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THE ANALYSIS OF PFAS IN AFFF PRODUCTS: APPLICATION OF ISOTOPE DILUTION MASS SPECTROMETRY AND TOP

Bharat Chandramouli, Million Woudneh, Coreen Hamilton, Richard Grace

Battelle Chlorinated 2018

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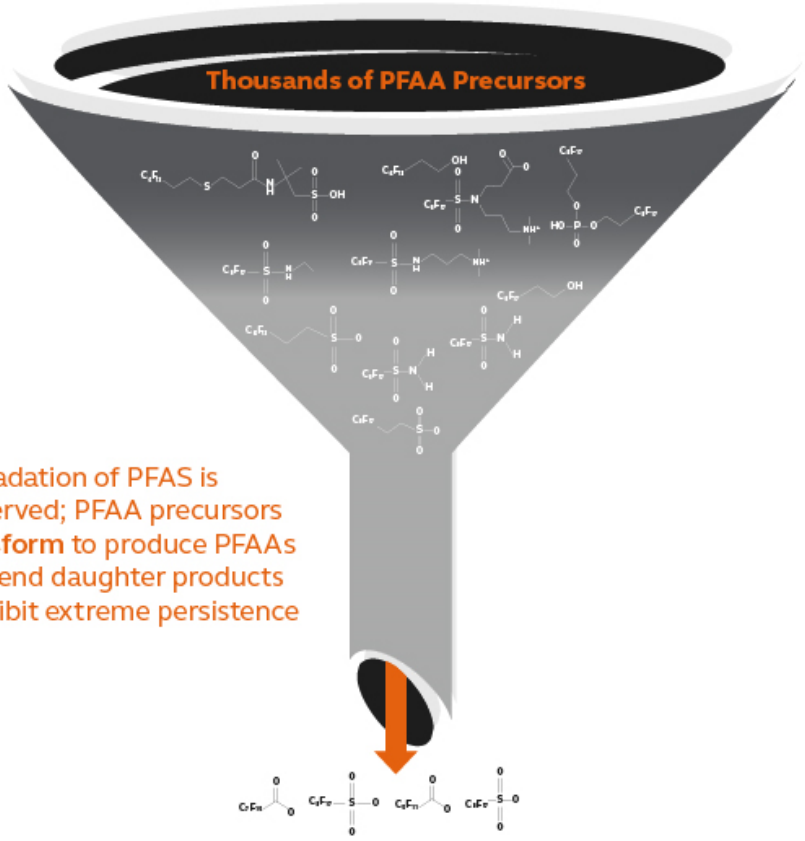
THE PFAS CHALLENGE



Biodegradation of PFAS is not observed; PFAA precursors **biotransform** to produce PFAAs as dead end daughter products that exhibit extreme persistence

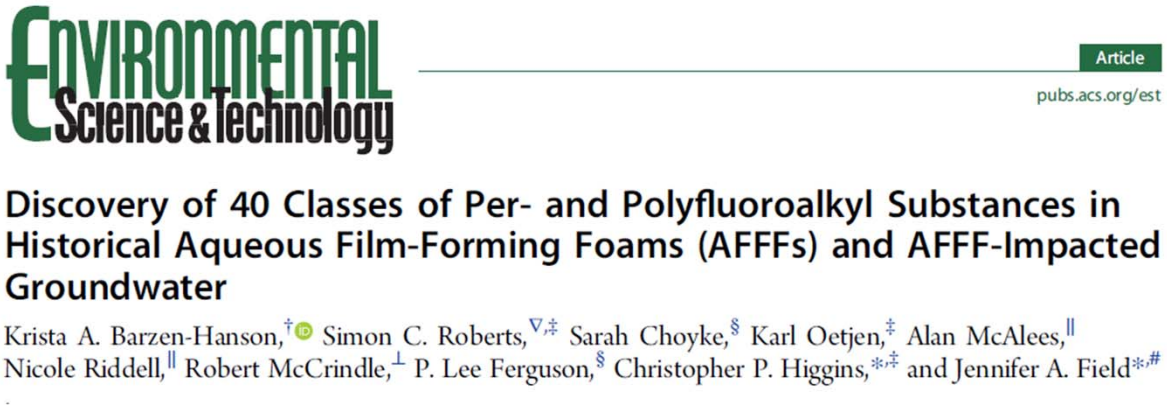
All Polyfluorinated / PFAA Precursor Compounds in Commerce ("Dark Matter")

Hundreds of Common Intermediate Transformation Products

Approximately 25 PFAAs

No PFAS biodegrade.

