Measuring Poly/Perfluorinated Alkyl Substances (PFASs) in the Environment

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photo: dupont.com

Contaminants of Emerging Concern (CECs)

- Includes physical, chemical, or biological pollutants

- Limited information regarding:

  - Previously unknown human health effects
  - Exposures to humans and wildlife not widely documented
  - Effects of exposures not completely characterized
  - New materials whose environmental behavior, toxicity, and risk management are not fully understood
  - Generally, currently not included in routine monitoring programs

- May be candidates for future regulation depending on information collected

(adapted from the EU NORMAN project: www.norman-network.com , Sept 2006)

Common CECs Categories

Class	Information	Examples of use
EDCs	Endocrine Disrupting Chemicals: Exogenous substance that causes adverse health effects in an intact organism, or its progeny, secondary to changes in endocrine function (IPCS/WHO, 2002)	• Steroid Hormones • Surfactants (APEs) • Pharmaceuticals
PPCPs	Pharmaceuticals and Personal Care products: Broad group including industrial, agriculture, and home use products Often lower concentrations but higher biological activity than traditional contaminants	• Human and Vet Drugs - Antidepressants, hormone supplements, antibiotics, ibuprofen, acetaminophen • Food and lifestyle – nicotine metabolites, caffeine, soy products • Personal Care Products - Bactericides, sunscreens, synthetic musks, detergents
Nano	Nanoparticles: Particles < 100 nm in size Form of particle may affect fate, transport, toxicity, and risk management as well as chemical species	• Sunscreens (TiO_2) • Silver antibacterials
Biological	Biological: New biological materials Organisms where limited knowledge is available	• Proteins –prions, genetically modified products (Bt corn) • *Helicobacter pylori*, *Mycobacterium avium*, *Toxoplasma gondii*, adenovirus, norovirus
PFASs	Poly & Perfluoroalkylated (PFASs) substances: Precursors (polymers and monomers) Poly & Perfluoroalkylated Acids (PFAAs)	• Stain guards • Fire fighting agents • Paper and Food packaging

Emerging Contaminants enter the environment

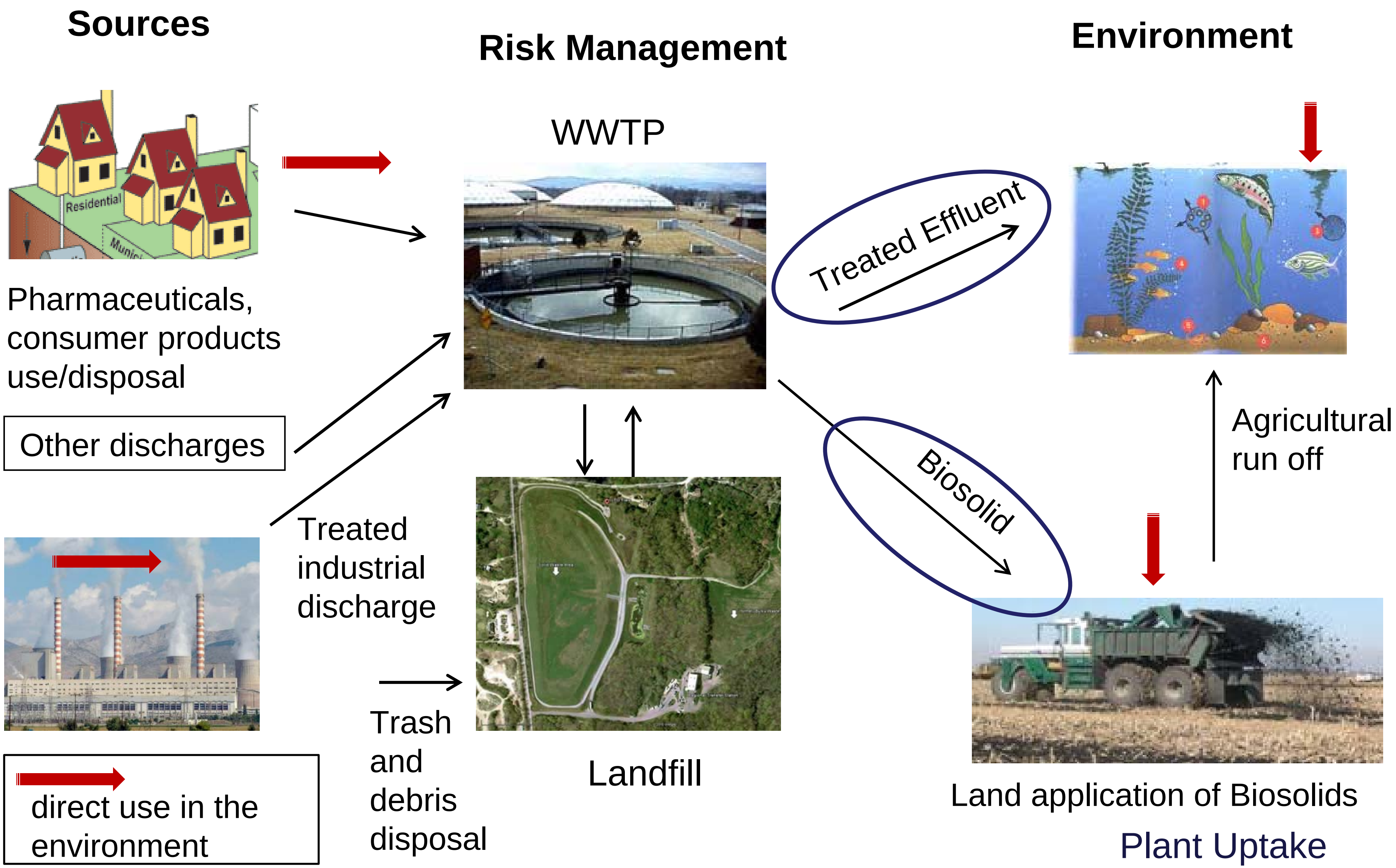
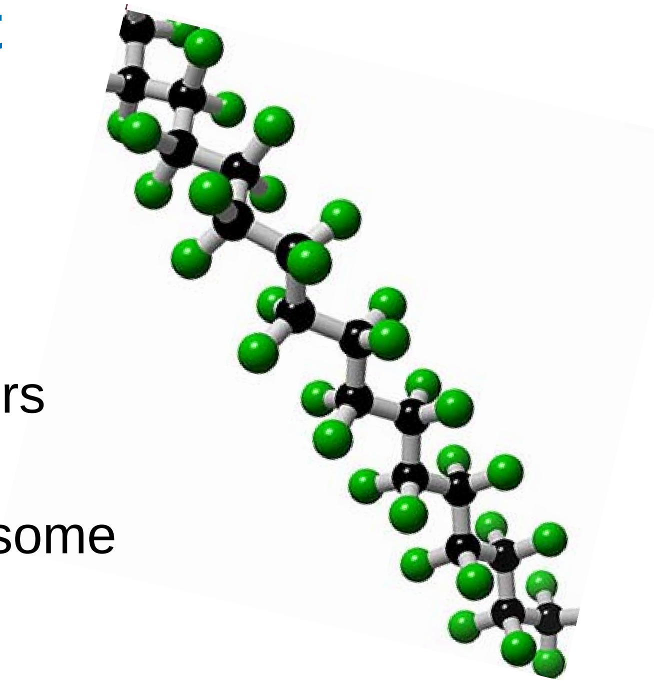


