Charge Question 1: Total PFAS Methods

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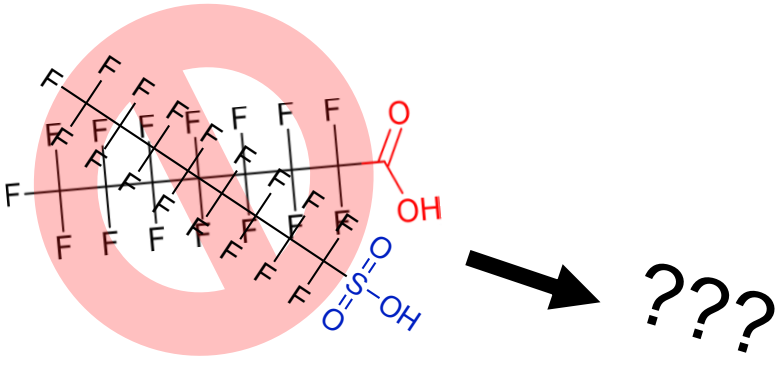
Goals

- To provide an overview on non-targeted methods, including descriptions of suspect screening and non-targeted analyses, total or adsorbable organic fluorine, total oxidizable precursor methods
- What do these different methods do and what technologies are (generally) used?
  - Suspect Screening Analysis and Non-Targeted Analysis (NTA)
  - Total or Adsorbable Organic Fluorine (TOF or AOF)
  - Total Oxidizable Precursor (TOP)

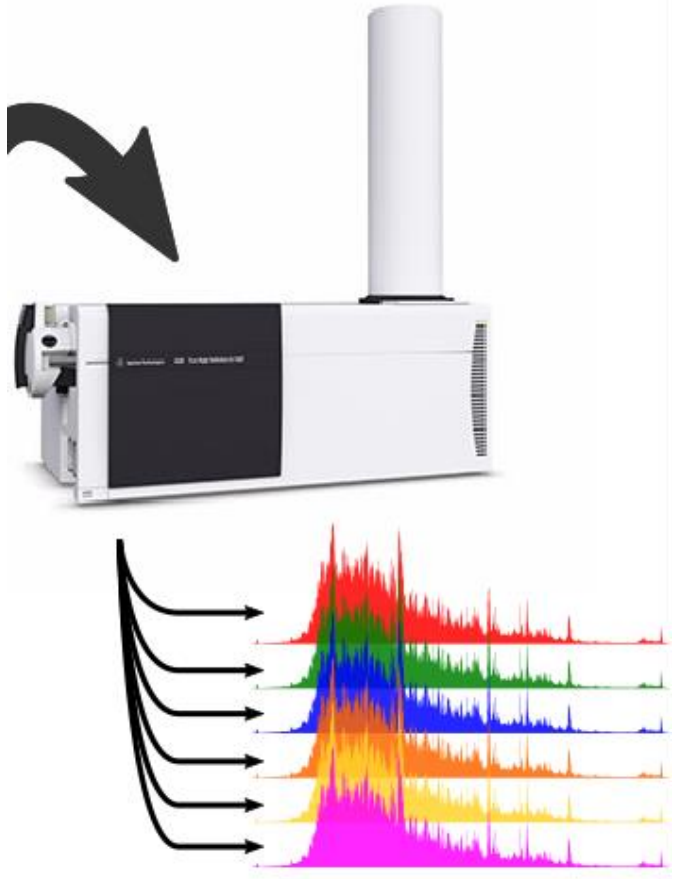
PFAS Non-Targeted Measurements and Analysis

- Why do we need NTA? Modern commerce introduces large numbers of novel chemicals with unknown properties
- Post-PFOA stewardship agreement / PFOS phaseout, proliferation of replacement species that are unknown
- Pressing need for comprehensive, quantitative, and rapid analysis to identify these unknowns
- NTA allows straightforward exploratory investigation of wide ranges of environmental media, consistent with existing sample preparation