THE ANALYTICAL CHALLENGE



Environmental Science & Technology

Article

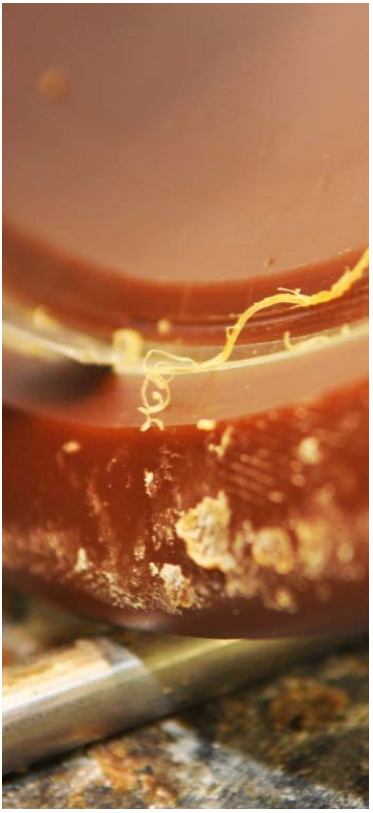
pubs.acs.org/est

Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

Krista A. Barzen-Hanson,[†] Simon C. Roberts,[▽,‡] Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,[∥] Nicole Riddell,[∥] Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,[*,‡] and Jennifer A. Field[*,#]

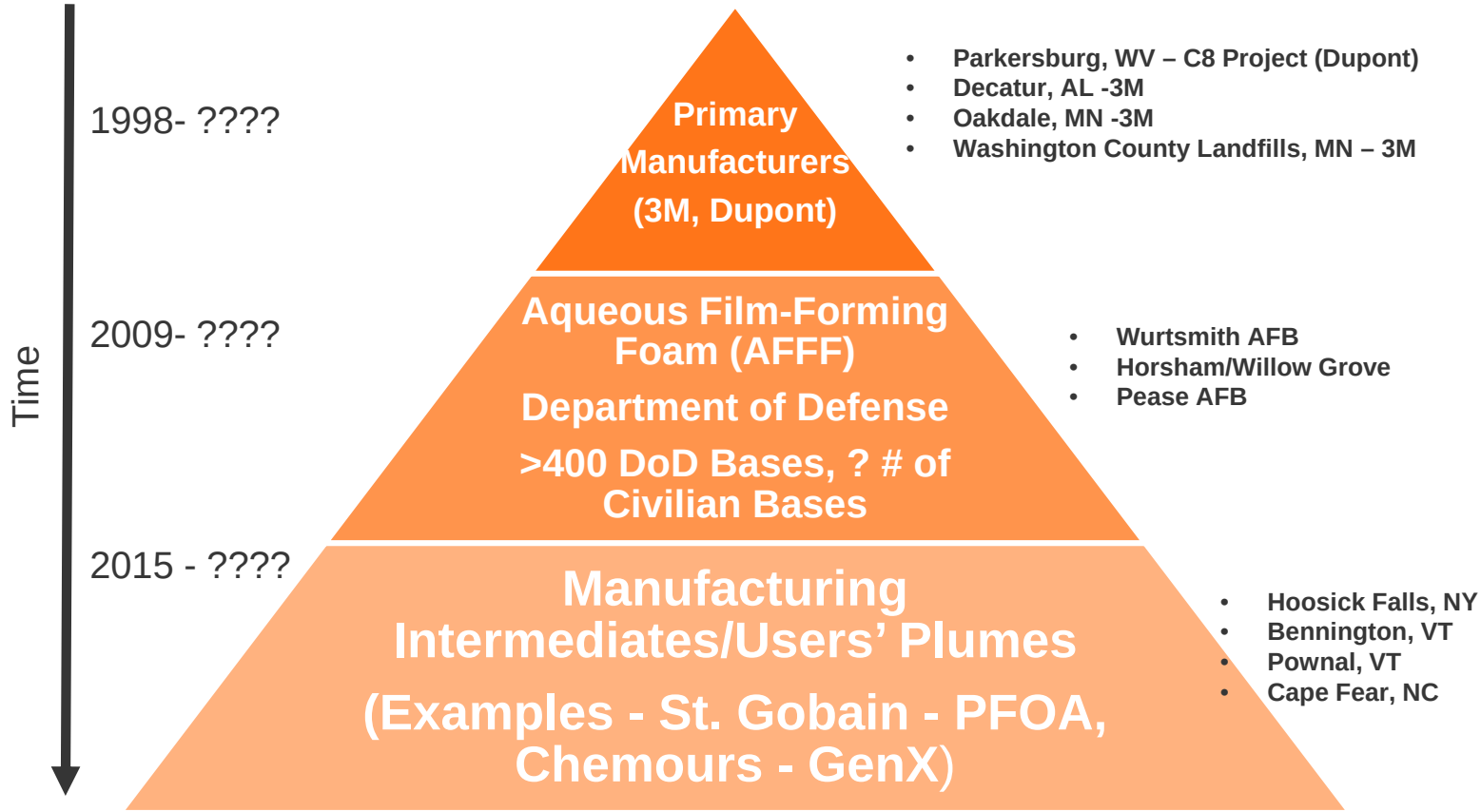
- Thousands of per and poly fluorinated compounds to potentially measure
- LC-MS/MS methods available (commercially) for about 40-50 of these
- Isotope-Dilution LC-MS/MS best available tool for quantitation. However, workflows are cost-additive: New analytes = New standards = More data processing = More $$$, and will never be exhaustive