Photo Courtesy: USEPA, USGS, Artsyltech, West basin, Royer

PFASs Fate and transport



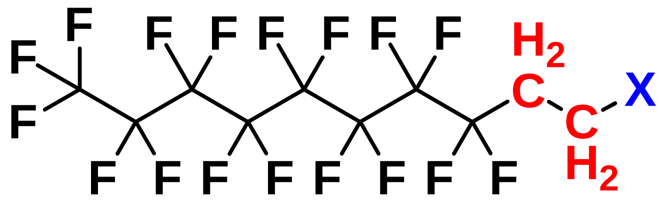
- Environmental concerns
  - Ubiquitous - found world-wide
  - Residuals during production of fluoropolymers released directly
  - Preliminary research shows degradation of some fluorotelomers
    - urethanes and acrylates
    - kinetics subject of continued research
- Fate and transport data is limited due to analytical limitations and minimum physical, chemical, and biological data on the wide range of PFASs in use and their degradation products

Effects and Fate

- Bioaccumulative in wildlife and humans (rising blood levels)
- Adverse effects in laboratory animals and wildlife
  - PFOS and PFOA shown developmental toxicity [1]
  - Highly persistent and bioaccumulative (t $_{1/2}$ PFOA ~4 yrs in humans)
  - Alter biosynthesis of gender-specific steroid hormones[1,2]
  - Decline in thyroid hormone levels[1,3]
- Little data about presence in environment (soils, water, groundwater, biosolids, etc)
- Environmental controls
  - Water - 0.4 µg/L for PFOA (US EPA OW, PHA)
  - Residential soil – 16 mg/kg (US EPA Reg 4, screening level)
  - PFOS, its salts and perfluorooctane sulfonyl fluoride have been listed under Annex B of the Stockholm Convention on POPs
  - EPA initiated 2010/2015 PFOA Stewardship Program with 8 global manufacturers - 95% reduction in direct emissions and residuals in products by 2010. Complete elimination by 2015

[1]Lau et al., 2007; [2]Biegel et al., 1995 ; [3]Chang et al., 2009

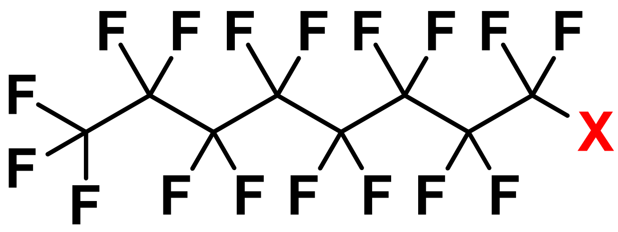
PFASs



x = halides, alcohol, olefin, ester

Polyfluorinated Compounds (Fluorotelomer)