PFAS Non-Targeted Measurements and Analysis

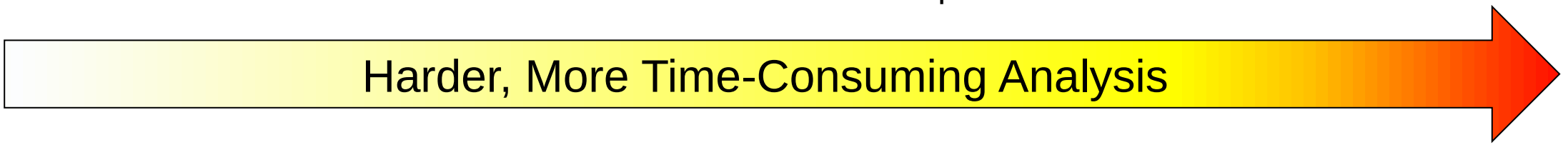
- Modern, high resolution, non-targeted mass spectrometry provides the tools to address these issues
  - Identification of unknowns
  - Quantitative (*if standards exist*) /Semi-quantitative (*using surrogates*) measurements
  - Level of detection ~0.001 ppb*
  - High-throughput analysis *(parallelized compound examination, rapid analysis workflow)*
- NTA does not require presuppositions about sample contents; ***necessary for discovery of emerging contaminants***
- Processing of NTA data requires many different software tools and approaches; ***expertise is required for high-quality results***
- NTA data can support early-stage monitoring and treatment experiments in absence of absolute quantitation



* Ateia et al., **2019** *Chemosphere,* 220: 866-882

Chemical Measurement Approaches

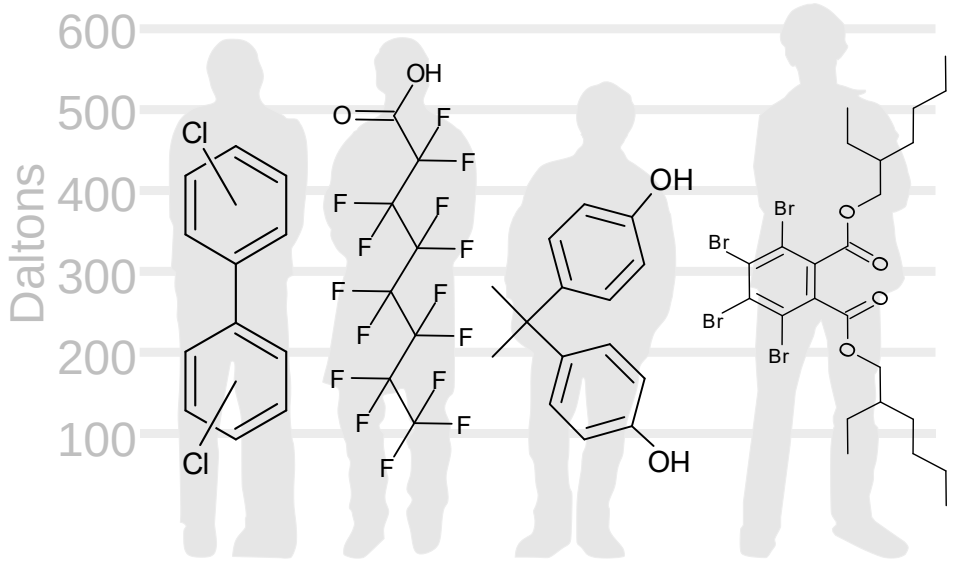
	Targeted	Screening	Discovery
Chemical Targets	Few, selected chemicals	100s – 100,000s per library	Any chemical
Method of Analysis	Focused method	Non-Targeted Method	Non-Targeted Method(s)
Chemical Structure	Known	Known in library	Unknown
Reference Data	Available	Some	Some, maybe simulated
Standards	Available	Maybe, for common compounds	Unlikely



Non-Targeted Data Analyses

Suspect screening analysis (SSA)

- Match unknowns to expected chemical set
- Can be custom list or compound library
  - Vendor Libraries, DSSTox, Transformation Products



Non-Targeted Analysis (NTA)

- Identify unknown structures of chemicals *without a chemical list*
- Relies on multiple experiments and techniques to build an identification

