Understanding PFAS Fate and Transport

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Agenda

- Background and Characteristics
- Regulatory Updates
- Atmospheric and Subsurface Fate & Transport
- PFAS F&T Case Studies:
  - PFAS manufacturing facility
  - Site model for multiple AFFF releases
  - Land application of industrial sludge
  - Fate of AFFF in a WWTP
- Conclusions

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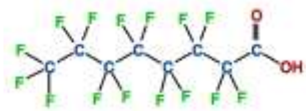
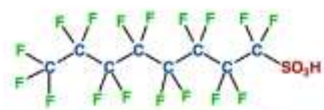
Background - What are PFAS Compounds?

- Synthetic class of compounds used in manufacturing fluoropolymers
  - PFOA – perfluorooctanoic acid and its principle salts, manufactured starting in 1947[1], 8 manufacturers phased out production by 2015
  - PFOS – perfluorooctane sulfonate, manufactured from 1949-2002
- Used in the manufacturing of many articles of commerce



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

[1] Prevedouros ES&T, 2006
[2] Paul et al. ES&T, 2009

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Background - Where do we find PFASs?

- Oil and water-repellent
- Stain-resistant upholstery, carpeting
- Non-stick coatings in cookware (Teflon®)
- Breathable, all weather clothing (Gore-tex®)
- Paper and packaging protectors (food packaging)
- Paints and adhesives
- Fluoro-elastomers (gaskets, O-rings, Hoses)
- Mining and oil surfactants
- Metal plating baths (chromium)
- Pesticides/Insecticides
- Aqueous film-forming foams (AFFF) for fire fighting

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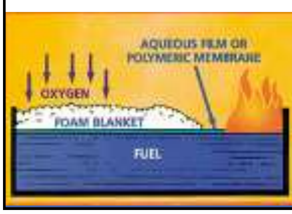
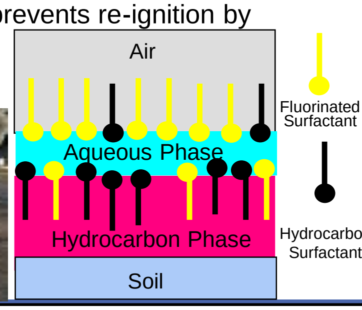
Aqueous Film Forming Foams (AFFF)

- Developed by the Navy in 1960s
- PFASs are used in AFFFs that were routinely used for fire fighter training at municipal and military fire training areas
- Used for Class B fires (highly flammable or combustible liquid fires, including jet fuels, gas tankers & refineries)
- AFFFs have the ability to spread over the surface of hydrocarbon-based liquids (i.e., create a film)
- AFFF blankets fuel, cools the fuel surface, prevents re-ignition by suppressing release of flammable vapors





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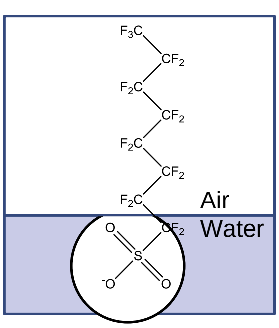
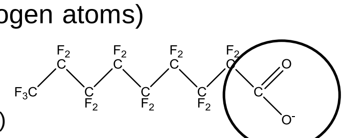
Characteristics - Unique Chemistry

- C-F bond is one of the shortest and strongest bonds
- Few degradation processes: too much energy to break bonds
  - stable in acids, bases, oxidants, heat
  - microorganisms cannot gain energy from breaking the bond

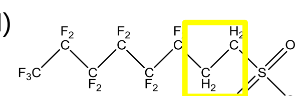


- Perfluorinated = all carbon atoms fully fluorinated (no hydrogen atoms)



PFOA (**per**fluorooctanoate)

- Polyfluorinated = some carbons are not fully fluorinated (have H)



(*Poly*)**fluorotelomer sulfonate (FtS)**

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Characteristic - PFAS Properties

Chemical Properties	PCB (Arochlor 1260)	PFOA	PFOS	TCE	Benzene
Molecular Weight	357.7	414.07	538	131.5	78.11
Solubility	0.0027 mg/L @24°C	**3400–9500 mg/L @25°C**	519 mg/L @20°C	1100 mg/L @ 20°C	1780 mg/L @20°C
Vapor Pressure (25°C)	$4.05x10^{-5}$ mmHg	**0.5-10 mmHg**	**$2.48x10^{-6}$ mmHg**	77.5 mmHg	97 mmHg
Henry's Constant	$4.6x10^{-3}$ atm-m³/mol	0.0908 atm-m³/mol	**$3.05 x10^{-6}$ atm-m³/mol**	0.0103 atm-m³/mol	0.0056 atm-m³/mol
Organic Carbon Part. Coeff. (Log K_{oc})	4.8-6.8	2.06	**2.57**	2.42	2.15

- High solubility, low volatility in water
- High detection frequency in soil and sediment

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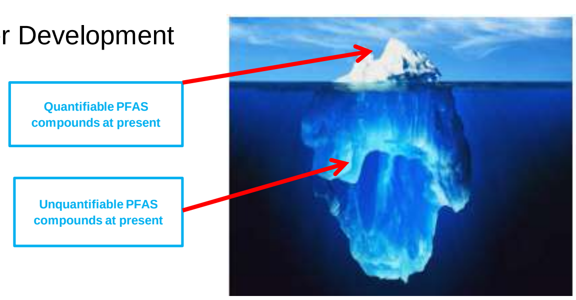
PFAS Laboratory Status