- Even Numbered Chains
  - precursors
  - residuals

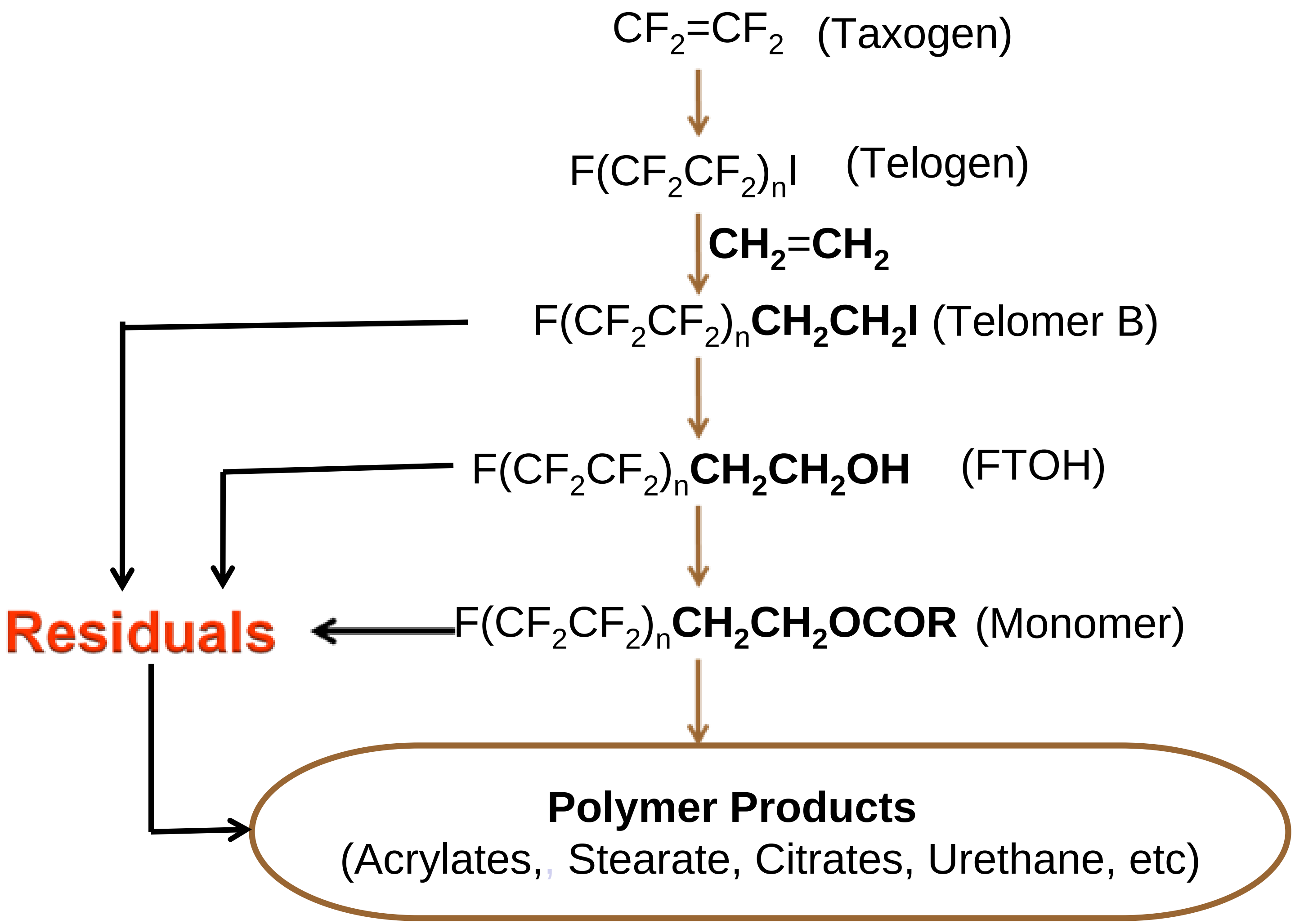


x = carboxyl, sulfonyl

Perfluorinated Compounds

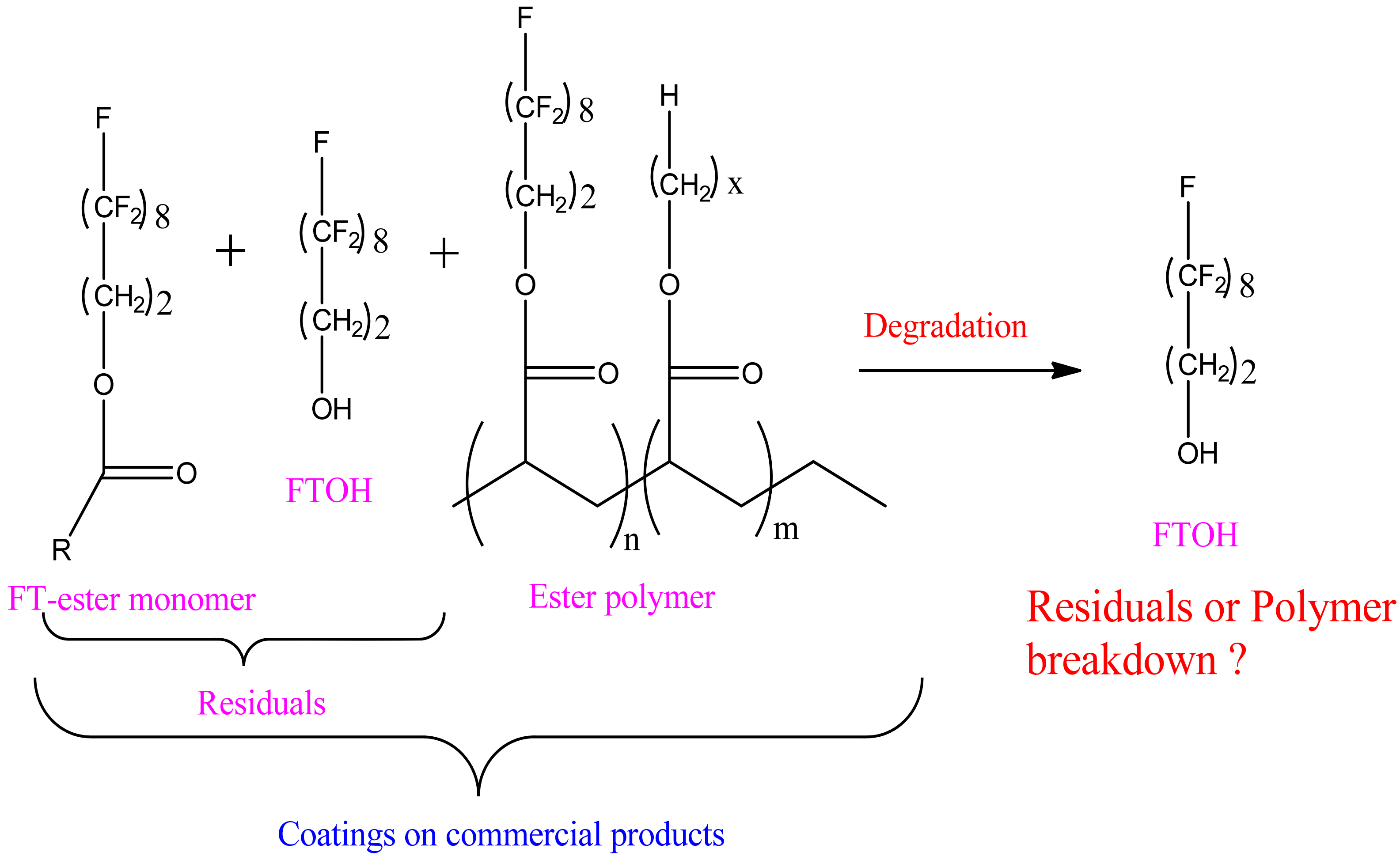
- Two primary types of chemistry
  - perfluoroalkylsulfonates (PFSA)
  - perfluoroalkylcarboxylate (PFCA)
  - Different production methods results in different mixtures of even and odd chains

Telomerization Process



- Only even numbered products are formed
- > 80% of the fluorotelomer compounds are used as polymers

Fluorotelomer polymer coatings



5 to 6.5 $\times 10^6$ kg of fluorotelomer-based products produced annually

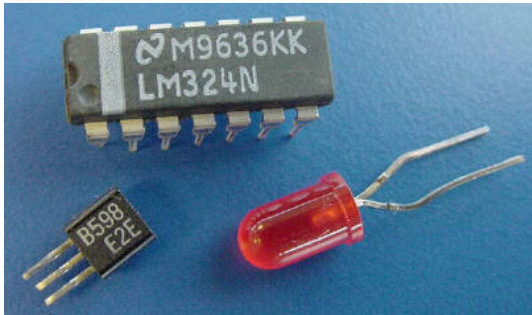
U.S. EPA Public Docket AR226-1141, 2002

EPA United States Environmental Protection Agency

PFASs use and production

- Uses
  - coatings for textile and apparel
  - fire fighting foams
  - manufactured in US or elsewhere
  - imported or processed to generate commercial goods
  - many industry segments including aerospace, automotive, building/construction, chemical processing, semiconductors, textiles

- Production
  - PFSA – total production 1970 to 2002 ~100,000 tons
  - PFCA – world wide in 2006 ~ 10,000 tons



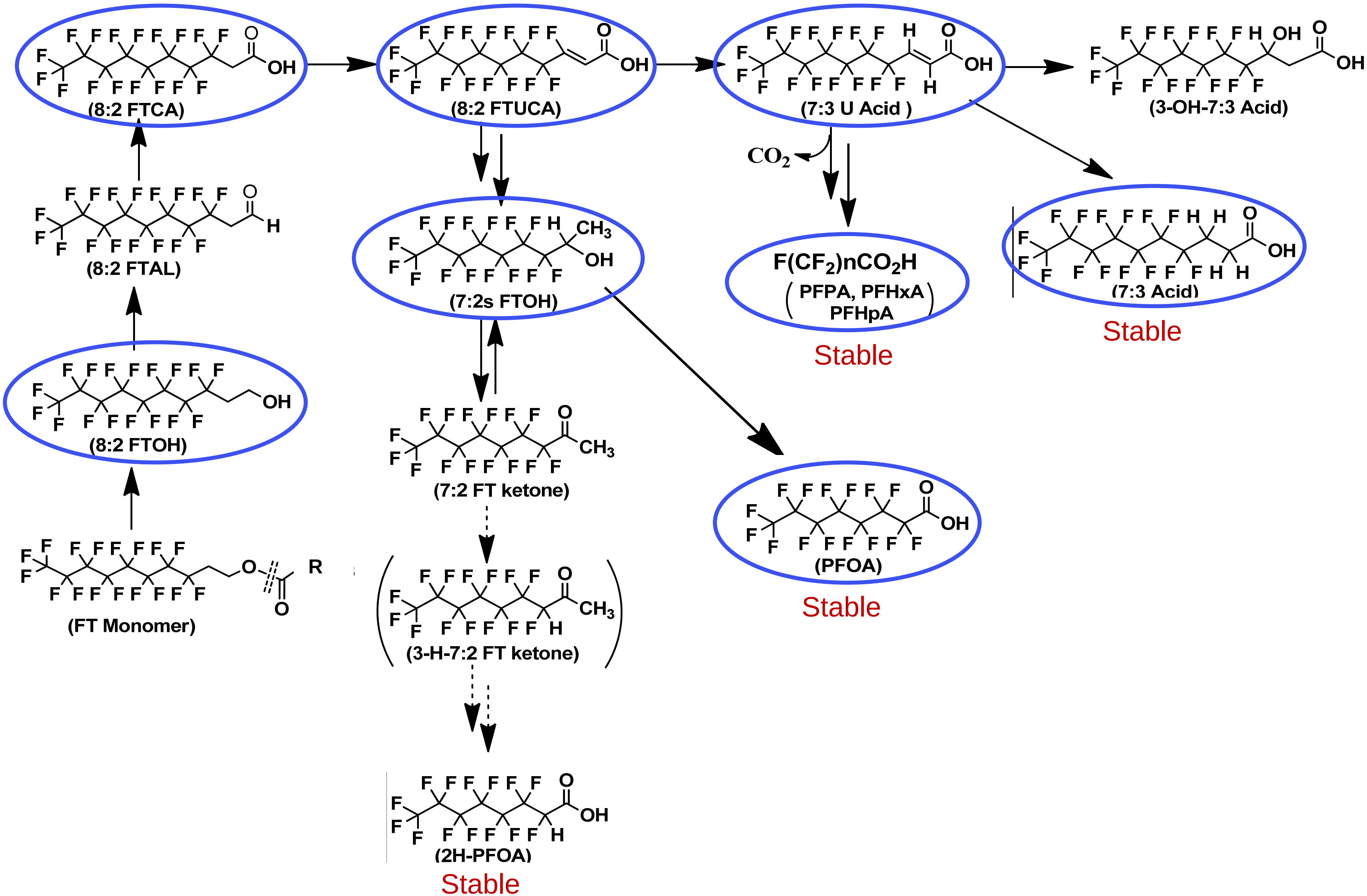
Fate and Transformation

- Due to difficulty in quantitatively measuring these compounds, environmental data of fate and transport are limited and subject to significant uncertainties