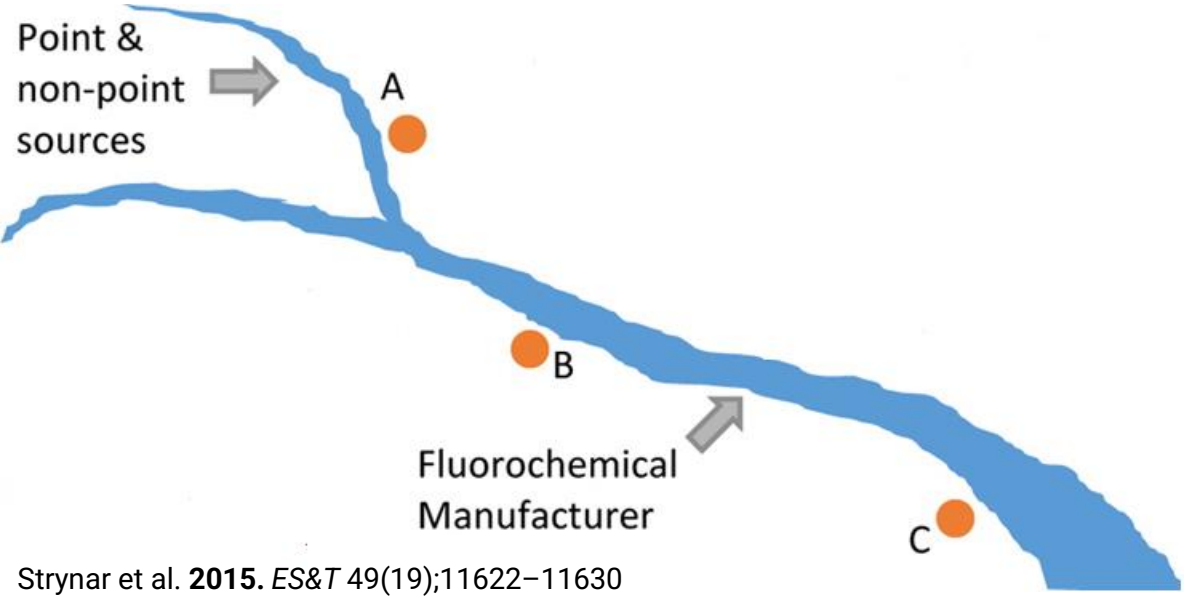
Cape Fear Case Study: Water NTA

Environmental Science & Technology — November 2015

Article

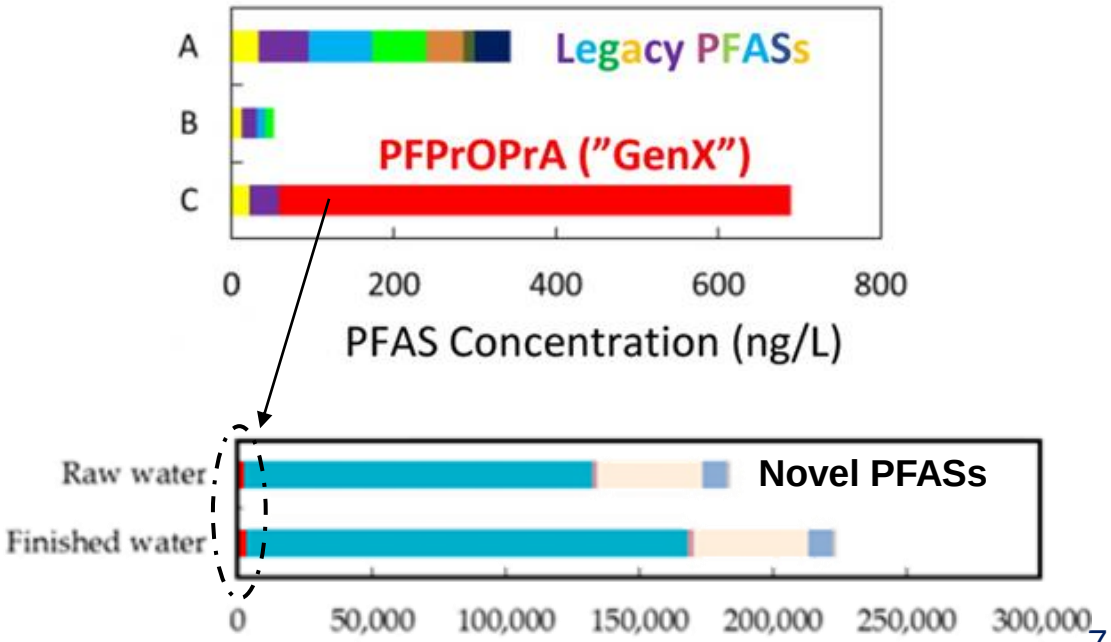
pubs.acs.org/est

Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS)