- 10's of thousands of potential PFASs
- Minimum of 100's that could be environmentally relevant
- Current commercial labs can quantify 20-35
  - Branched and linear standards
- Screening Methods under Development



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Regulatory Updates

- 1999 - concerns originated and by 2002 3M phased out PFOS production
- 2015 Texas TCEQ first cleanup criteria established PCLs for 16 PFASs
- May 2016 - USEPA OSWER established Final Lifetime Health Advisory Levels (HALs) for PFOS, PFOA and PFOS+PFOA at 70 ppt
- 9/23/16 - New Jersey DWQI proposed PFOA drinking water MCL of 14 ppt
- 11/6/16 - Alaska DEC just established cleanup levels for PFOS/PFOA in soil and groundwater
- 11/15/16 - USEPA OSWER HAL clarification, should not be used to identify risk levels in food sources

Stockholm Convention on persistent organic pollutants (POPs)

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Sense of Scale

- 70 parts per trillion = 70/1,000,000,000,000

Equivalent to 3.5 drops of water in an Olympic swimming pool

World Population = 7.4 billion
70 ppt ~ 1 person / 2 world populations

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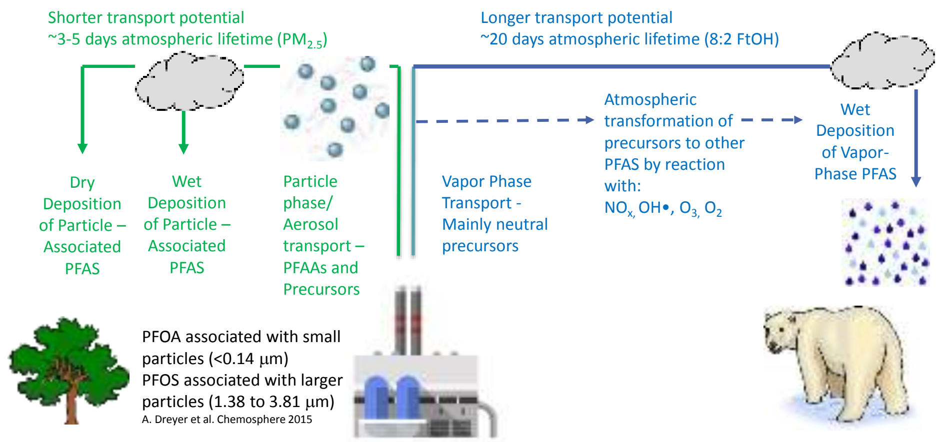
PFAS Atmospheric Fate & Transport



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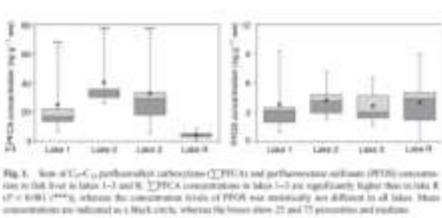
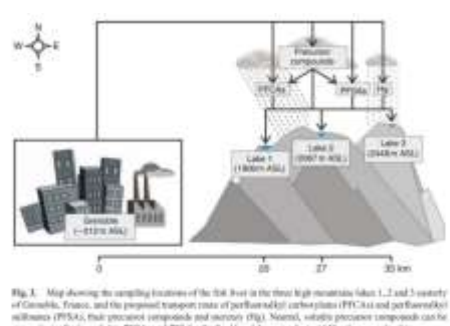
Air Deposition of PFAS to Remote Lakes - Grenoble, France

- Air deposition is sole source of PFAS to mountainous lakes outside of Grenoble
- Concentrations of PFOS and PFOS precursors in fish were similar between reference lake and lakes near Grenoble
- Concentrations of PFCAs and PFCA precursors in fish were dependent on proximity to local industrial sources





Ahrens et al., Environ. Chem. 2010

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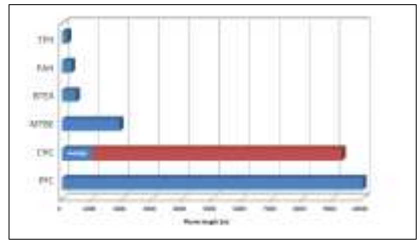
PFAS Groundwater Fate & Transport: Chemical Properties and Implications

PFAA plumes are generally longer

- High solubility
- Low log K_{OC}
- Recalcitrant
- Mostly anionic
- PFAA sorption increases with perfluorinated chain length, e.g. PFOS (C8) is more sorptive than PFBS (C4)



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Vapor Pressure (@25°C), mmHg	$4.1x10^{-5}$	0.5-10	$2.5x10^{-6}$	78	97
Log Koc	5 – 7	2.06	2.57	2.47	2.13

Persistence and mobility can lead to large plumes

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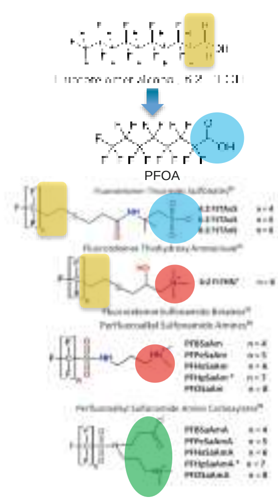
Polyfluorinated Compounds – PFAA Precursors

- Thousands of polyfluorinated precursors to PFAAs have been commercially synthesized
- The common feature of the precursors is that they will **biotransform** to make PFAAs as persistent “dead end” daughter products
- Neither PFAAs nor their PFAAs biodegrade, i.e. mineralize
- Some precursors are fluorotelomers
- Some are cationic (positively charged) or zwitterionic (mixed charges) –this influences their fate and transport in the environment
- Cationic / zwitterionic PFAS tend to be less mobile than anionic PFAAs and so can potentially be retained longer in “source zones”
- Environmental fate and transport of precursors is complex and structure dependent