- Some species are volatile
  - fluorotelomer alcohols (FTOHs)
  - protonated PFOA

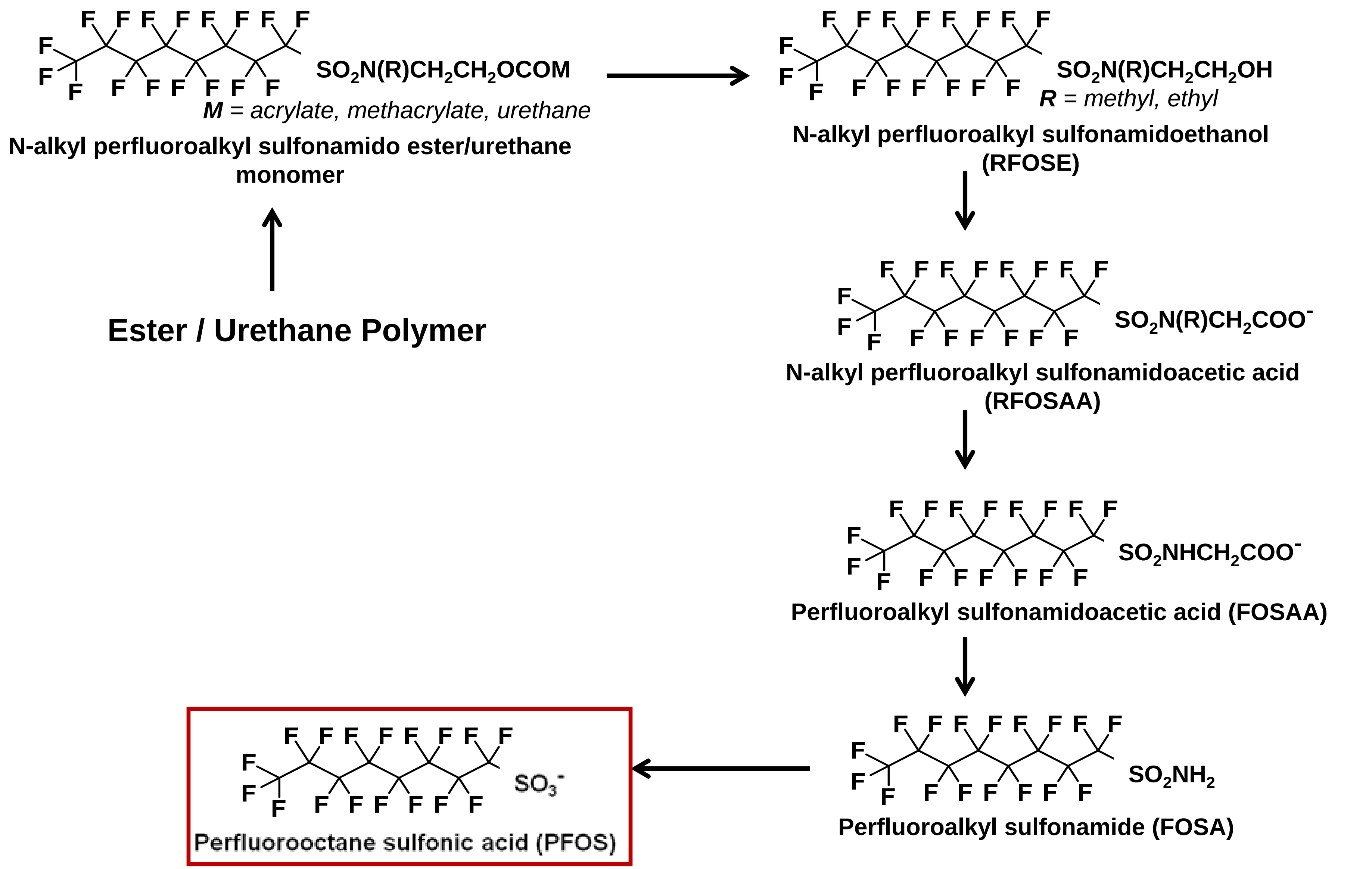
- Aerobic reactions
  - complex reaction pathway
  - some compounds present as residuals in commercial products
  - must be able to distinguish degradation from transformation of process residuals
- Anaerobic reactions - reports of reductive dehalogenation

Biodegradation Pathway of Fluorotelomer Derivatives

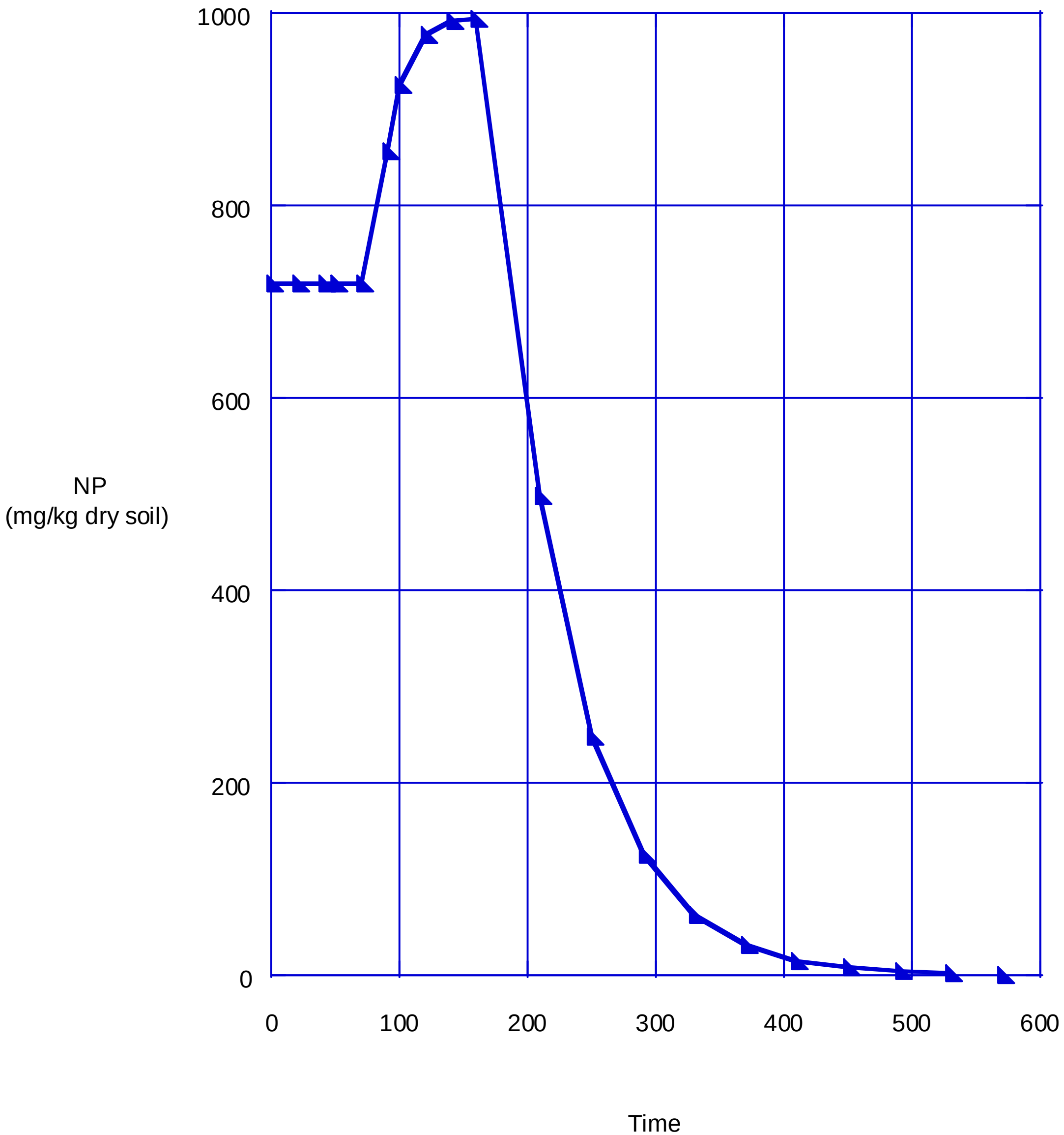


(Modified from Wang et al., 2009)