Environmental Science & Technology Letters — December 2016

Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina



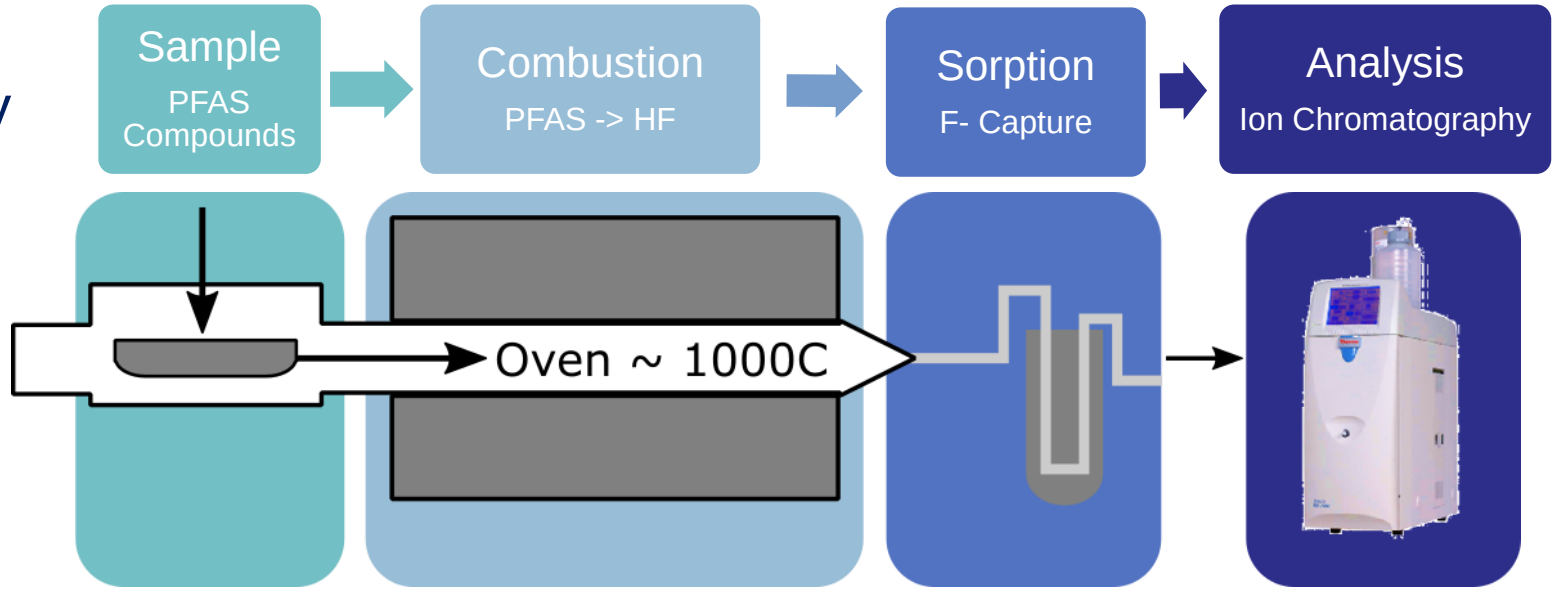
Peak Area Counts of Emerging PFASs at Community C