PFAS PRODUCT USES

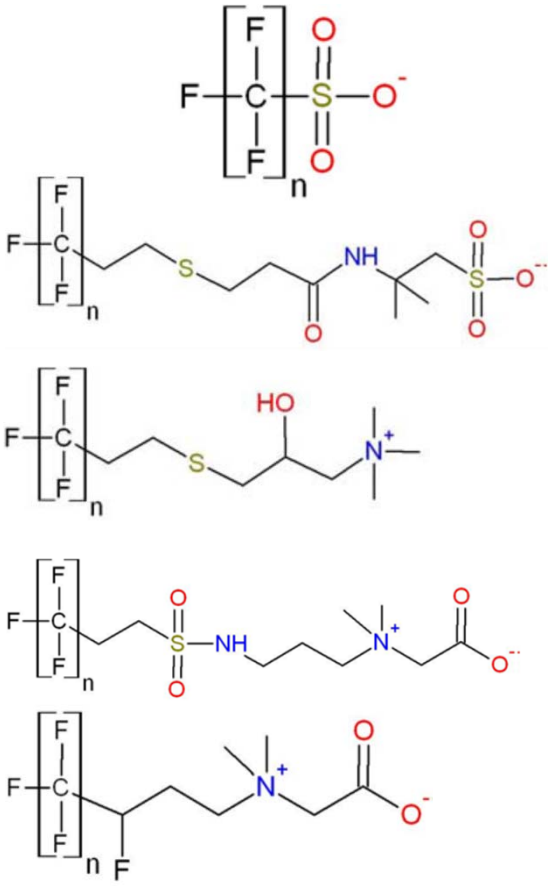


- Aqueous film forming foams (AFFF - < 3% of all fluorinated)
- Chrome plating (acid mist suppression)
- Waterproofing
- Specialty plastics
- Electronics/semi-conductors
- Pesticide additives
- Refrigeration/cooling
- Manufacturing intermediates in production of other more complex chemistries

PFAS PRODUCT PYRAMID



AFFF PRODUCTS ARE CHANGING



- PFOS-based surfactants being phased out
- Replacements primarily 6:2 telomer based (since the 70s)
- Active ingredients are generally proprietary – Untargeted research can shine light
- However, residual levels of perfluorinated acids (PFAA) in new products still under study
- Long term potential to form PFAAs still unknown
- Fate, transport and health consequences still under study
- Analytical methods in flux: Lower reporting limits

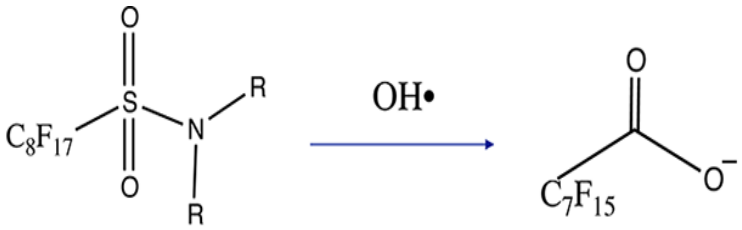
AFFF PRODUCT REGULATION

- US DoD MIL-PRF-24385F(SH) Sep 2017
  - PFOS <800 ppb
  - PFOA <800 ppb
- Queensland Australia
  - PFOS + PFHxS = 10,000 ppb
  - PFOA + other long chain analogues measured using TOP assay = 50,000 ppb F

