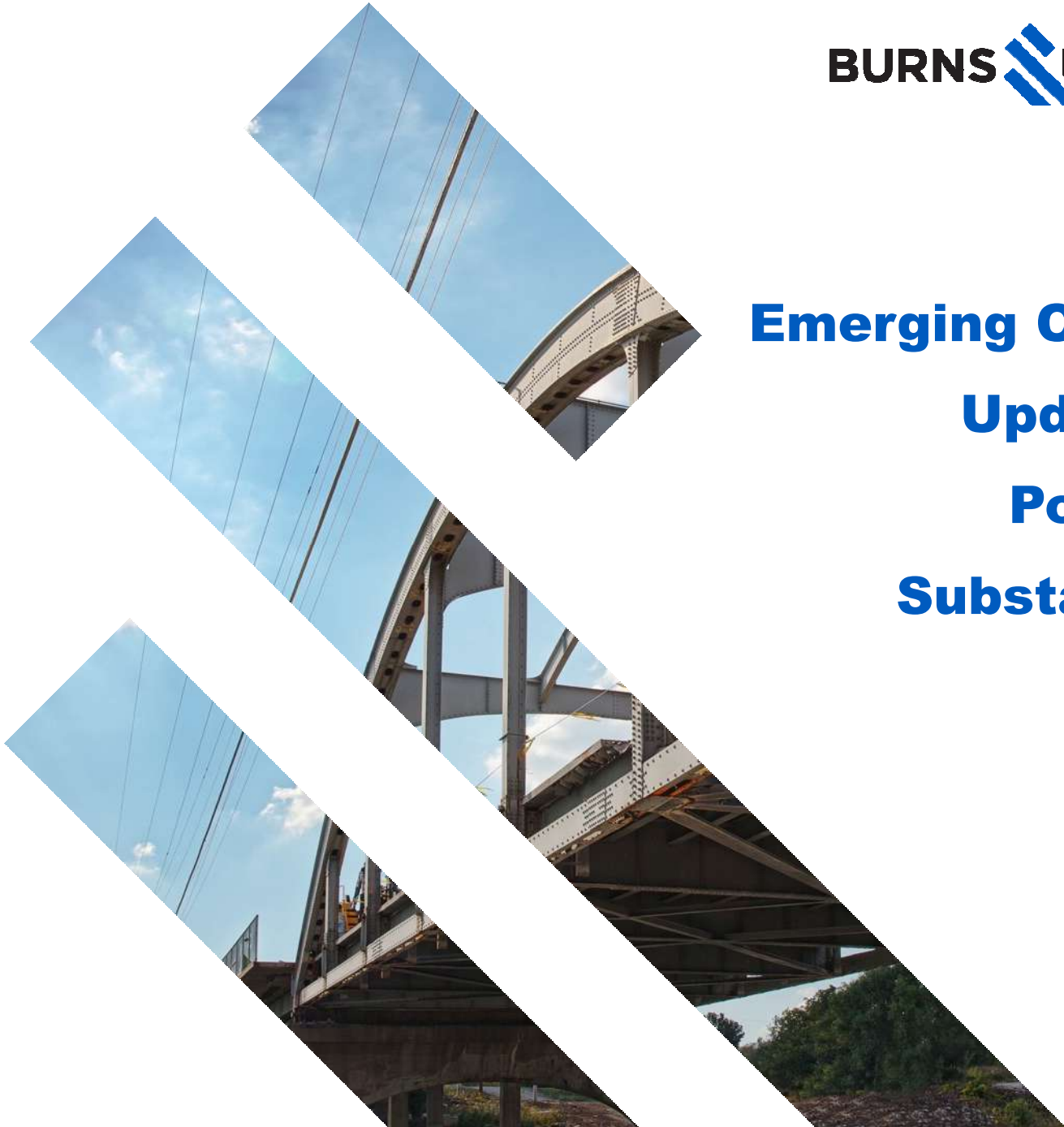




Emerging Contaminants Update: Per- and Polyfluoroalkyl Substances (PFAS)

Brian Hoyer, PG

February 27, 2018



Introduction to PFAS

PFAS vs. PFCs

Importance of Nomenclature

Per- and Polyfluoroalkyl Substances (PFAS)

Per-fluorinated Compounds

Perfluoroalkyl Acids (PFAAs)

Perfluorocarboxylic Acids (PFCAs)

Perfluorobutanoic acid (PFBA)
Perfluoroheptanoic acid (PFHpA)
Perfluorohexanoic acid (PFHxA)
Perfluorononanoic acid (PFNA)
Perfluorooctanoic acid (PFOA)
Perfluorodecanoic acid (PFDA)
Perfluoroundecanoic acid (PFUA)
Perfluorododecanoic acid (PFDoA)

Perfluoroalkane Sulfonates (PFASs)

Perfluorobutane sulfonate (PFBS)
Perfluoroheptane sulfonate (PFHpS)
Perfluorohexane sulfonate (PFHxS)
Perfluorooctane sulfonate (PFOS)
Perfluorodecane sulfonate (PFDS)

Perfluoroalkane Sulfonamides (FASAs)

Poly-fluorinated Compounds

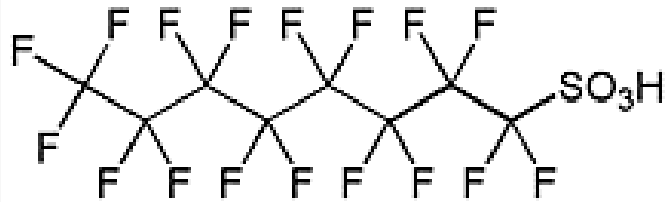
Thousands of compounds

Fluorotelomer alcohols
Sulfonamido carboxylates
Fluorotelomer betaines
Sulfanomidoethanol
Fluorotelomers
Sulfonamide ketones, aldehydes and ethers
And more
INCLUDES PERFLUORINATED PRECURSORS

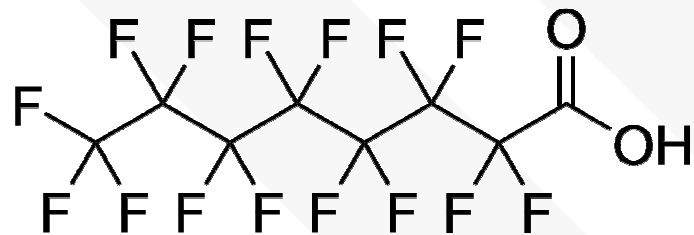
Note: Diagram presents common compounds and chemical groups and may not be complete.