Transformation Pathway of Sulfonamide derivatives



Importance of precursors and pathways



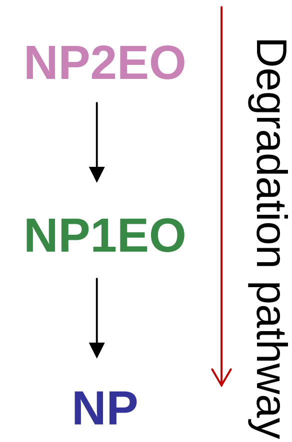
- Example:

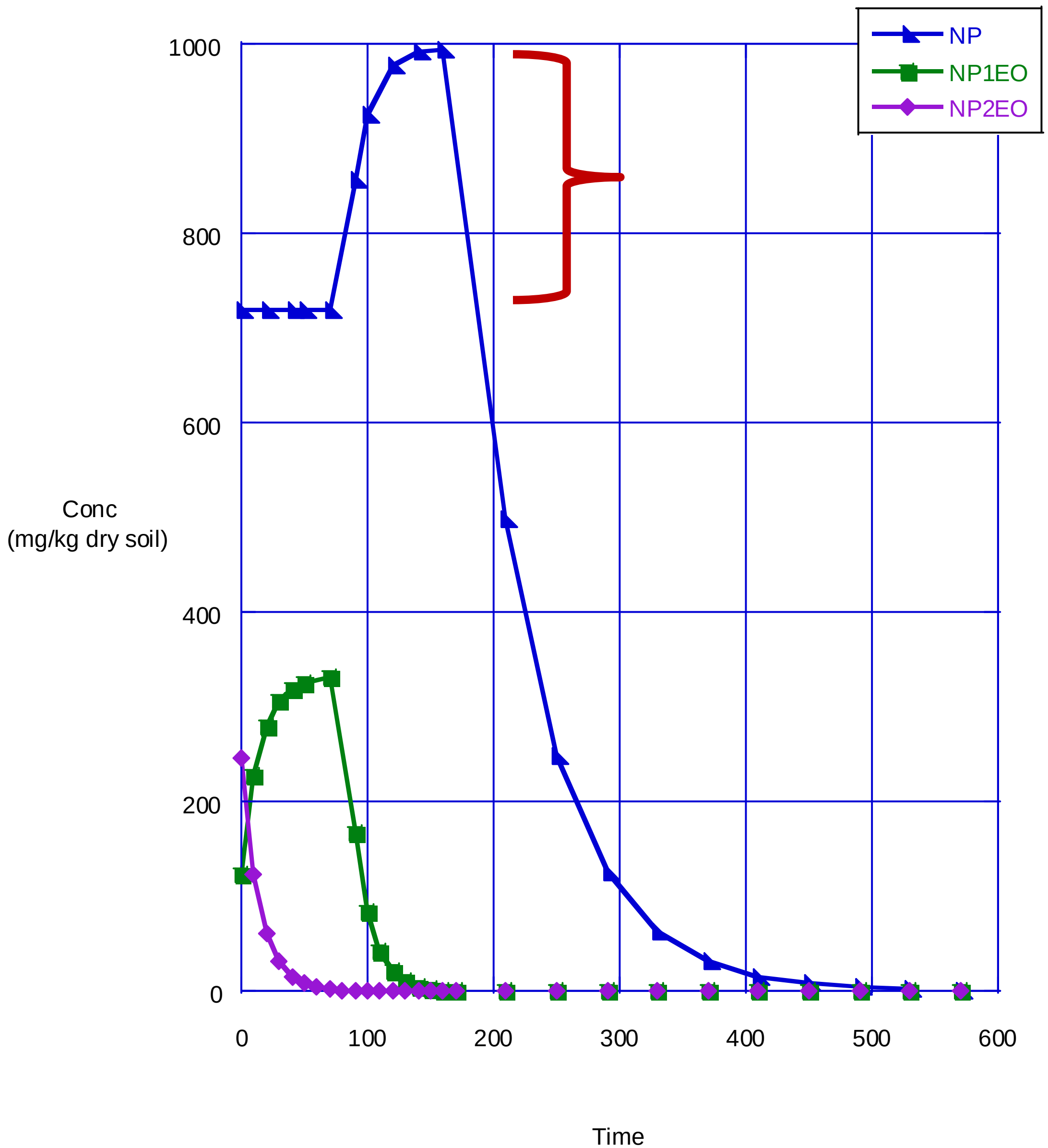
  NP as a function of Time

- If only monitoring NP:
  - flat initially
  - 40% increase between 70 and 170 days
  - decrease after 170 days

United States Environmental Protection Agency

Degradation of precursors to NP – “Created” NP





- Accounting for the precursors and their degradation pattern explains observations
- 240 mg of NP2EO converted to 200 mg of NP1EO
- eventually 300 mg additional of NP produced
- transformation rate and masses affect observation

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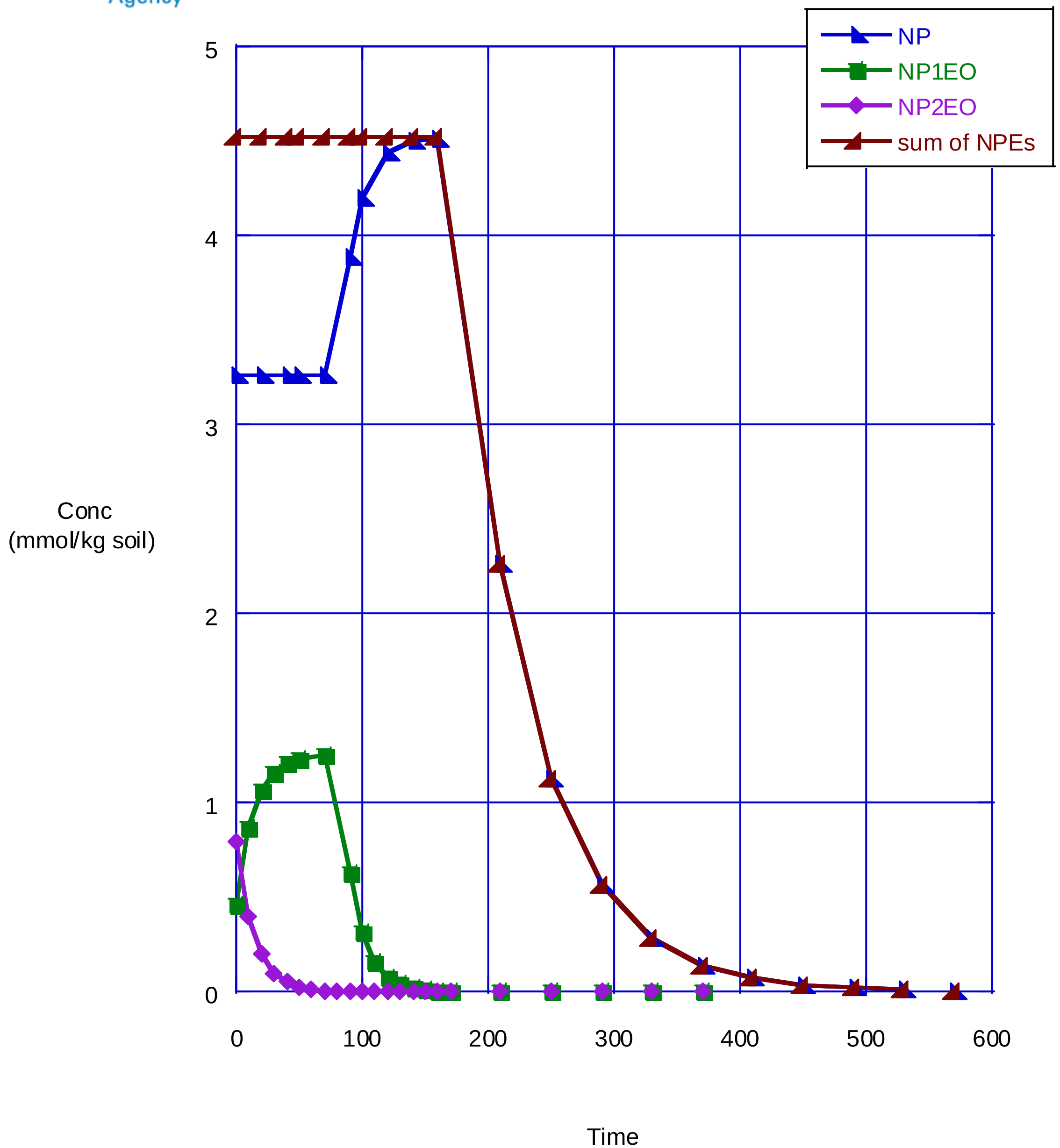
All NPE Data graphed - molar basis