Strynar et al. **2015.** *ES&T* 49(19);11622−11630

Sun et al. **2016** *ES&T Letters* 3(12):415−419

Combustion Ion Chromatography for Total F

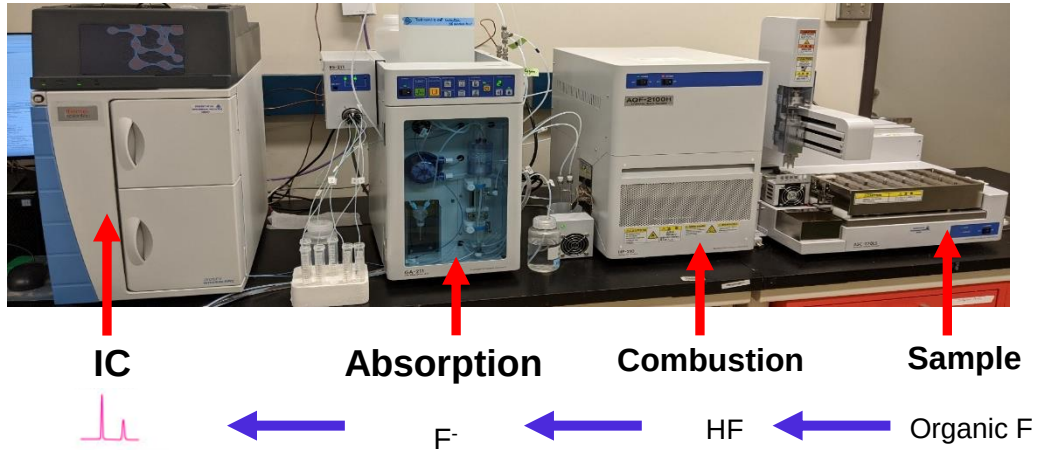
- Conversion of sample (solid, liquid, or extract) to F- and analysis by Ion Chromatography
- Total Extractable or Adsorbable Fluorine mass measurements
  - *Adsorbable or Total Organic Fluorine (AOF or TOF) – depends on extraction process*
  - *Level of Detection of 1.0 ppb**