BASIC CHEMISTRY

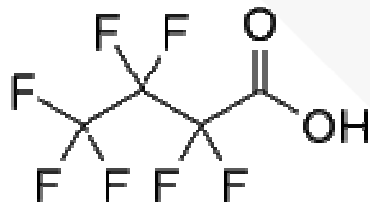
Per-fluoroalkyl substance



Perfluorooctane sulfonate (PFOS)

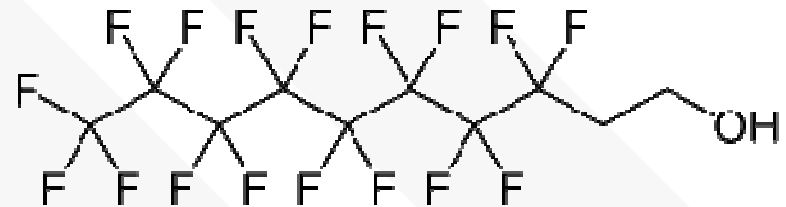


Perfluorooctanoic Acid (PFOA)



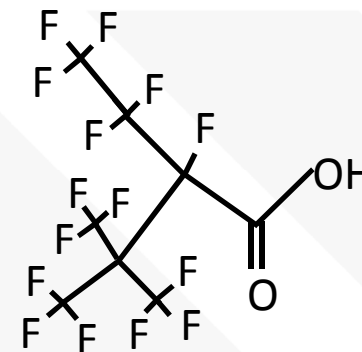
Perfluorobutanoic Acid (PFBA)

Poly-fluoroalkyl substance



Fluorotelomer alcohol, (8:2 FTOH)

Branched Per-fluoroalkyl substance



HISTORICAL USE OF PFAS

- ▶ 1950s - US Manufacturing began
- ▶ Aqueous Film Forming Foams (AFFF)
 - 1960s – U.S. Navy develops first AFFF
 - Chemically Complex – Mixture of 100s or 1,000s of PFAS.
 - Primary AFFF manufacturers - 3M, Ansul, National Foam, Angus, Chemguard, Buckeye, and Fire Service Plus, Inc.
- ▶ Products
 - Teflon™, Scotchgard™
 - Textiles, paper, and surface treatment (shoes, mattresses, food packaging, rubber, plastics, leather...)
- ▶ Manufacturing Processes
 - Primary manufacturing
 - Secondary Manufacturing
 - Metal plating and coating mist control
 - Surfactant/Additive
- ▶ TSCA SNURs Established in early 2000s



REPLACEMENT PFAS

- ▶ Early 2000s – Begin phasing out PFOA/PFOS and related compounds.
- ▶ Shift in Manufacturing Focus:
 - “Short Chain” \leq C6 PFCAs and PFSA.
 - Perfluoropolyethers
 - GenX
 - ADONA
 - Asahi’s Product
 - Solvay’s Product
 - Fluorotelomer products
- ▶ Historically not the focus of regulation
- ▶ Recent increase in scrutiny and subject of regulatory focus (e.g. – GenX)

PRECURSOR COMPOUNDS

Types of Precursors

- ▶ Fluorotelomer Sulfonates
 - 4:2 FTS, 6:2 FTS, 8:2 FTS
- ▶ Sulfonamides
 - FOSA, N-MeFOSAA, N-EtFOSAA
- ▶ Phosphate Ester/DiEsters
- ▶ Phosphinates
- ▶ Fluorotelomer Acids
- ▶ Fluorotelomer Alcohols

Why this Matters

- ▶ Slowly Degrade to PFAAs.
- ▶ Cannot measure all precursors in a sample.
- ▶ Degradation mechanics are not well understood.
- ▶ Can confuse delineation and CSM.
- ▶ Do they affect treatment objectives/approach?
- ▶ How to we account for them?