NP2EO

↓

NP1EO

↓

NP

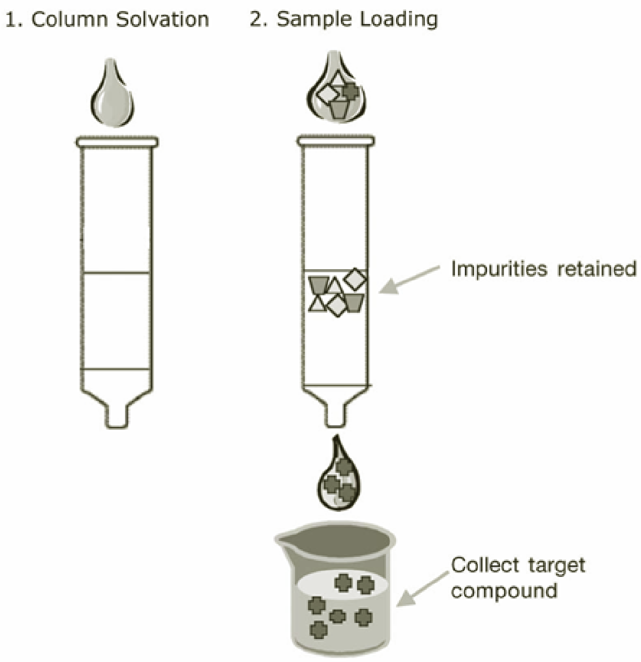
Degradation pathway

- include all relevant precursors and metabolites in the pathway to track transformation and removal
- molar basis simplifies quantitative tracking
- molar sum of NPEs – unified variable

Analytical Methods for PFASs

- Compounds are chemically different than traditional contaminants
  - more hydrophilic
  - fluorocarbon chemistry
  - levels are typically very low and often in difficult matrices (e.g WWT residuals)

- Typical analytical methods
  - extraction
  - solid phase
  - ASE (accelerated solvent extraction)
  - clean up
  - measurement using chromatography paired with MS/MS

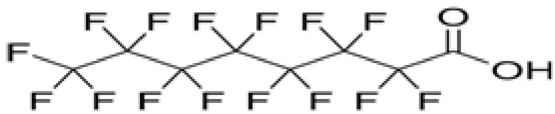


- QA/QC checks are critical to assuring data quality
  - Analysis of blanks to identify sample contamination
  - Accounting for ion suppression/enhancement
  - Surrogate recoveries
  - Matrix spikes

Measuring Selected Perfluorinated Alkyl Acids (PFAA) in biosolids and waste water by LC/MS/MS

Shoji Nakayama (NIES, Japan), Kavitha Dasu (NRC/EPA)
Marc Mills (USEPA, ORD) 513-569-7322

Example:PFOA - perfluorinated octanoic acid



Warning: PFCs are present in most Teflon materials. Anything used in this sampling and analysis effort must be free of Teflon. So test tubes, pipets, glassware have to be non-Teflon and rinsed well with methanol before use. Blanks must be carried through sample and analysis processes to identify interferences.

Sample preparation

Weigh 0.5 g Biosolid

1. Add 2mL of KOH into sample and vortex
2. Add 5 mL MeOH and mix

3. Sonicate sample for 30 min

1

1

4.Shake sample for another 30 min

5. Centrifuge the sample
6. Collect the supernatant portion

7. Add 45ml DI water to the supernatant

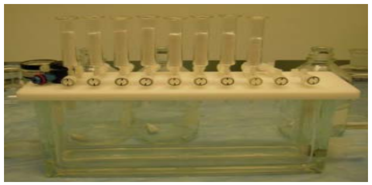
2

Draft method. Not endorsed by EPA. Please do not cite or quote.

2

SPE extraction and Clean up

8. SPE cartridge : Condition a WAX and ENVI-Carb Cartridge



9. Sample Loading:
About 50 mL of sample was passed through the WAX Cartridge then followed by Elution through the ENVI –Carb cartridge. To Elute use 0.1% ammonia in MeOH

11. Concentrate the elute to about 1 mL
12. Add 100uL of IS
13. Adjust sample volume to 1 mL with MeOH

14. Prep for Instrument
Blank = 1: 1 of MeOH/ mobile phase (10mM Formic Acid).
Samples= 100uL of mobile phase with 100uL of sample.

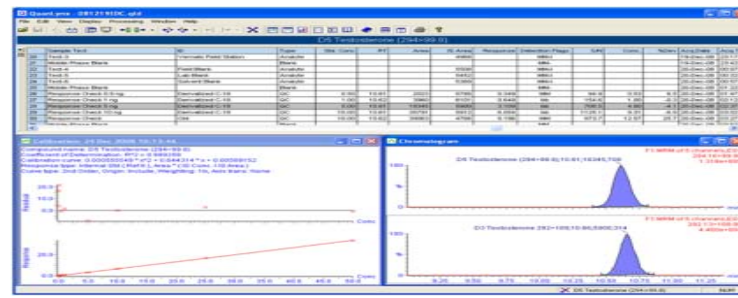
3

3

Measurement

15. Load onto LC/MS/MS

Data Analysis/QC

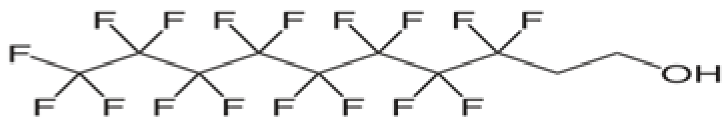


Check spectra for ion suppression or enhancement.
Check Surrogate recovery within **70 – 130%.**
Check calibration standards within **70 – 130%** of true value.
Lab and solvent blanks should not contain targets (no peaks present).
Flag data as suspect if QC fails. Repeat analysis if sufficient sample.
For frequent violation (> 10% samples), investigate problem, and repeat the sampling event.