PRODUCT ANALYSIS OBJECTIVES

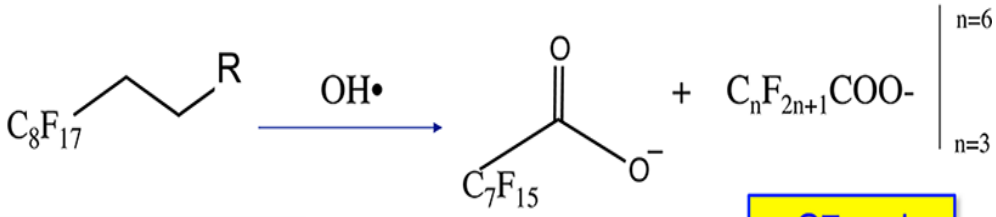
- Measure low ppb levels of PFAA in
  - Similar fluorinated active ingredient - % levels
  - Additives, other surfactants, interferences
  - Higher molecular weight substances – polymers, gelling agents, etc – sample prep difficulties
- Understand potential for PFAA formation down the line
  - Total oxidizable precursor approaches (TOP)
  - *Untargeted profiling*
  - *Total fluorine methods (PIGE, EOF)*

TOP: PERFLUORINATED POTENTIAL



C8 ECF Precursor

PFOA



C8 Fluorotelomer Precursor

PFOA

C7 and shorter PFCAs

- Can we estimate the potential of a sample containing a complex mixture of PFAS to eventually transform to stable perfluorinated end-products?
- Measure PFCAs/PFSAs in sample before and after oxidation to report conversion rates
- TOP is a strategy to simplify the measurement of precursors by transforming them into PFAAs

Houtz & Sedlak, D. L. (2012). Environmental Science & Technology, 46(17), 9342–9349.

METHODS

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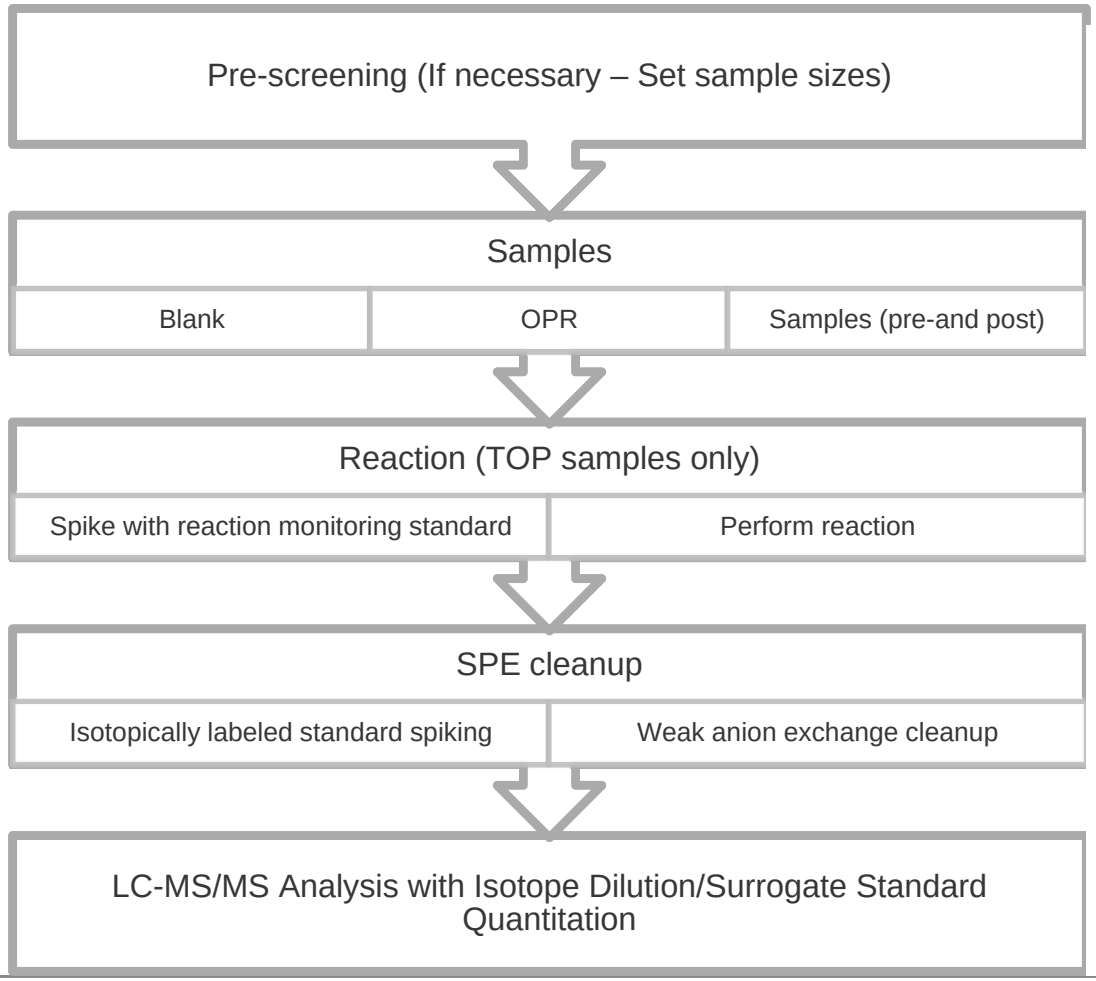
ANALYTICAL PROTOCOLS

