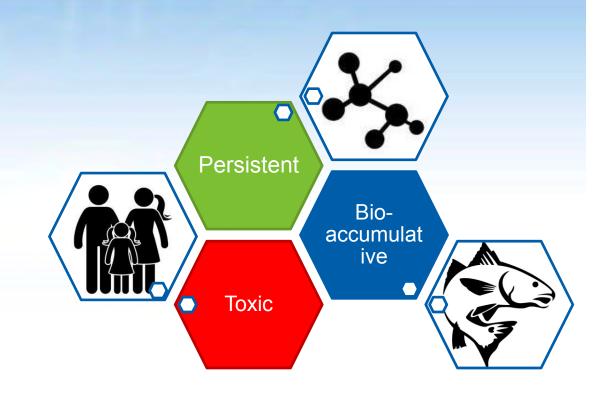




The C-F bond is one of the shortest and strongest in nature

**Environment Testing** 

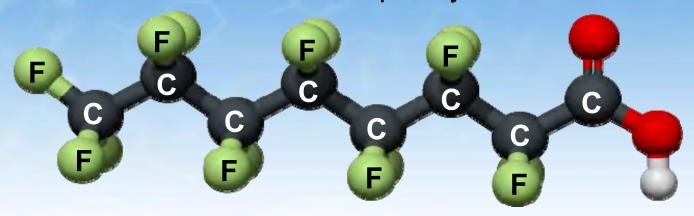
**TestAmerica** 



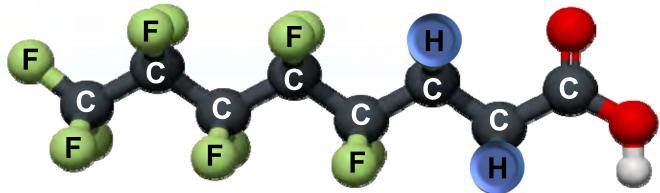


# Per and Poly?

Perfluorinated = Completely Fluorinated

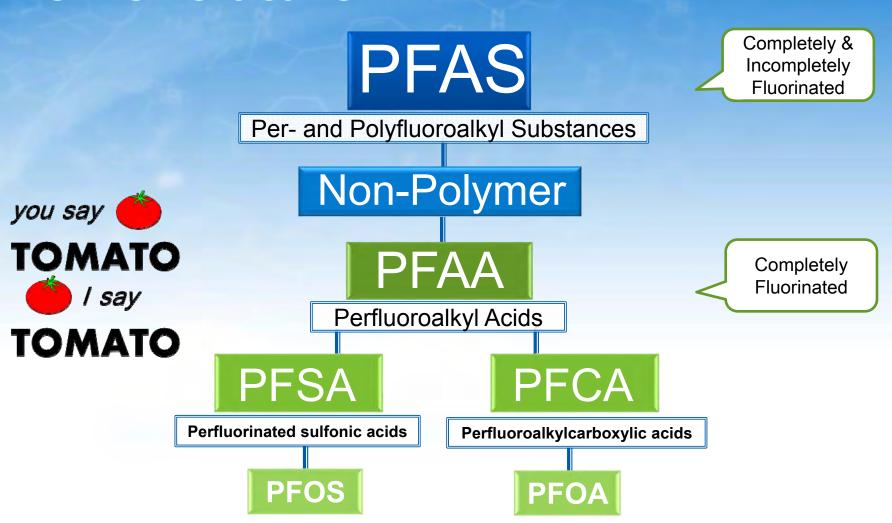


Polyfluorinated = Incompletely Fluorinated





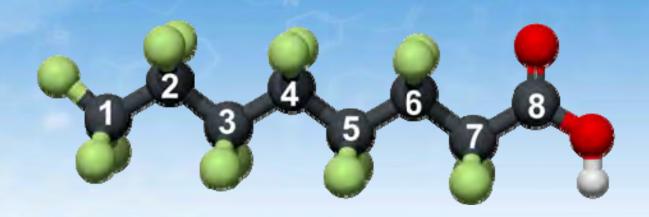
## Nomenclature





**Environment Testing TestAmerica** 

## **Carbon Chain Nomenclature**



Acronym	Compound Name	Chain Length
PFDA	Perfluoro <u>deca</u> noic acid	C10
PFOA	Perfluoro <u>octa</u> noic acid	C8
PFHxS	Perfluoro <u>hexa</u> nesulfonic acid	C6