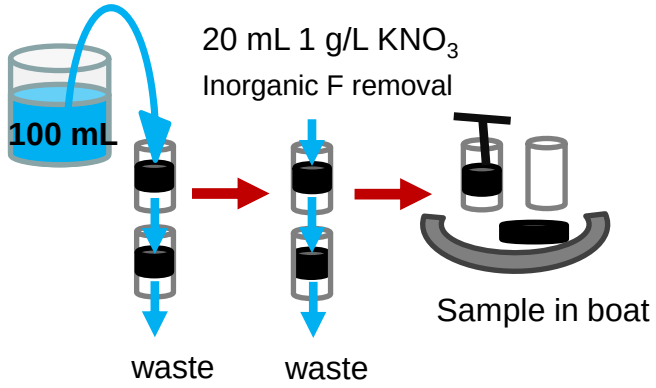


*Ateia et al., **2019** *Chemosphere,* 220: 866-882

ORD Draft AOF Method for Wastewater

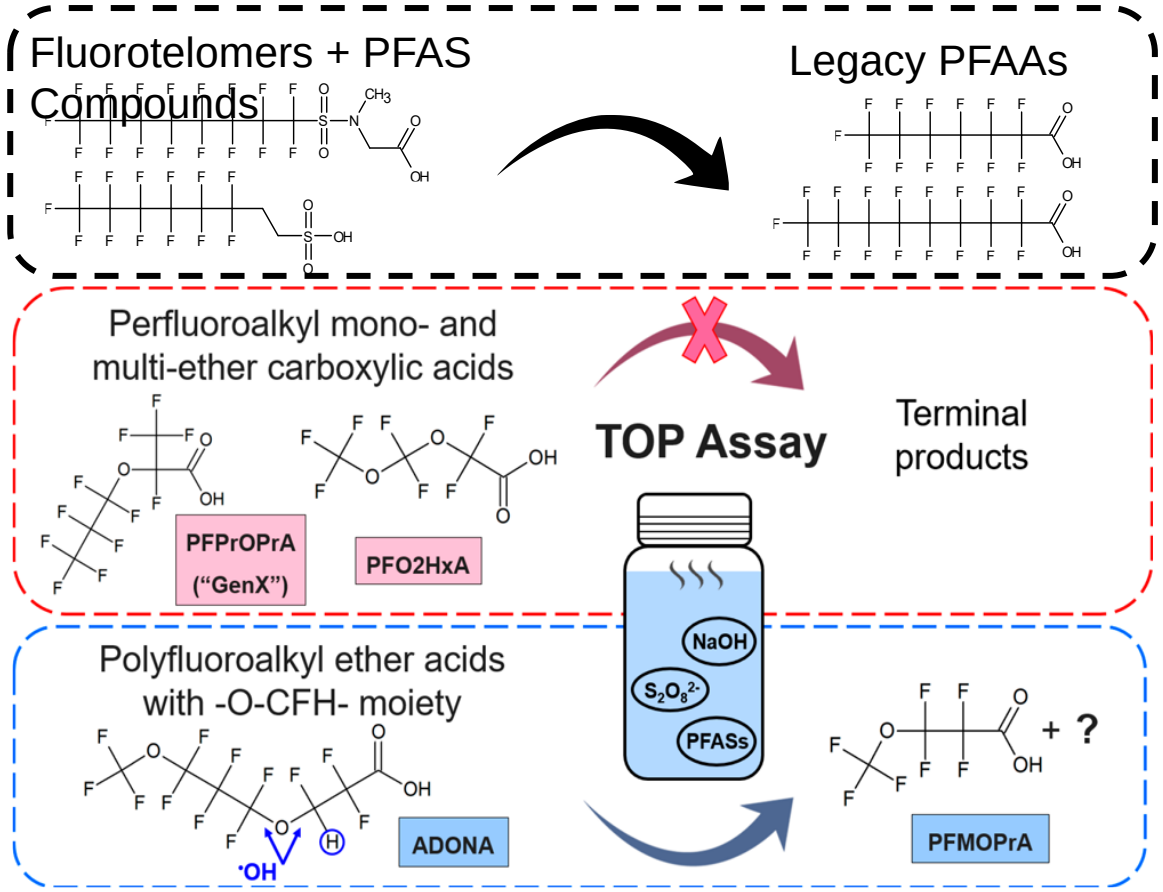
- ORD will deliver to OW October 2021
- Screening method adsorbs contaminants onto granular activated carbon, removal of inorganic fluoride with nitrate solution, followed by combustion of the carbon
- Organofluorine compounds are converted to fluoride in the combustion process and measured by ion chromatography
- Will aid in assessing total PFAS contamination, recognizing this technique measures more than PFAS
- Likely only useful for wastewater or highly contaminated situations (>1 µg/L)





Total Oxidizable Precursor (TOP) Assay

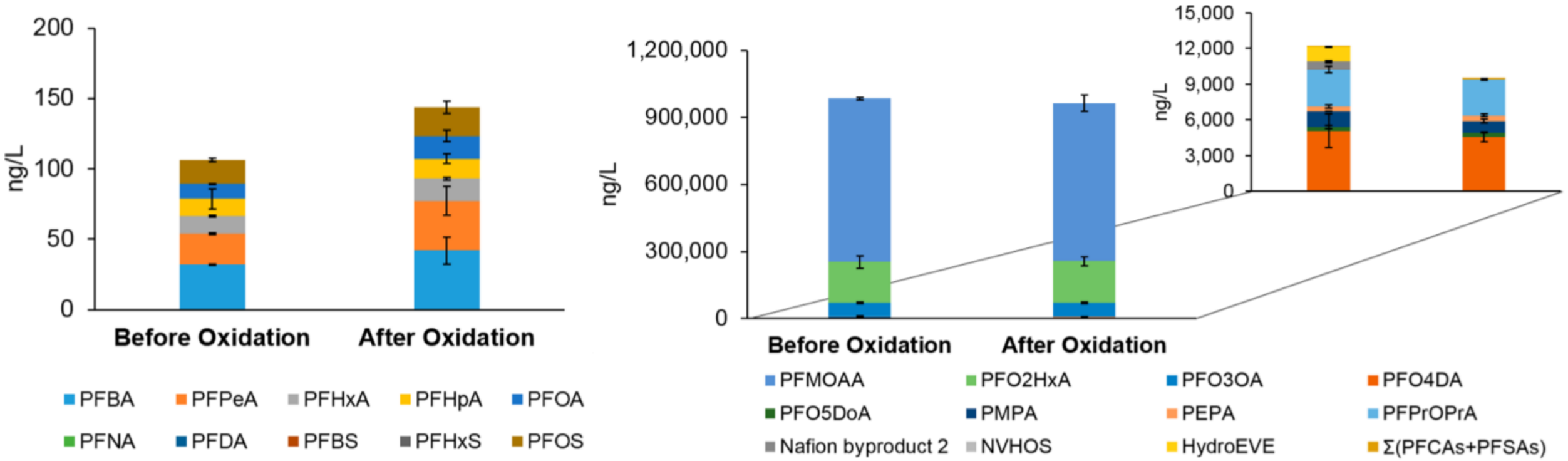
- Oxidation procedure converts PFAS precursors not identified by standard targeted analysis to measurable PFAS
- Post oxidized samples (water, soil, sediment, tissue) are extracted and measured via EPA method 537 (targeted) or similar technique using LC-MS-MS
- Increase in PFAS concentration after undergoing TOP assay indicates PFAS precursors present in sample
- Useful in determining if follow up using non-target or suspect screening analysis is indicated
- Level of Detection ~0.002 ppb*
- Limitations: Precursor identity not confirmable; no standardized TOP method currently exists; Not all PFAS are converted by TOP procedure (e.g., GenX)