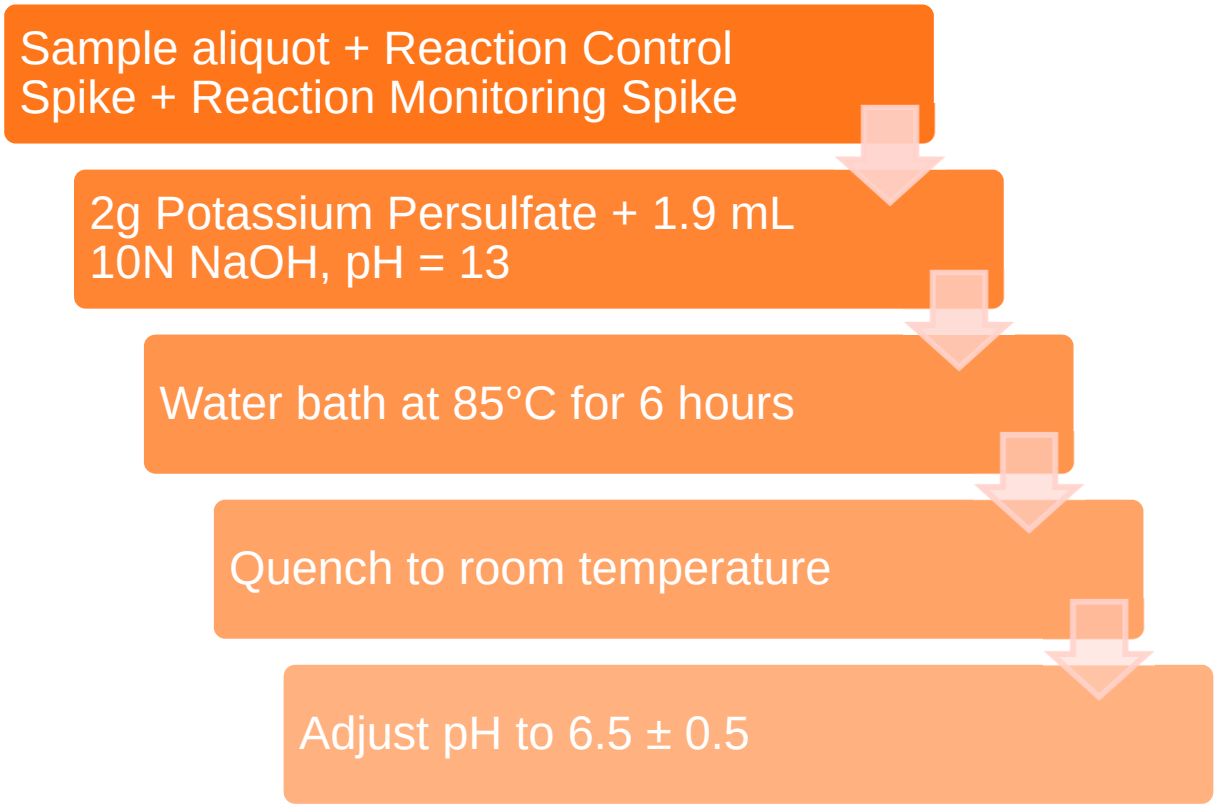


- Default sample sizes 0.1- 100 µL
- Reporting limits 2 ppb and upward – Depends on product information as available
- Uses full suite of isotopes as practicable