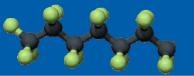


#### **Chemical Structure**

Chain Length

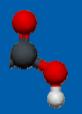
- ≥8 carbon atom PFCAs
- ≥6 carbon atom PFSAs

Carbon backbone



 Inert, Persistent & Bioaccumulative

Functional Group



Our ability to capitalize on the desirable qualities



# **Surfactant Properties**

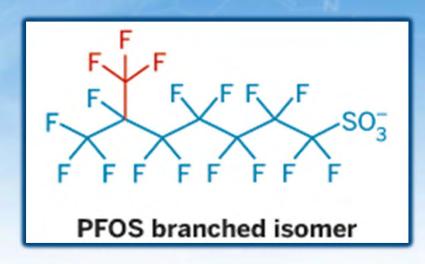
Fluorocarbon "Tail" = Hydrophobic and Oleophobic

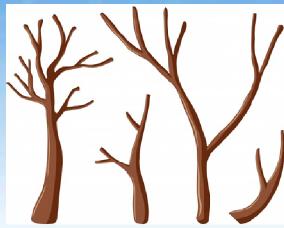


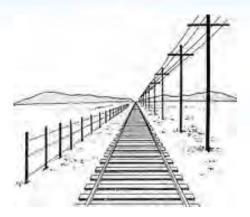
Functional Group "Head" = Hydrophilic

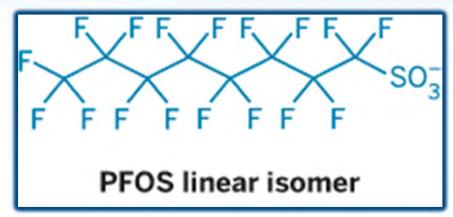


## **Branched & Linear Isomers**











#### **PFAS Formation**

#### **ECF Reaction =** B&L & Unintended Byproducts

#### Telomer Reaction: Unintended Byproducts & Precursors



# Where do they come from?

Raw Materials
Industrial Chemicals

Fire Training
Emergency Response

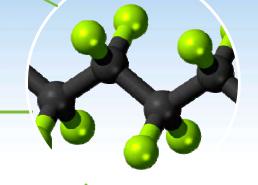
Stain Resistant,
Water Repellant,
Non-Stick Products

**eurofins** 

**Environment Testing TestAmerica** 

Manufacturing

**AFFF** 



Consumer Products

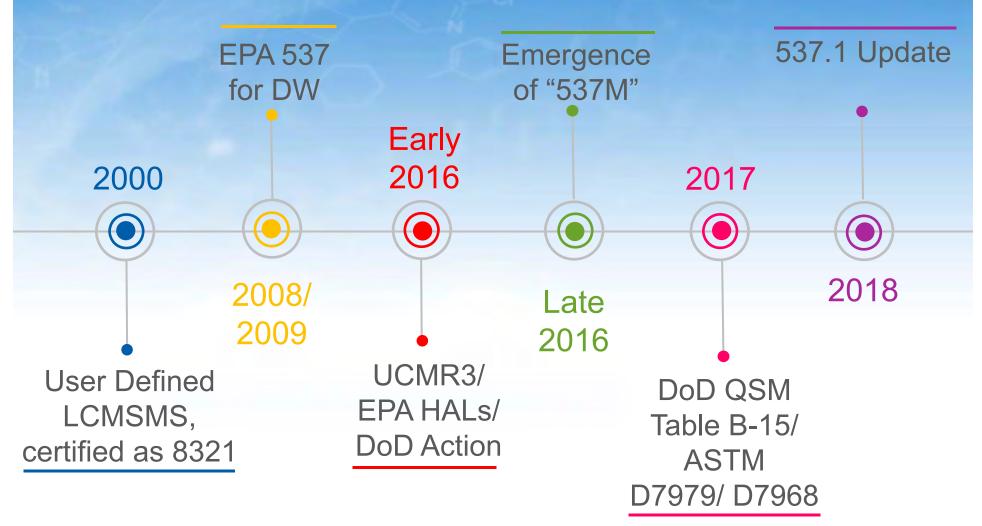
# **Replacement Chemicals**

	Legacy Manufacturers		
Original Chemical	PFOA	PFOS	PFOS
Replacement Chemical	HFPO-DA "GenX"	DONA	F-53B