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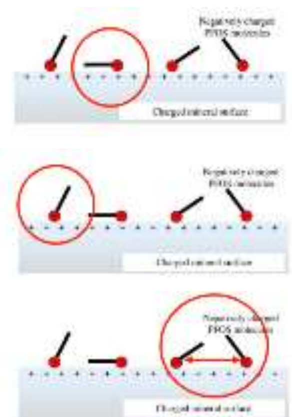
Subsurface Retardation of PFAS in Groundwater

- Hydrophobic interaction
  - Predominant sorption mechanism for long chain PFAS
  - Organic rich soils retard movement of PFAS
  - f_{oc} increases -> K_d increases
  - Oil and other organics may also increase sorption
- Electrostatic effects
  - Positively charged PFAS (i.e. some precursors) sorb to negatively charged minerals
  - Negatively charged PFAS sorb to positively charged minerals
  - Electrostatic repulsion can decrease PFAS sorption
  - High ionic strength dulls electrostatic repulsion and attraction



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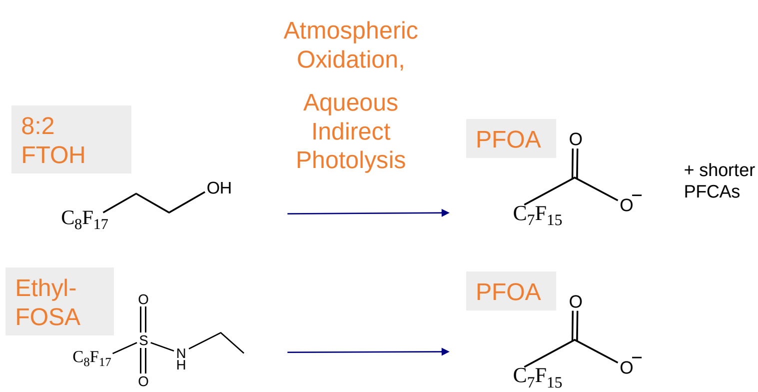
Abiotic Transformation of PFAA Precursors

Both Sulfonamido and Fluorotelomer Precursors predominately oxidize to form PFCAs



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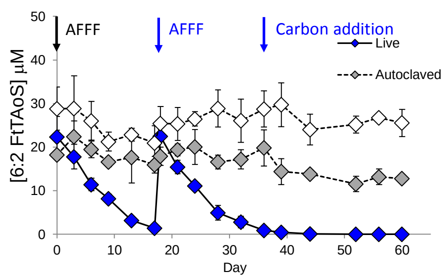
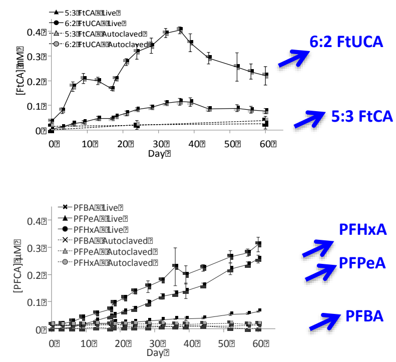
Aerobic Biotransformation of Fluorotelomer Precursors Forms PFCAs

Example of Soil Microcosms with Ansul AFFF
(Harding-Marjanovic et al. ES&T 2015)





Similar results with fluorotelomer compounds seen in:
Dinglasan et al. 2004, Wang et al. 2005, Lee et al. 2010, Liu et al 2010, Dasu et al. 2012, Zhang et al. 2013

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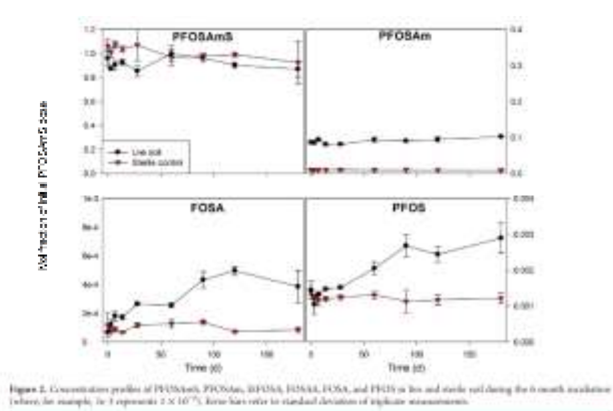
Slow Transformation of Sulfonamido Precursors to PFOS

Aerobic Soil Microcosms from Mejia-Avendano et al. ES&T 2016



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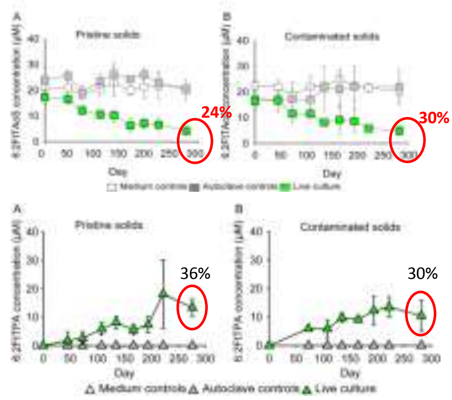
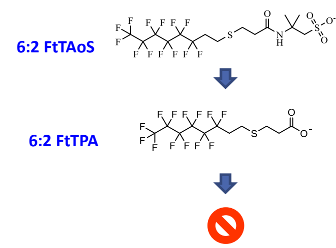
Biotransformation of Fluorotelomer Precursor under Sulfate-Reducing Conditions: No PFCAs observed