Zhang et al. **2019** *ES&T Letters* 6(11): 662−668

* Ateia et al., **2019** *Chemosphere,* 220: 866-882

TOP Analysis of Cape Fear Water

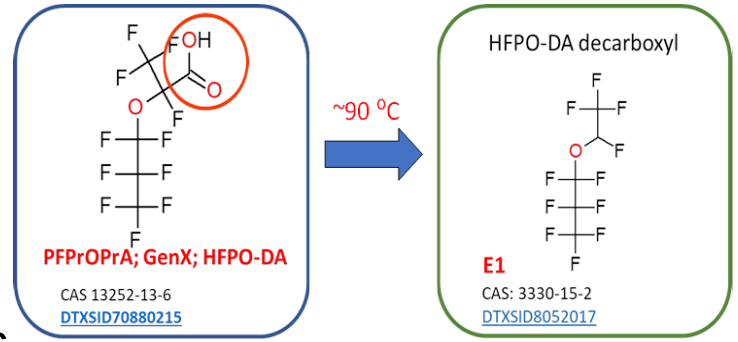


An expanded targeted list for a TOP assay is necessary to capture the scope of contamination

Zhang et al. **2019** *ES&T Letters* 6(11): 662−668

PFAS in Air: Additional Measurement Challenges

- Multiple sources: PFAS manufacturers, industrial users, treatment/destruction facilities: *How will heat affect/transform PFAS?*
- **TOF** as a screening tool for PFAS emission estimates: *mass balance of organic fluorine (HF, targeted PFAS, nontargeted/unknown PFAS)*
- High resolution mass spectrometry and **NTA** can help detect unknowns and identify PFAS to add to targeted methods
- However, unique sampling challenges exist for PFAS in air
  - Unlike in water, large portion of total PFAS in air is volatile, nonpolars*: Potential loss throughout method (e.g., breakthrough, evaporation)*
  - Need to efficiently capture and measure PFAS from a variety of sources (e.g., waste treatment, industrial emissions, coating processes)
- *No "one-size-fits-all" sampling solution:* Will likely require multiple methods (e.g., whole air, preconcentration of PFAS in aqueous or sorbent sampling)



Summary Points

- Screening Survey and Non-Targeted Analyses are powerful tools for identifying unknown PFAS compounds in environment and biological endpoints (e.g., fish tissue)
  - Sensitive detection levels (ppt), semi-quantitative (based on surrogate(s))/quantitative (if standards exist)
  - Can discover unknown PFAS sources (e.g., GenX in Cape Fear River)
  - Requires extensive expertise and time intensive

- Total Organic Fluorine (AOF or TOF) methods provide a screening level estimate for PFAS mass balance (e.g., air emissions, waste streams, treatment technologies)
  - Relatively inexpensive and easy to use
  - Less sensitive detection levels (ppb)
  - Draft AOF wastewater method developed by ORD for single lab validation by OW

- Total Oxidizable Precursors Assay
  - Relatively easy to use, accessible without NTA expertise and equipment
  - Sensitive detection levels (ppt)
  - Includes both precursors (non-targeted total) and existing terminal PFAS

- Methods are accessible for all matrices, but sampling challenges exist for measuring PFAS in air emissions