Measuring Selected PFAA precursors (FTOHs) in biosolids and waste water by GC/MS/MS

Shoji Nakayama (NIES, Japan), Kavitha Dasu (NRC/EPA)
Marc Mills(USEPA, ORD) 513-569-7322

Example :8-2 FTOH: 8-2 fluorotelomer alcohol



Warning: PFCs are present in most Teflon materials. Anything used in this sampling and analysis effort must be free of Teflon. So test tubes, pipets, glassware have to be non-Teflon and rinsed well with methanol before use. Blanks must be carried through sample and analysis processes to identify interferences.

Sample preparation

Weigh 0.5 g Biosolid

1. Add 2mL of KOH into sample and vortex
2. Add 5 mL EtOAc and mix

3. Sonicate sample for 30 min

1

1

4.Shake sample for another 30 min

5. Centrifuge the sample
6. Collect the EtOAc portion

7. Repeat steps 2-5 two times and each time collect the EtOAc portion. Combine all extracts

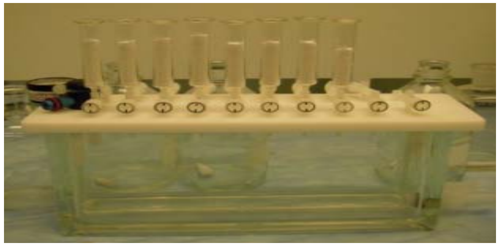
2

Draft method. Not endorsed by EPA. Please do not cite or quote.

2

SPE extraction and Clean up

8. SPE cartridge conditioning:
Pass 4 mL EtOAc and keep cartridge wet



9. Sample Loading: The EtOAc portion is passed through ENVI-Carb cartridge
10. SPE extract: The Elute is collected

11. Concentrate the elute to about 800uL
12. Add 100uL of IS
13. Adjust sample volume to 1 mL with EtOAc

14. Prep for Instrument
Blank = EtOAc
Samples= 100uL in a 200-uL
Glass insert GC auto sample vial.

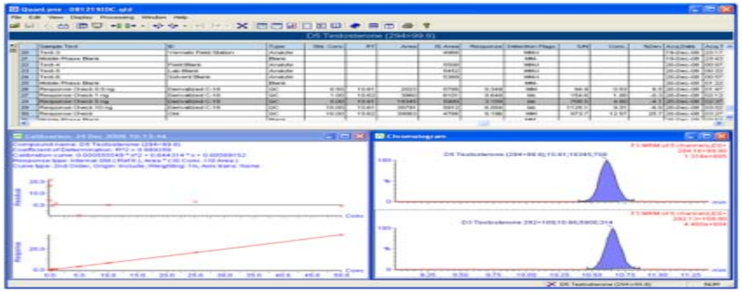
3

3

Measurement

15. Load onto GC/MS/MS

Data Analysis/QC



Check spectra for ion suppression or enhancement. Check Surrogate recovery within **70 – 130%.** Check calibration standards within **70 – 130%** of true value. Lab and solvent blanks should not contain targets (no peaks present). Flag data as suspect if QC fails. Repeat analysis if sufficient sample.
For frequent violation (> 10% samples), investigate problem, and repeat the sampling event.

Unknown Analysis

United States Environmental Protection Agency

Initial Full scan on UPLC-TOF/MS

↓ Accurate mass spectrum

Identification of relevant intensity signals and prominent chromatographic peaks

↓

Additional MS/MS experiments at different collision energies to analyze fragmentation pattern for structural elucidation and identification

← Further confirmation

Fragmentation is further confirmed on Orbitrap MS using multiple MS^n experiments

↓ Further confirmation

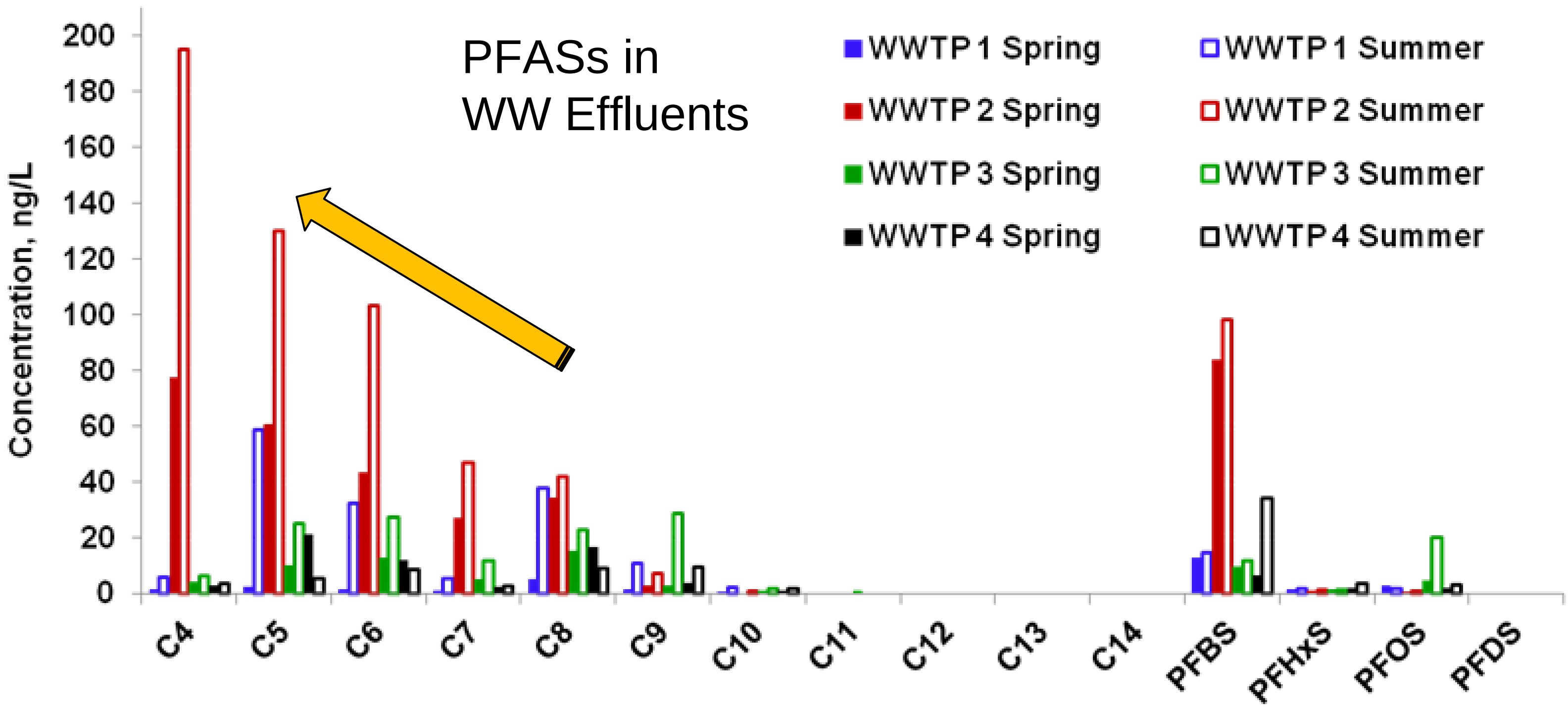
Fraction collected based on retention times of the respective peak

↓

Analyzed on the ^{13}C and ^{19}F NMR for further structural confirmation

Changing targets with changing formulations

- Industry continues to modify their formulations to meet consumer needs and regulatory drivers.
- Changes include:
  - Shorter carbon chain lengths (<C6) – no longer just C8 chemistry
  - Use of polyfluorinated chemistries – not completely saturated with fluorines
  - Use of alternative chemistries for linkages – more ether and oxetane linkages to polymer



SERDP Project (ER-2426): Quantification of In Situ Chemical Reductive Defluorination (ISCRD) of Perfluoroalkyl Acids in Groundwater Impacted by Aqueous Film-Forming Foams (AFFF)s

- Project leads: Dr. Linda Lee and Dr. Loring Nies, Purdue University,
  Dr. Victor Medina, USACE ERDC
  Dr. Marc Mills and Dr. Kavitha Dasu, USEPA ORD
  Dr. Hongtao Yu, Jackson State University

- Project schedule: FY14 New start
  3 year project

- Project Need:
  - Targeting Perfluoroalkyl substances (PFASs) found in aqueous film-forming foams used to fight fires
  - Training with AFFFs at DOD sites for more than 30 years has resulted in repeated short-term releases of AFFFs at training areas resulting in nearly 600 military sites being exposed to AFFFs.