EXAMPLE OF PRECURSOR DEGRADATION

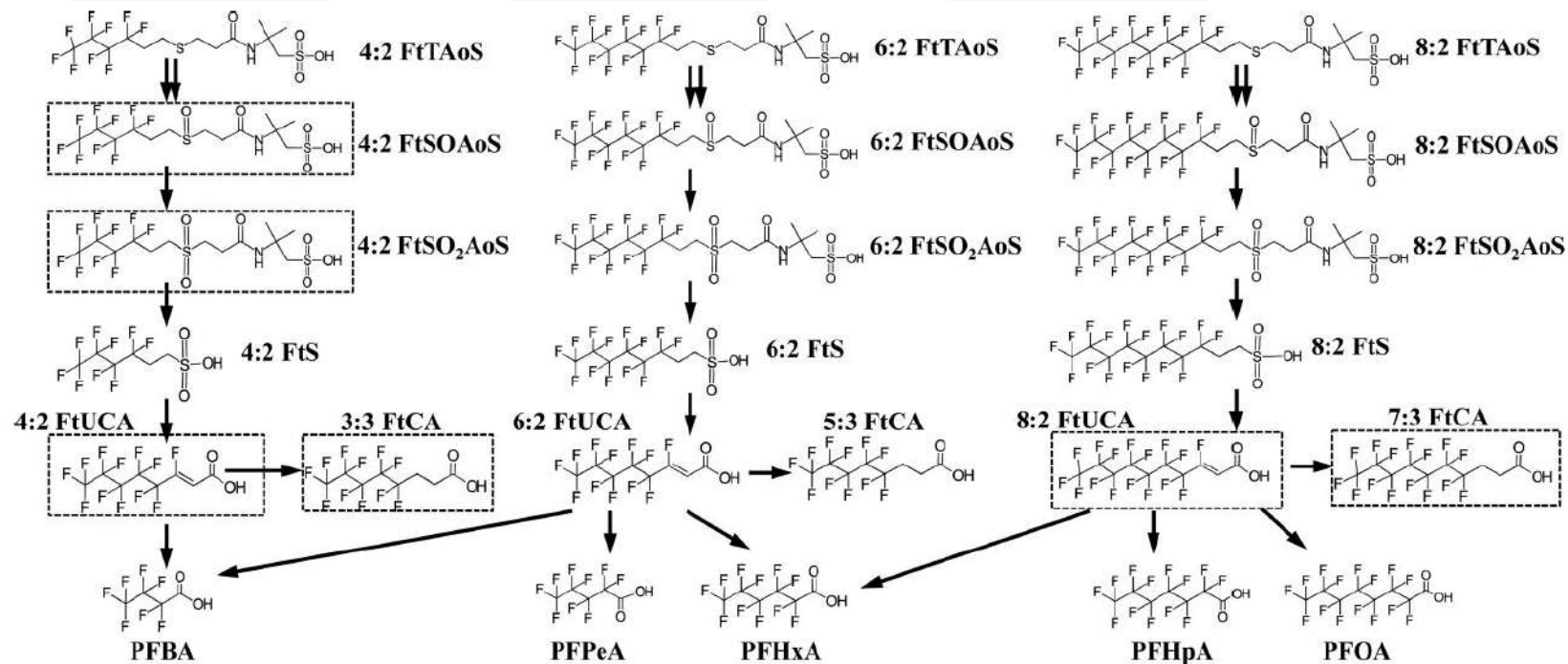


Figure 4. Proposed biotransformation pathways of 4:2, 6:2, and 8:2 FtTAoS by aerobic soil microcosms. Compounds in dashed boxes are proposed biotransformation intermediates and were not directly detected in microcosms. The double arrow indicates that the reaction occurs both biologically and abiotically.

Diagram from Harding-Marjanovic, K. C., Houtz, E. F., Yi, S., Field, J. A., Sedlak, D. L., & Alvarez-Cohen, L. (2015). Aerobic Biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environmental science & technology*, 49(13), 7666-7674. doi:10.1021/acs.est.5b01219

Chemical Properties of PFOS and PFOA

Parameter	PFOS	PFOA	Benzene	TCE	PCB (Arochlor 1260)
CAS number	1763-23-1	335-67-1	71-43-2	79-01-6	11096-82-5
Chemical Formula	C ₅ F ₁₇ SO ₃ H	C ₇ H ₁₅ COOH	C ₆ H ₆	C ₂ HCl ₃	C ₁₂ H ₄ Cl ₆
Molar Weight	500 g/mol	414 g/mol	78.1 g/mol	131.5 g/mol	357.7 g/mol
Solubility	680 mg/l (pure water) 370 mg/l (fresh water) 12.4 mg/l (sea water)	3,400-9,500 mg/l	1780 mg/l	1,100 mg/l	0.0027 mg/l
Log K _{oc}	2.57	2.56	2.3	2.13	5 - 7
Henry's law constant	3.05 x 10 ⁻⁹ atm. m ³ ·/mol-(pure water)	not measured	5.5 x 10 ⁻³ atm. m ³ ·/mol	1,0 x 10 ⁻² atm. m ³ ·/mol	4.6 10 ⁻³
Vapor pressure	2.48 x 10 ⁻⁸ mm Hg	0.017 mm Hg	95 mm Hg	77.5 mm Hg	4.05x10 ⁻⁵ mm Hg

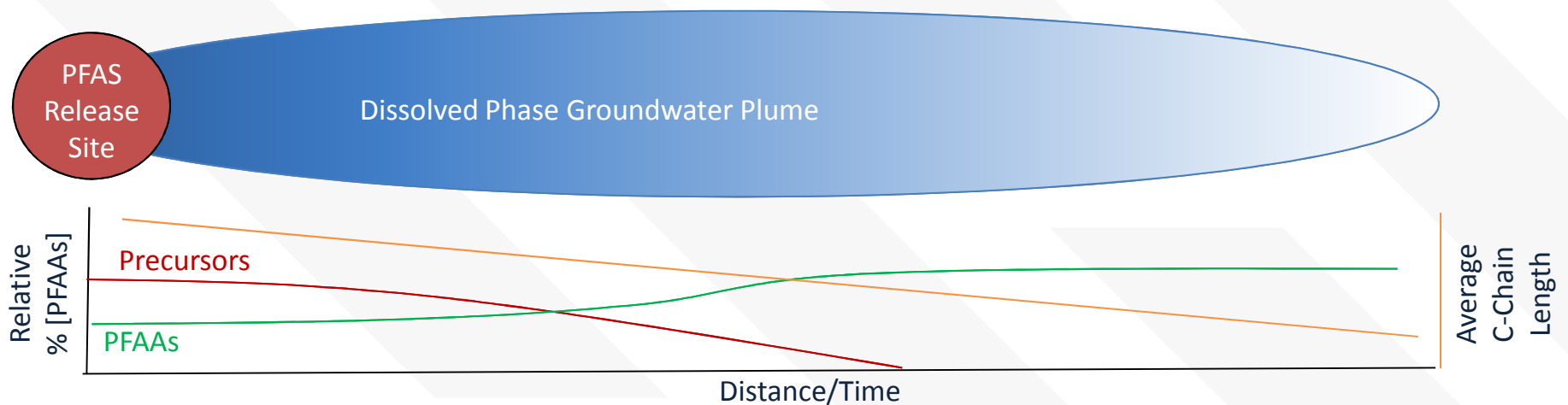
Note: Physiochemical properties for other PFAS are not well understood. Historic focus on PFOA and PFOS.