Shan Yi – American Chemical Society Philadelphia 2016





Related study - Zhang et al. 2016, Chemosphere: no transformation of 6:2 fluorotelomer sulfonate observed in anaerobic sediment, transformation of 6:2 FtOH did not yield significant PFCA products

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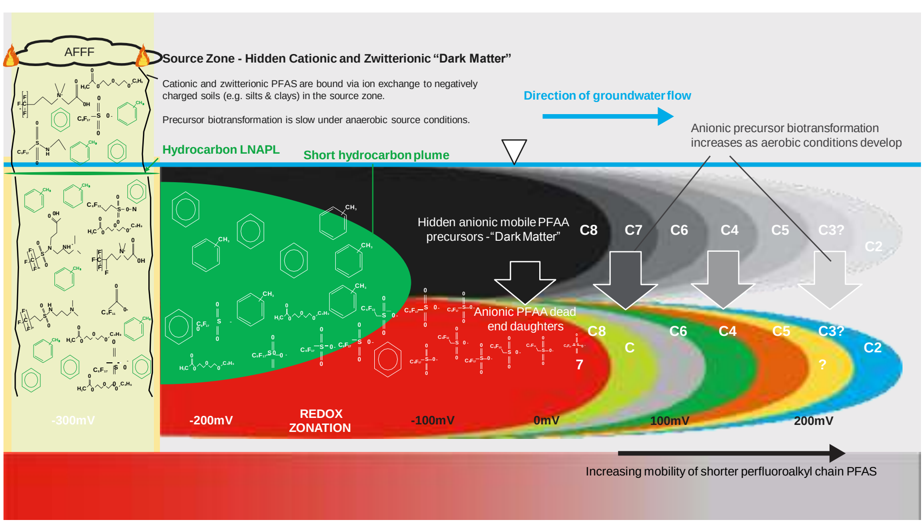
Conceptual Site Model of a Fire Training Area



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Case Study 1: SCM for a Fluoropolymer Manufacturing Facility

- PFOA used since the 1950s
- In 2000 PFOA found in a nearby Public Water Supply
- Investigation of the presence of PFOA in environmental media
- Site sources – air emissions, water discharges, on-site landfill

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SCM for a Fluoropolymer Manufacturing Facility

Public and Private Well Sampling

- Surveying and Sampling Program
- ~110 samples collected and analyzed
- Concentrations decreased with increasing distance from the site
- PFOA in cistern samples
- Concentrations higher in primary wind flow direction

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SCM for a Fluoropolymer Manufacturing Facility

Groundwater Flow – On-site and Off-site

- No off-site migration of groundwater
- Additional modeling needed to prove no transport pathway under or through river
- Multiple pumping scenarios modeled
- All showed no transport pathway under or through river

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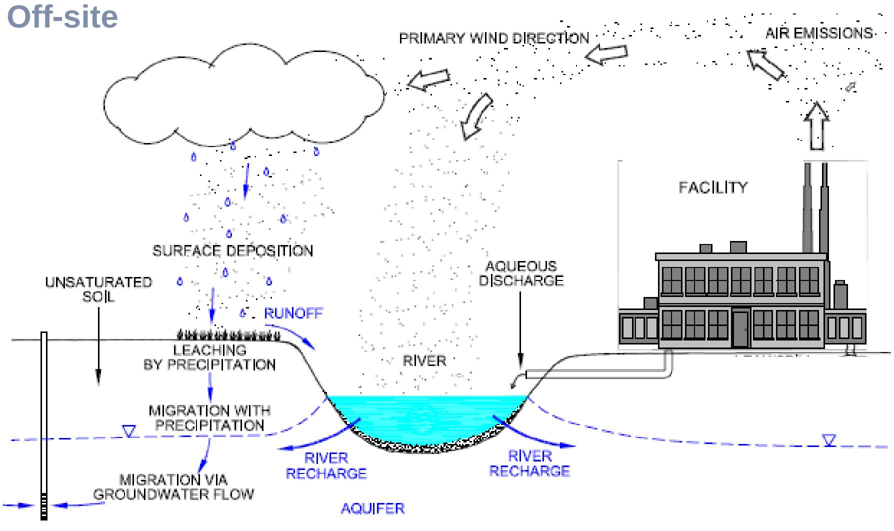
SCM for a Fluoropolymer Manufacturing Facility

Off-site



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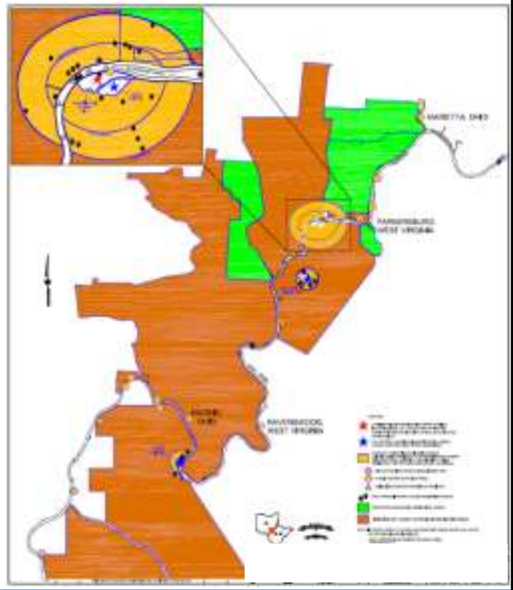
SCM for a Fluoropolymer Manufacturing Facility