# Why are PFAS an Analytical Challenge? Unique Ubiquitous **Properties** Lack of Consensus Best Method Surface Active Range of Concentrations 12

#### **Methods Timeline – Past to Present**





# EPA Method <u>537.1</u> "A Drinking Water Method Only"



Features	<b>Method 537.1</b>	
Matrices	Drinking Water	
Analyte List	14 + 4 replacement chemicals	
Sample size	250 mls	
Holding times	14 days for extraction	
Aqueous Extraction	SPE SDVB	
Analysis	LCMSMS - no confirmation ion	
Branched and Linear Isomers	Yes, for available standards	
Quantitation	Internal standard	
Reporting Limits	(2 ppt - 40 ppt)	
Isotope Recovery Correction	No	
LCS recovery limits	70-130	



14

# Groundwater, Soil, Tissue?

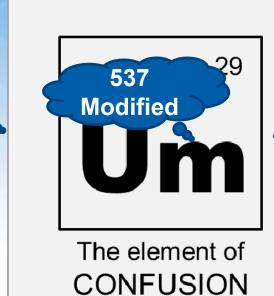


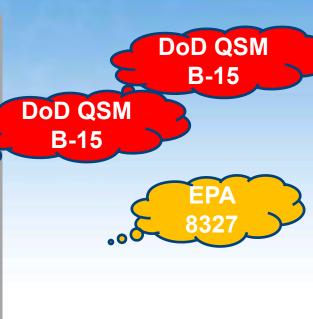
What method do we use for non-potable water & solid matrices?

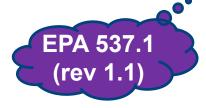
# 537 "Modified"

ISO 25101 EPA 537.1 (rev 1.1) ASTM D7979















#### Available vs. Future

7979

- Non-potable Aqueous
- No SPE, Direct Inject, External Standard

8327

- SW-846 Draft Method for Non-potable Aqueous
- No SPE, Direct Inject, External Standard
- Public Comment Period Closed Aug 23, 2019

53<sup>7</sup>M

"8328"

- User Defined Method, All Matrices
- SPE, Isotope Dilution, Comparable to DoD QSM Table B-15

EPA Draft Method, All Matrices other than DW

- SPE, Isotope Dilution, Comparable to DoD QSM Table B-15
- Unknown, perhaps 2020

537.1

533

- EPA Published Method, Drinking Water Only
- SPE, Internal Standard

.

- EPA Draft Method, Drinking Water, possibly non-potable
- SPE, Isotope Dilution and/or Internal Standard, TBD
- Undergoing 3<sup>rd</sup> Party Validation NOW



Analyte Description
Perfluorobutanoic acid (PFBA)
Perfluoropentanoic acid (PFPeA)
Perfluorohexanoic acid (PFHxA)
Perfluoroheptanoic acid (PFHpA)
Perfluorooctanoic acid (PFOA)
Perfluorononanoic acid (PFNA)
Perfluorodecanoic acid (PFDA)
Perfluoroundecanoic acid (PFUnA)
Perfluorododecanoic acid (PFDoA)
Perfluorotridecanoic Acid (PFTriA)
Perfluorotetradecanoic acid (PFTeA)
Perfluorobutanesulfonic acid (PFBS)
Perfluorohexanesulfonic acid (PFHxS)
Perfluoroheptanesulfonic Acid (PFHpS)
Perfluorooctanesulfonic acid (PFOS)
Perfluorodecanesulfonic acid (PFDS)
Perfluorooctane Sulfonamide (FOSA)
N-methyl perfluorooctane sulfonamidoacetic acid (NMeFOSAA)
N-ethyl perfluorooctane sulfonamidoacetic acid (NEtFOSAA)
Perfluoro-1-pentanesulfonate (PFPeS)
Perfluoro-1-nonanesulfonate (PFNS)
6:2FTS
8:2FTS
4:2FTS
DONA
HFPO-DA (GenX)
F-53B Major
F-53B Minor

#### NPW & Solids

# EPA Draft Target Analyte List

Replacement Chemicals

# Questions