PFOS (Giesv, 2010, OECD, 2002) PFOA (EFSA, 2008)

Benzene, TCE, PCB 1260 (Payne, Suthersan, *In-Situ Remediation Engineering*, pp. 469-485, CRC Press, 2005)

BEHAVIOR IN THE ENVIRONMENT

- ▶ Soluble Under Normal pH
- ▶ Dead-end PFAAs will not Degrade – Attenuate via Physical Mechanisms Only
- ▶ Form Long Groundwater Plumes (Potentially Miles Long)
- ▶ Precursor Compounds can act as Source
- ▶ Low Compliance Limits.



Note – Overly simplified diagram, does not account for site-specific interactions (e.g. – complex hydrogeology, back diffusion, commingled plume)

Regulatory Status

Quickly Changing

FEDERAL ACTIONS

- ▶ Toxic Substance Control Act (TSCA)
 - 2002 – Significant new use rules (SNURs) under TSCA for 88 PFOS-related substances.
 - 2007 – SNURs were modified to include 183 PFOS-related additional substances.
 - 2013 – Final SNUR issued for C7-C20 PFCAs. Requires 90 day advanced notice of all new uses.

- ▶ 2006 – EPA Launches PFOA/PFOS Stewardship Program w/ goal of 95% reduction of long chained PFAAs and precursors by 2010/2015.

- ▶ Drinking Water Health Advisories
 - 2009 – USEPA established a provisional health advisory (PHA) of 0.2 µg/L for PFOS and 0.4 µg/L for PFOA.
 - May 2016 – USEPA established a health advisory (HA) of 0.07 µg/L for PFOA and PFOS.

FEDERAL ACTIONS

▶ Risk-Based Screening Levels – See Calculator

- Resident RSL for Tap Water = 0.401 µg/L (PFOA and PFOS); 401 µg/L (PFBuS)
- Resident RSL for Soil = 1.26 mg/kg (PFOA and PFOS); 1,260 mg/kg (PFBuS)
- Worker RSL for Soil = 46.7 mg/kg (PFOA and PFOS) 46,700 mg/kg (PFBuS)

▶ Showing up in 5-Year Reviews

▶ December 2017 – EPA Launched Cross-Agency Effort to Address PFAS

- Identify Near-Term Actions
- Enhance Coordination across States, Tribes, Fed. Partners
- Increase Ongoing Efforts to Identify Lab Methods
- Expand Protective Communication Efforts

RESPONSE BY THE STATES

- ▶ In many cases, states are leading efforts to introduce enforceable standards.
 - Drinking water, surface water, and/or groundwater = AK, CT, CO, DE, IA, ME, MI, MN, NV, NH, NJ, NC, OR, TX, VT.
 - Soil = AK, DE, MI, MN, NV, NH, NC, TX.
 - Others may have qualitative standards (e.g. – California Prop 65)
- ▶ Many collaborative efforts are underway to provide scientific basis for regulation - *Anticipate more in 2018*
 - Technical societies focused generating guidance documents (e.g. – ITRC, NGWA).
 - EPA's cross-agency effort
 - CDC study as part of National Defense Authorization Act.
- ▶ Developing patch-work of regulation.
 - Variability in compounds
 - Variability in compliance limits

Note: The information presented on this slide may soon be out of date. Check state-specific websites for current list of standards and related regulation.

Source Scenarios

Common Sources

COMMON PFAS SOURCE AREAS

AFFF Point Sources

- ▶ Fire Fighting Training Grounds
- ▶ Hot Crash Sites
- ▶ Hangers
- ▶ AFFF Storage Areas
- ▶ Deluge Areas
- ▶ Fueling Stations
- ▶ Calibration Areas
- ▶ Aviation
- ▶ Oil and Gas

Industrial / Manufacturing

- ▶ PFAS Manufacturing
- ▶ Metal Plating
- ▶ Textile Coating
- ▶ Non-Stick Cookware (PTFE Coating)
- ▶ Insecticides
- ▶ Paper and Packaging
- ▶ Surfactants
- ▶ Consumer Products
 - Cleaners
 - Waxes
 - Hygiene Products

Other PFAS Sources

- ▶ Landfills
 - Infiltration to Groundwater
 - Leachate Management
- ▶ Equipment Maintenance Areas
 - Aviation Fluids
- ▶ Water Treatment Systems
 - Effluent?
 - Bio-solids and Sludges?