Expanded Investigation Area

GAC treatment systems installed for drinking water remediation at public water supplies and private wells



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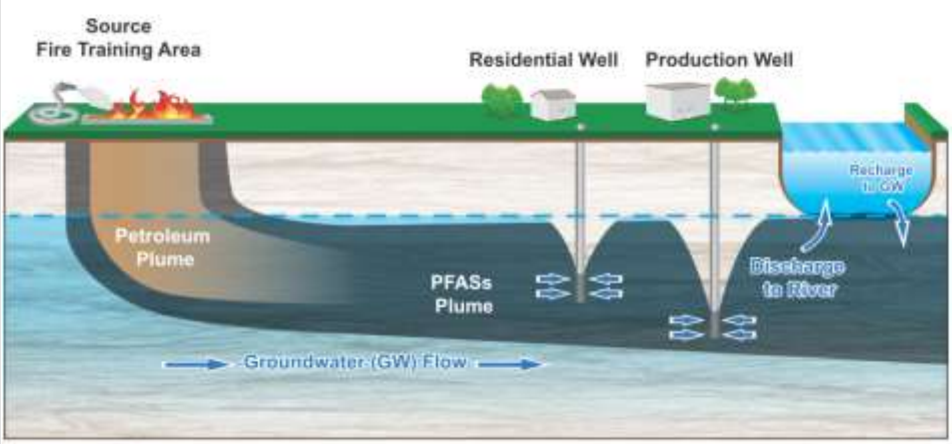
Case Study 2: Conceptual AFFF Site Model – What and Where?



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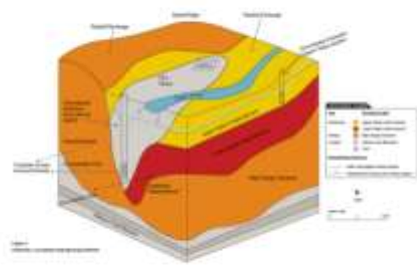
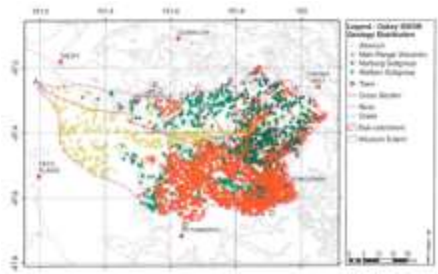
Site and Region Hydrogeological Setting





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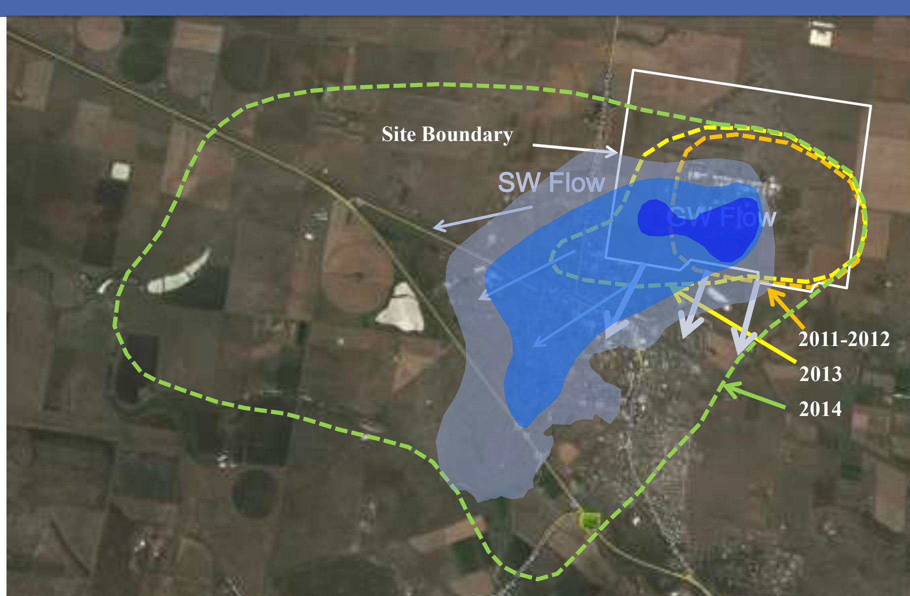
SCM AFFF Site – Characterization and F&T Evolution



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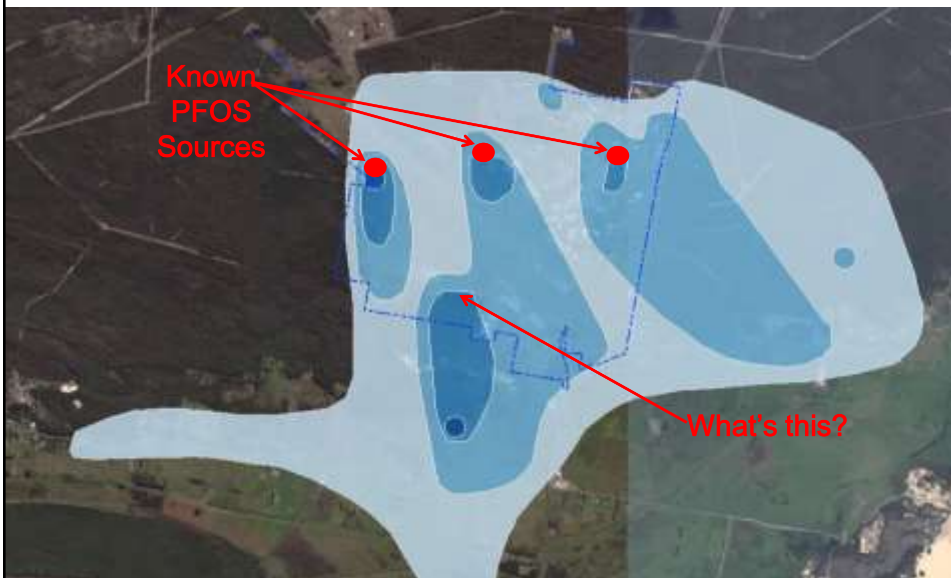
AFFF Precursor Oxidation – Impact on PFOS Concentrations