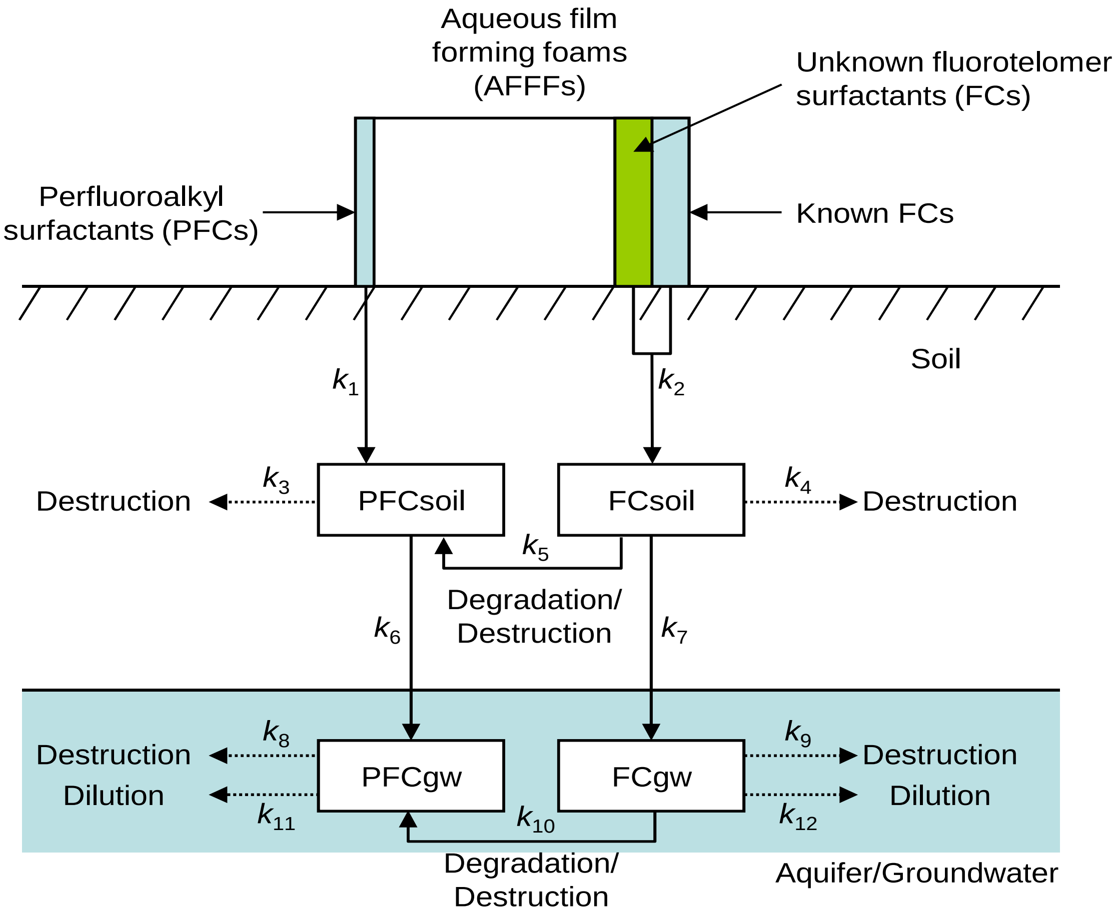


Figure 2. Two-dimensional conceptual site model (CSM) showing fate/transport and remediation of fluoroalkylchemicals

Project Objectives:

Evaluate the use of zero valent metals/bimetals (Pd_0/Fe_0, Mg_0, Pd/Mg_0) including Pd_0/Fe_0 synthesized within clay interlayers (for ease of injection and reduced loss of reactivity) as well as co-solvent assisted Vitamin B12 defluorination.

1. quantify the magnitude, rate, and effectiveness of abiotic reductive techniques to defluorinate linear PFOS in aqueous systems within an environmentally relevant conditions (ie concentration range, pH, temperature)
2. characterize intermediates resulting from incomplete defluorination
3. quantify effectiveness of smectite intercalated Pd0/Fe0 to defluorinate PFOS by measuring PFOS loss and generation of fluoride and sulfate
4. quantify the effect of ionic composition and co-contaminants in aqueous systems defluorination in a subset of reductive systems
5. evaluate defluorination in vadose zone soils and aquifer materials using a subset of the most favorable abiotic reductive transformation approaches
6. assess increased potential for oxidation of intermediates towards evaluating selected reductive/oxidative treatment trains

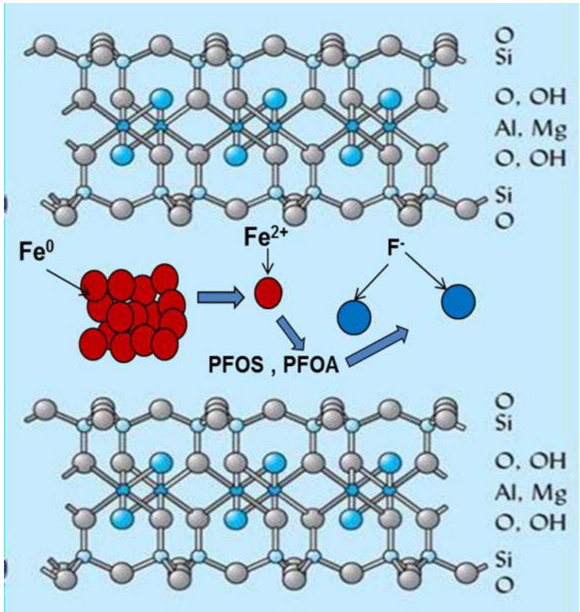


Figure. 2

<u>Benefits</u>: This research will address the reductive reaction mechanisms and pathways (intermediates) for defluorination of PFOS and associated PFASs, which will facilitate design of an in-situ strategy for remediation of PFAS-contaminated groundwater at military sites with minimal adverse impacts.

Sources of Information

- US EPA webpage
  - PFSAs
    - general information http://www.epa.gov/opptintr/existingchemicals/pubs/actionplans/pfcs.html
    - public health advisory http://www.epa.gov/opptintr/pfoa/pubs/pfoainfo.html#provisional
    - screening level http://www.epa.gov/region4/water/documents/d_final_pfc_soil_screening_values_11_20_09.pdf
    - Regulations - PFOS Stockholm Convention list- http://chm.pops.int/Implementation/NIPs/Guidance/GuidancefortheinventoryofPFOS/tabid/3169/Default.aspx
    - SNUR
    - http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html#final
  - Other Chemicals
    - TNSSS http://water.epa.gov/scitech/wastetech/biosolids/tnsss-overview.cfm
    - chemical action plans http://www.epa.gov/opptintr/existingchemicals/pubs/ecactionpln.html
  - Biosolids - http://water.epa.gov/polwaste/wastewater/treatment/biosolids/index.cfm

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  - Cathy Fehrenbacher
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