Challenge to Identifying Sources

- ▶ Proprietary Formulations Pose Challenges
- ▶ Defining PFAS/PFOS/PFOA-Free

AFFF

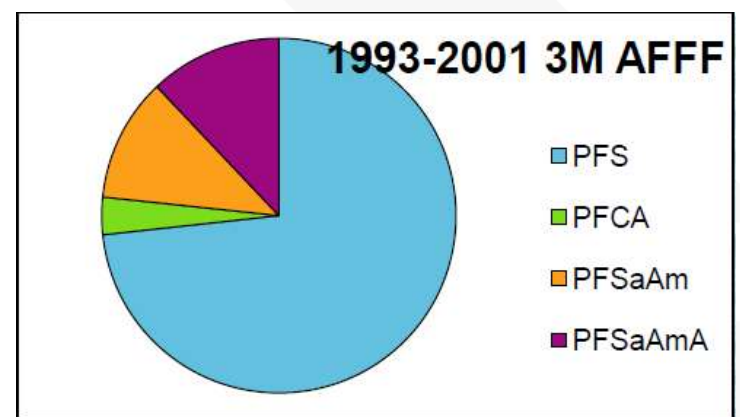
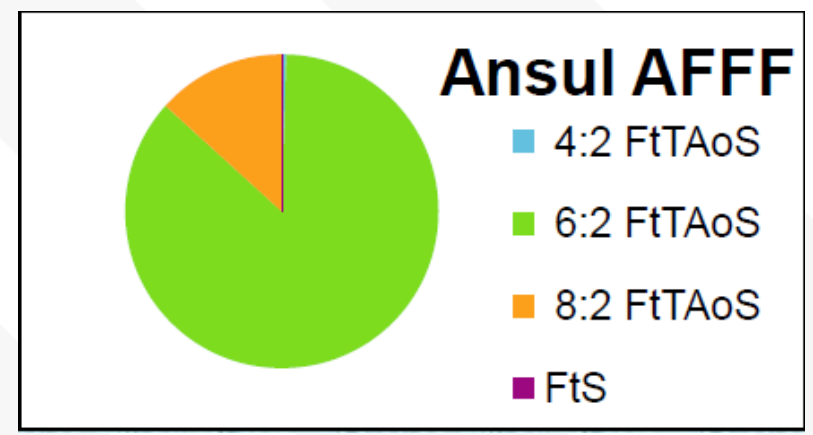
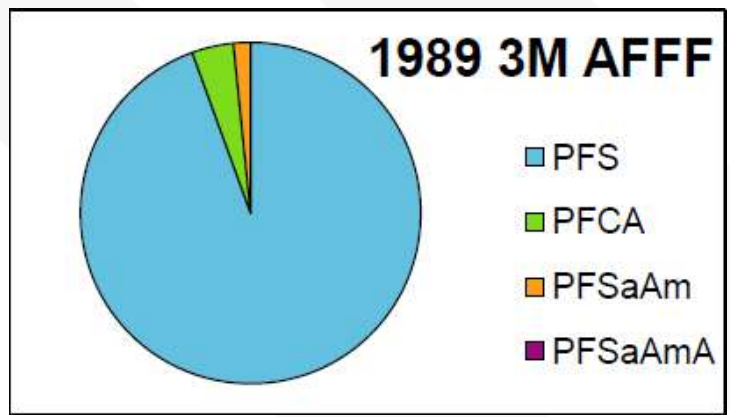
Military, Aviation, Oil & Gas, Emergency Response

- ▶ Fire Training Areas, Hot Crash Sites.
- ▶ Potential for environmental impact is a function of release volume and frequency.
- ▶ PFAS plumes are commonly comingled with hydrocarbons.
- ▶ PFSA dominate (PFOS).
- ▶ AFFF manufacturing process results in branched vs. straight-chain PFAS.
- ▶ PFOA and other PFCAs are primarily a result of precursor degradation.



HISTORIC AFFF FORMULATIONS

- ▶ 3M vs. Ansul
- ▶ Transition to new “PFOS and PFOA Free” formations (What does that mean?).



Diagrams from Fields, J., Overview of Per- and Polyfluoroalkyl Substances (PFAS)

INDUSTRIAL COMERCIAL

- ▶ Primary Manufacturing Facilities – Locations where PFAS-containing products are produced.
- ▶ Secondary Manufacturing Facilities – Locations that use PFAS-containing products as part of another process.
- ▶ Potential for concentrated source areas (local releases) and wide-spread surface deposition (stack emissions or mists)
- ▶ Composition depend on the type of PFAS produced and or used.
- ▶ Potential for impacts is a function of magnitude and frequency of releases.
- ▶ Disposal of PFAS-containing wastes.
- ▶ PFCA dominant (PFOA).

LANDFILLS

- ▶ PFAS composition is a function of materials placed in landfill.
- ▶ Greatest variation of PFAS.
- ▶ Relative Increase in Short-chained PFCAs (≤ 6).
- ▶ Slow rate of decomposition and degradation = Potential for sustained source of PFAS to environment.
- ▶ Leachate streams may transfer PFAS to other systems (e.g. – WWTPs).



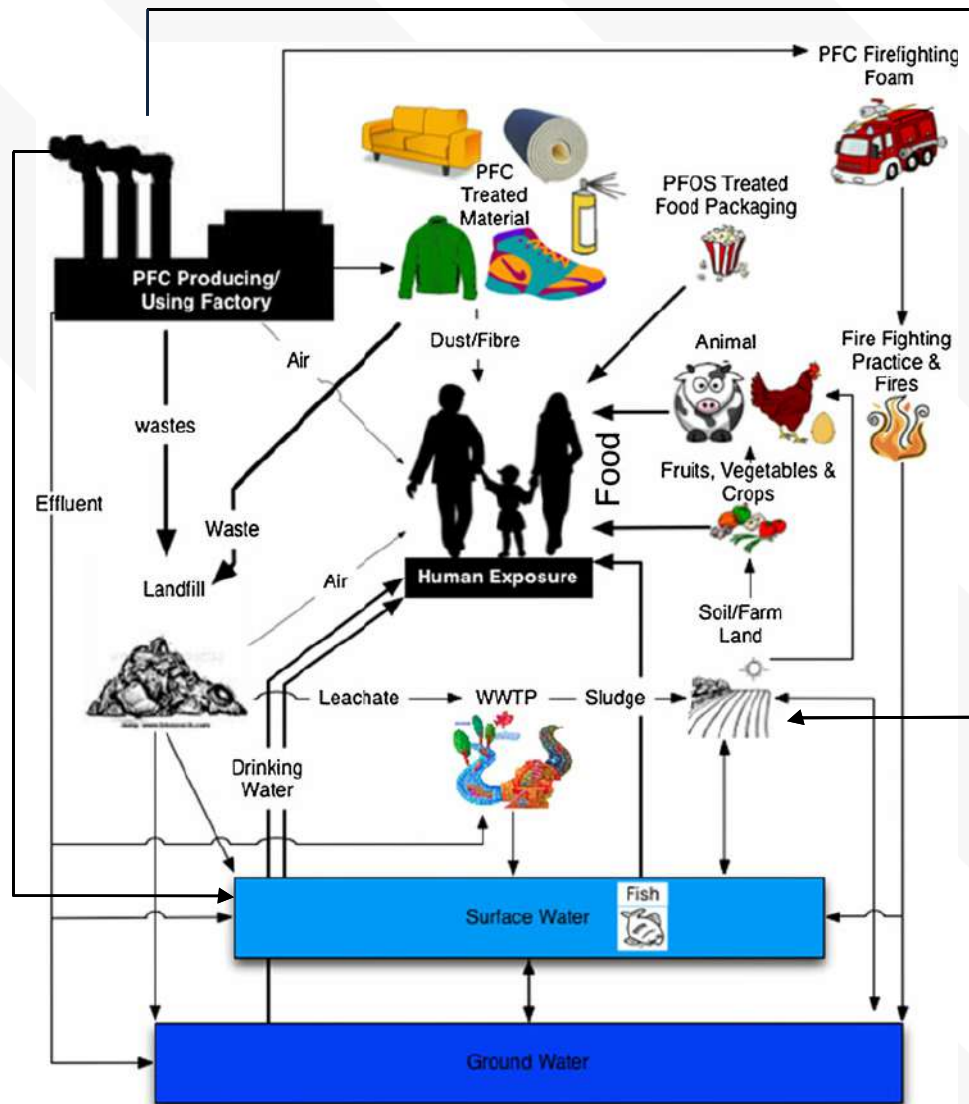
WASTE WATER TREATMENT PLANT / BIPRODUCTS