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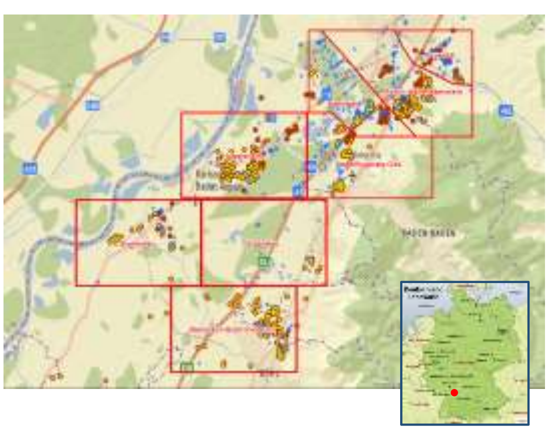
Case Study 3: PFAS-Impacted Industrial Sludges used as Agricultural Fertilizer, Southwest Germany



- ~1990's compost blended with industrial paper sludge used as agricultural fertilizer in SW Germany near Baden Baden
  - Sludge contained Polyfluoroalkyl Phosphates (PAPs) and fluorinated polymers
- Additional AFFF source from fire event
- Largest PFAS Site in Germany (3.7 Km^2); 3 Million m^3 of affected soil.
- **Underlying alluvial sandy aquifer used for drinking water**

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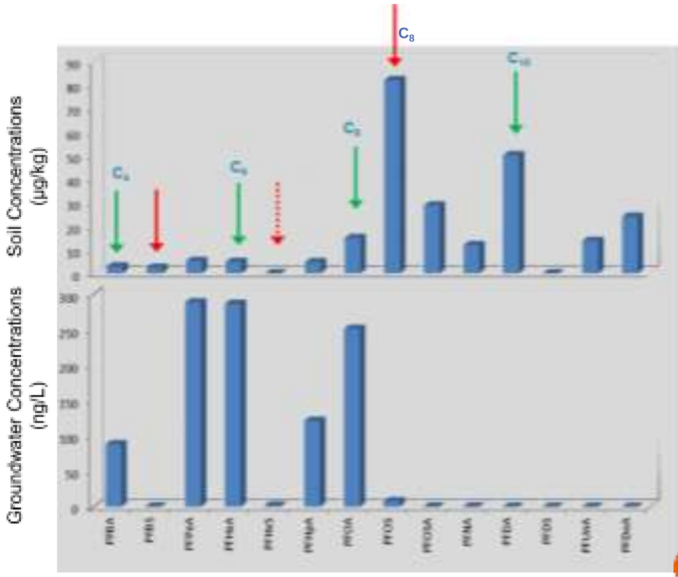
PFAS Fingerprint: Average Concentrations



- > 100 individual samples of soil and groundwater
- Soil fingerprint dominated by longer chain compounds; groundwater shows predominance of shorter chain compounds & PFOA – possibly reflective of a mixture of sources
- Lab scale K_D determinations (compounds with arrows) to evaluate adsorption
- Possible Influencing Factors: f_{oc}, carbon chain length, functional groups, anion exchange capacity, pH, ionic strength, PFAS concentration

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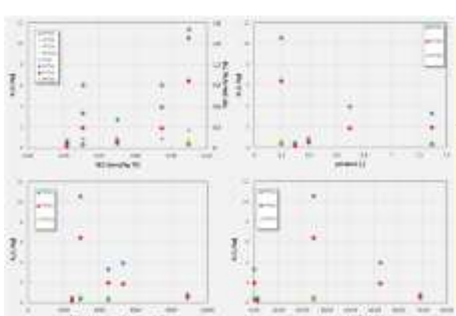
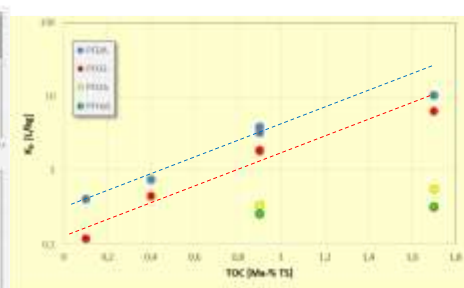
Adsorption strongly correlated with f_{OC}





K_D **did not** show strong relationship to
- Anion Exchange Capacity
- pH
- Grain size
- Clay content

K_D **did** show strong relationship to
- Total organic carbon (TOC)
- PFAS chain length

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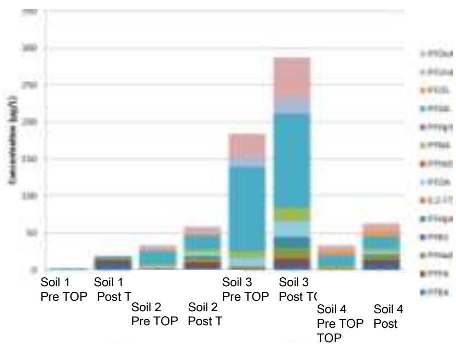
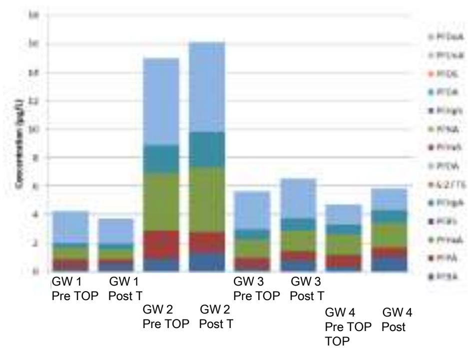
Precursor Analysis via TOP Assay: Most precursors found on soils

TOP Assay on soils:
~30-70% increase in PFAAs
C4 to C9 increases observed

TOP Assay on groundwater:
~5-10% increase in PFAAs
Minimal evidence of precursors





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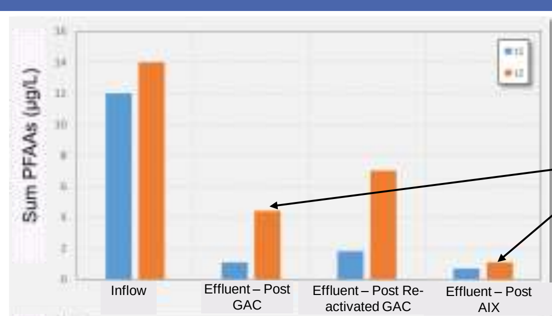
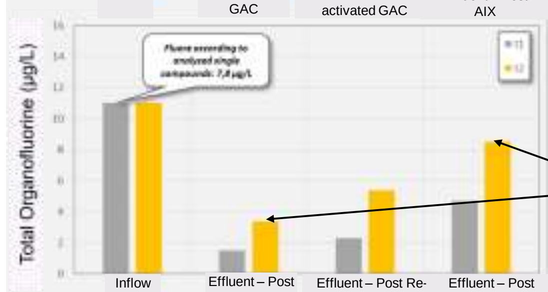
PFAAs sorbed better to anionic exchange resins (AIX) PFAA Precursors sorbed better to GAC





t1 ~ 2 weeks
t2 ~ 4 weeks

Faster breakthrough of PFAAs with GAC than AIX

Total organofluorine (i.e. PFAAs + PFAA precursors) show that total PFAS has faster breakthrough with AIX

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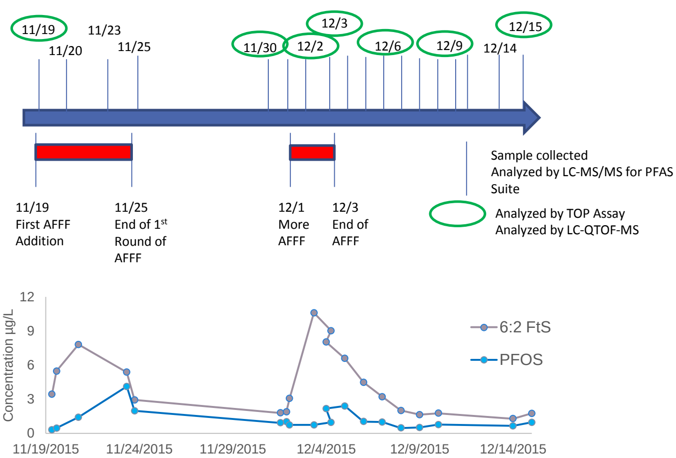
Case study 4: Fate of AFFF in a Wastewater Treatment Plant during Annual AFFF Testing

~ 15 days of testing performance of AFFF equipment and AFFF specs

AFFF waters conveyed via wash racks to industrial treatment system

Project undertaken by California DTSC Environmental Chemistry Lab



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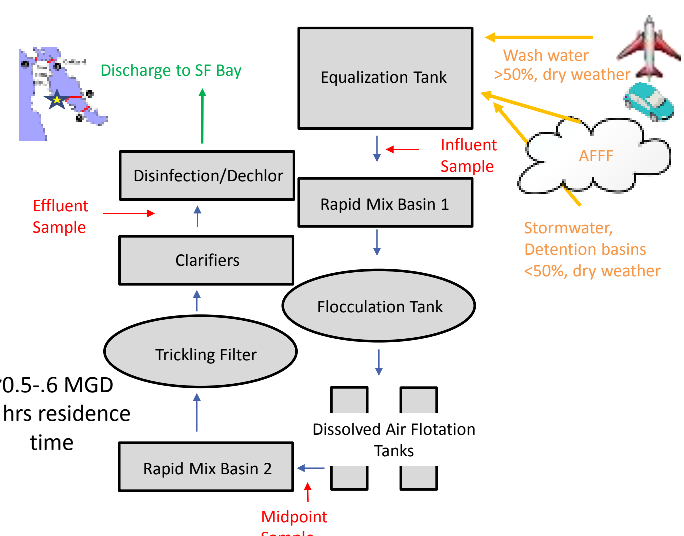
Schematic of SFO Industrial Treatment Plant