Municipal and Industrial WWTPs

- ▶ PFAS entering WWTP is a function of waste streams received.
- ▶ Common treatment technologies are incompatible with PFAS.
- ▶ Stimulate precursor degradation.
- ▶ Relative increase of PFCAs and PFSAAs in effluent have been observed.
- ▶ PFAS have potential to enter biosolids.
- ▶ May be significant in Regional F&T of PFAS



IDENTIFICATION OF POTENTIAL EXPOSURE MECHANISMS



- ▶ Potential for Multiple Exposure Routes
- ▶ Various media interactions
- ▶ Complex system
- ▶ What is the important pathway given your site?
 - Location
 - Surrounding land use
 - Hydrogeology
 - Hydrology
 - Climate
 - Receptors

Image adapted from Oliaei, F., et al, 2016.

Sampling and Analysis

HOW TO SAMPLE – THINGS TO DO

- ▶ Confirm that a **PFAS-free water source** is used for decontamination and drilling fluids.
- ▶ Only wear clothing that has been **washed 6 times** prior to use in the field.
- ▶ Utilize **field blanks, equipment rinsate blanks, PT samples and/or trip blanks.**
- ▶ **Triple-rinse** sampling tools and sampling equipment with distilled water following decontamination procedures.
- ▶ Use only **PFAS-free materials** when working on a PFAS site
 - Plastics
 - Detergents (Verify fluorine free) can use solvents.
 - Sheeting
 - PPE
- ▶ **Wash hands** and don new gloves frequently.
- ▶ Use **HDPE sample containers** unless specifically instructed otherwise by the project laboratory.

HOW TO SAMPLE – THINGS TO AVOID

- ▶ Do not **field filter** samples.
- ▶ Do not use any materials that contain **Teflon™**
- ▶ Do not allow **food or wrappers** on site.
- ▶ Do not wear clothing or boots that have been treated to be **water-resistant**.
- ▶ Do not use **water-resistant** paper, labels, self-sticking notes, aluminum foil, or blue-gel ice packs.
- ▶ Do not use **Tyvek** clothing.

Note: Current research is focused on addressing folklore and misconceptions of sampling materials.

ANALYTICAL METHODS

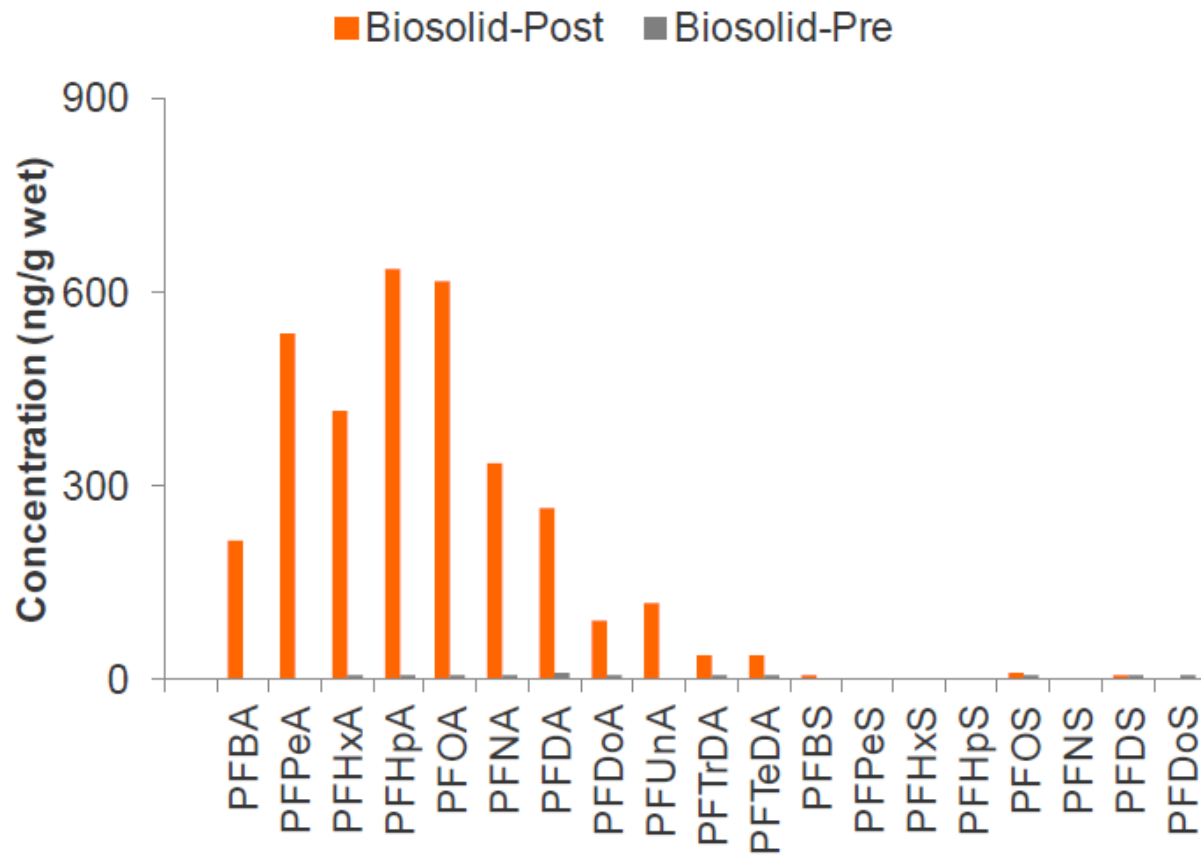
- ▶ **USEPA Method 537**
 - Developed for Drinking Water.
 - Does not report C4, C5, and C6 PFCAs are not readily picked up by 537 as written.

- ▶ **Modified Method 537 Rev 1.1 LC/MS/MS with Isotope Dilution**
 - Allows for quantification of branched PFOA.
 - Not all Modified Method 537 Procedures are the Same.
 - Understand Laboratory-Specific Protocols
 - Isotope Dilution and Corrections (QA)
 - Sample Cleanup
 - Analyte Lists and Reporting Limits

- ▶ **Analyte List – Up to ~40 Compounds Available**
 - Project-specific list should reflect goals and objectives
 - Consider objectives before selecting analyte list



TOTAL OXIDIZABLE PRECURSOR ASSAY (TOP)



Summary of TOP Assay

1. Prepare/Collect Split Sample
2. Introduce Potassium Persulfate and NaOH.
3. Hot Water Bath
4. Quench to Room Temperature
5. Adjust pH to Normal and Analyze
6. Compare Results to Parent Sample

Chandramouli, B., 2017. EMDQ Phoenix

MOBILE LABORATORY

- ▶ NELAP/DoD ELAP-accredited Mobile Laboratory has come to Market
- ▶ Running Modified Method 537 Rev 1.1 LC/MS/MS with Isotope Dilution
- ▶ Offers same-day results (25 samples per day)
- ▶ Cost effective approach for field efforts with large sample volumes.
- ▶ Allows for cost-effective QA sample analysis.
- ▶ Potential cross-contamination issues are identified in the field.
- ▶ Analysis of common co-contaminants (VOCs and SVOCs).

Remediation and Treatment

PFAS REMEDIATION TECHNIQUES

State of the Practice

- ▶ Limited selection of proven technologies
- ▶ Focus on R&D
- ▶ Proof concept is the first hurdle, then field application

- ▶ In situ vs. ex situ vs. well head
- ▶ Potential for combined remedy
- ▶ MNA (Physical Attenuation)



PROVEN TECHNOLOGIES – GW / DW

Groundwater Remediation / Water System Upgrades

- ▶ Well Head Treatment
- ▶ Pump & Treat / Hydraulic Containment
- ▶ In Situ Adsorption / Trap Dissolved Phase

Groundwater / Municipal Water Treatment

- ▶ GAC
- ▶ Ion Exchange
- ▶ Nanofiltration
- ▶ Reverse Osmosis

Municipal Water Alternative Strategies

- ▶ Identify & Mitigate Sources
- ▶ Seek Alternate water source
(e.g., bottled water, new wells)



PROVEN TECHNOLOGIES – GW / DW

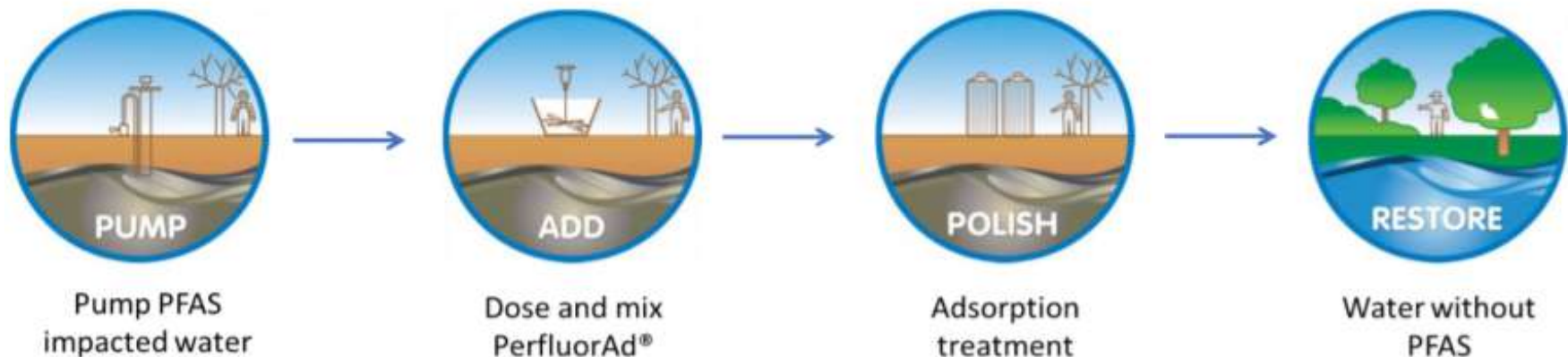
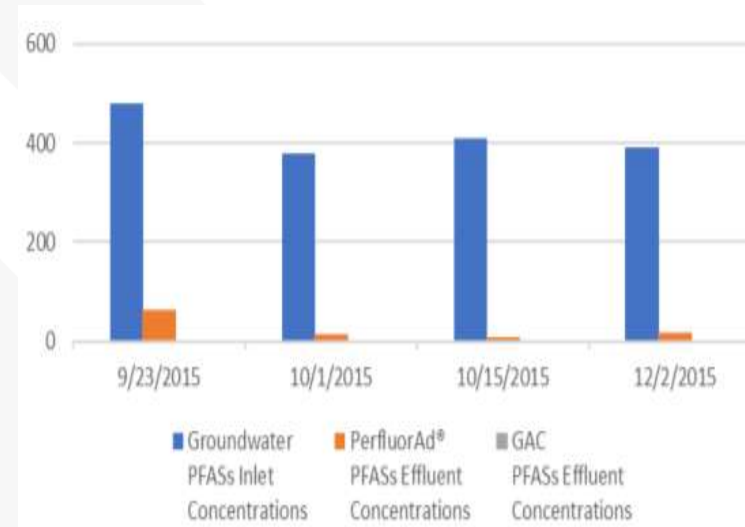
▶ Disadvantages of Proven Water Treatment Options