~0.5-.6 MGD
<3 hrs residence time

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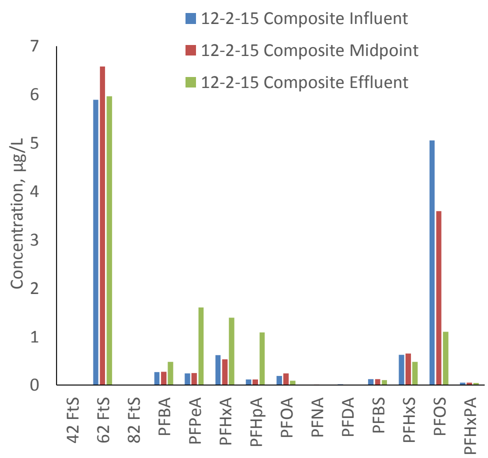
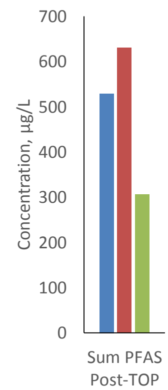
Directly Measured Analytes vs. Post-TOP Assay Total PFAS Mass



~95-98% of PFAS mass is not directly measured by target analyte list



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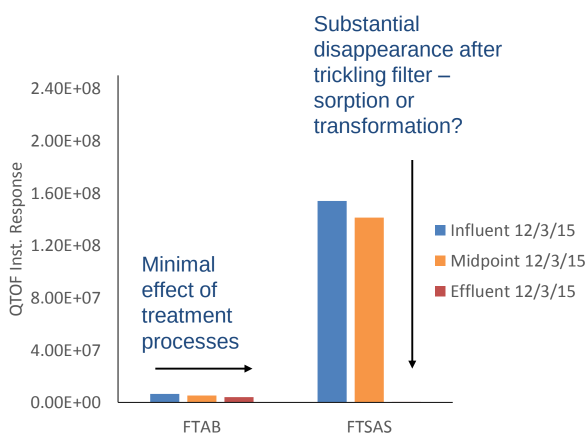
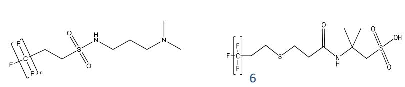
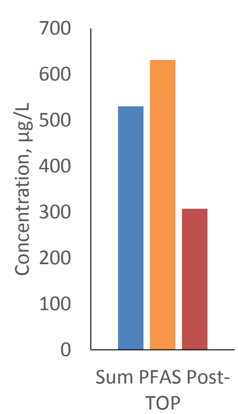
Influent to Effluent: >99% loss of 6:2 FTSAoS, ~50% loss of Total PFAS







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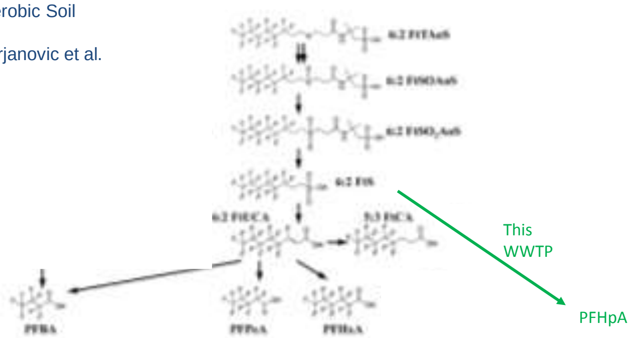
Biotransformation Pathway in WWTP Resembles Aerobic Soil Microcosm Pathway

Biotransformation of Ansul 6:2 FtTAoS in Aerobic Soil Microcosms (Harding-Marjanovic et al. 2015)



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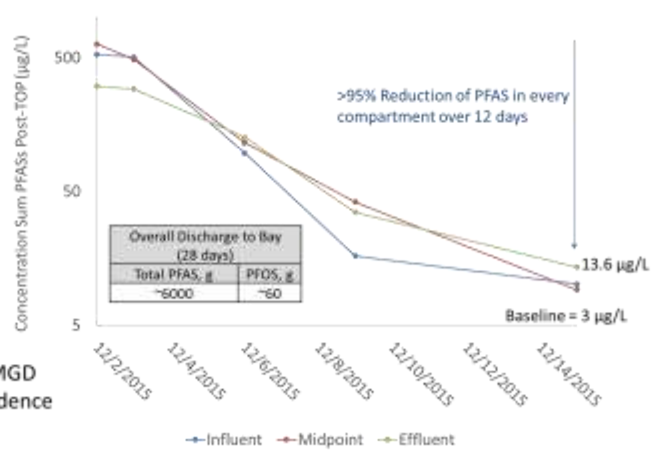
Plant Clearance of PFAS



Overall Discharge to Bay (28 days)	
Total PFAS, g	PFOS, g
~6000	~60

~0.5-.6 MGD
<3 hrs residence time

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AECOM

Conclusions

- Transport depends on chemical structure:
  - Precursors have many different kinds of functional groups
  - PFAAs are generally non-volatile and mobile in groundwater
- PFAAs are non-reactive
- PFAA precursors biotransform more rapidly under aerobic than anaerobic conditions
  - Similar transformation pathways seen in lab studies and full-scale wastewater treatment plants

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Conclusions

- Atmospheric deposition of PFAS can occur tens of miles away from the release location
- Long chain PFAA retardation in subsurface is dominated by hydrophobic sorption
  - Electrostatic effects may be more significant for cationic precursors and short chain PFAAs
- Multiple sources and local hydrogeology contribute to PFAS distribution at specific sites
- Subsurface fate and transport concepts have implications on performance of GAC, AIX, and other sorptive treatment technologies

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Questions?

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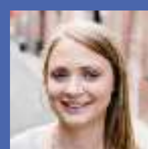

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