- GAC
 - Reduced adsorption capacity as compared to common applications
 - Regeneration costs 10 to 100 times higher in comparison to other hydrocarbons
 - Reduced effectiveness when high TOC is present
 - Requires regeneration/incineration
- Ion Exchange
 - Reduced adsorption capacity as compared to common applications
 - Waste streams associated with spent media
 - Currently less cost-effective than GAC; R&D ongoing
- Reverse Osmosis
 - Highest cost
 - Waste streams associated with reject/concentrate



PRETREATMENT (E.G. - PERFLUORAD®)

- ▶ Removal of PFAS from Water
- ▶ Liquid reagent that bind PFAS and creates flocs
- ▶ Flocs are removed and disposed (may require destruction).
- ▶ 97% removal of PFAS.
- ▶ Mobile approach
- ▶ Extends life of GAC ion exchange, or reverse osmosis.



<http://tersusenv.com/resources/library/tech-briefs/243-perfluorad/file>

IN SITU ADSORPTION AND IMMOBILIZATION

Trapping Dissolved-Phase PFAS

- ▶ Introduction of colloidal sorbents or coagulants to trap PFAS in-situ
- ▶ Identify most effective treatment media types and dosage
- ▶ Determine effects of co-contaminants on performance
- ▶ Potential deployment as permeable reactive barrier
 - Understanding of site hydrogeology is key to placing effective barrier
 - Formation must support injection
- ▶ Can be a cost effective approach to groundwater treatment
- ▶ Success of these remedies relies on application design
 - Product must make contact
 - Particular focus should be placed on hydrogeology

PROVEN TECHNOLOGIES - SOIL

Source Remediation

- ▶ Excavation and Off-site Treatment
 - Incineration
- ▶ Advantages
 - Bulk Mass Removal
 - Mass Flux Reduction
 - Long-Term Risk and Cost Reduction
- ▶ Challenges
 - *Cost*
 - *Accessibility - existing infrastructure*



STABILIZATION (E.G. - REMBIND®)

▶ Activated Carbon / Aluminum Hydroxide

Table 1: Leachability Reduction of PFOS & PFOA for Soil 1

Site 1	ASLP Analysis			
	PFOS µg/L	%	PFOA µg/L	%
Untreated Soil	34.15	-	0.65	-
RemBind®	0.50	98.5	0.04	93.8
RemBind® PLUS	0.29	99.2	<0.02	>96.9

Table 2: Leachability reduction of PFOS & PFOA for Soil 2

Site 2	ASLP Analysis			
	PFOS µg/L	%	PFOA µg/L	%
Untreated Soil	376	-	5.51	-
RemBind®	1.76	99.5	0.27	95.1
RemBind® PLUS	0.10	99.9	<0.02	>99.6

- ▶ Reduce Leachability
- ▶ Increases Sorption
- ▶ Reduce Leaching to GW
- ▶ Effective on Co-Contaminants
- ▶ Longevity?



<http://tersusenv.com/resources/library/tech-briefs/239-rembind-product-overview-1/file>

EMERGING TECHNOLOGIES – R&D FOCUS

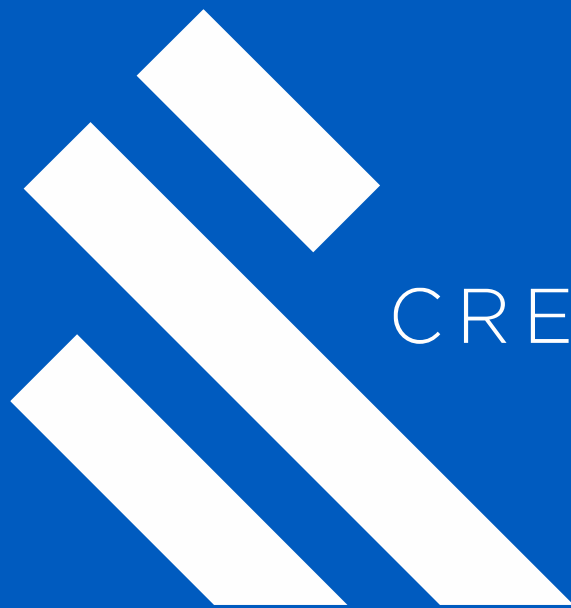
- ▶ On Site Thermal Desorption/Destruction
- ▶ Chemical Oxidation/Reduction
 - Proof of concept in lab. Challenges in field-scale applications
 - Increased Performance on PFCAs than PFSA
 - Potential to Degrade Precursors
 - Potential to Couple with In Situ Immobilization
- ▶ Pyrolysis (plasma arc)
- ▶ Catalytic/Electro-Catalytic Reactions
- ▶ Biologically-mediated destruction
 - Research to ID potential fungi/enzymes capable of degrading PFAS.

Risk Communication

RISK COMMUNICATION AND STAKEHOLDER INTERACTION

- ▶ Body of toxicological research includes variable results. Focused primarily on PFOA and PFOS.
- ▶ HA and compliance limits have been established to be protective despite uncertainties in the toxicological dataset.
- ▶ Results in low (ppt) compliance limits.
- ▶ How do we clearly discuss risk with stakeholders?
- ▶ This subject is complex. Care should be taken when communicating to be sure the proper message and position is communicated.





CREATE AMAZING.