ANALYTES AND ISOTOPE DILUTION

Perfluorinated Carboxylates	Perfluorinated sulfonates	Fluorotelomer sulfonates	Sulfonamides and related (legacy compounds)
C4-C14, all isotope dilution except C13 (uses C14 surrogate)	C4-C10 , C12 Uses C4, C6 and C8 isotopically labeled surrogates	C4, C6 and C8, all isotope dilution	MeFOSAA, EtFOSAA. PFOSA, MeFOSA, EtFOSA, MeFOSE, EtFOSE (all isotope dilution)

TOP REACTION PROTOCOL



From Houtz and Sedlak, 2012

RESULTS (PRELIMINARY), DEVELOPMENT SAMPLES

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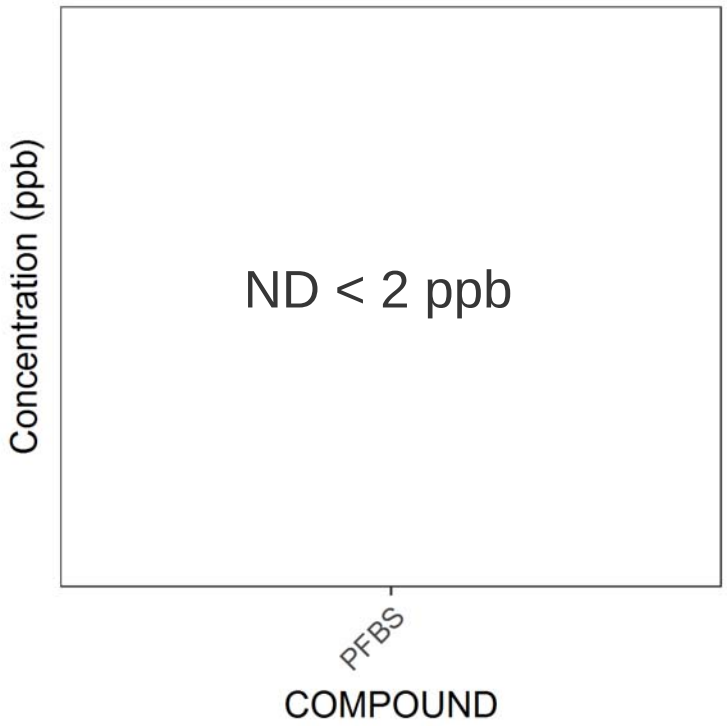
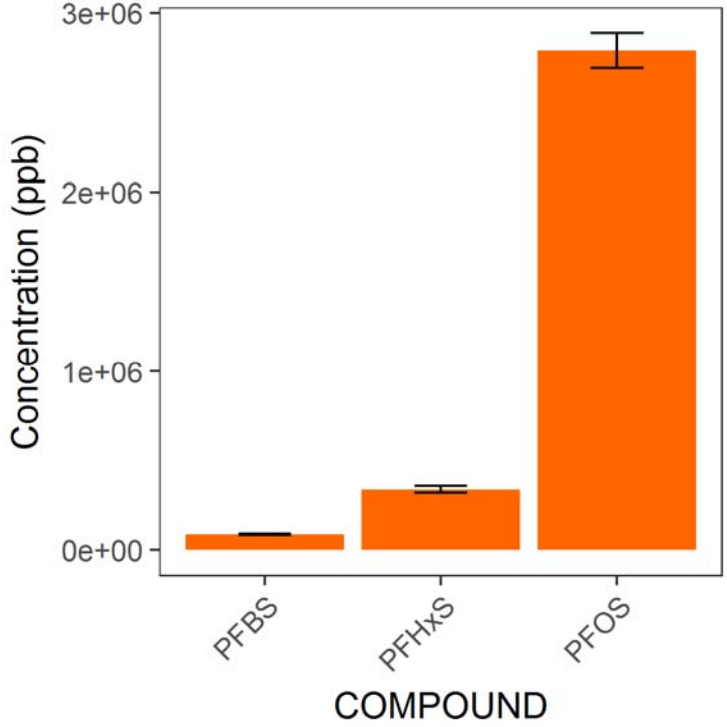
PRODUCT DATA - SULFONATES

6:2 based

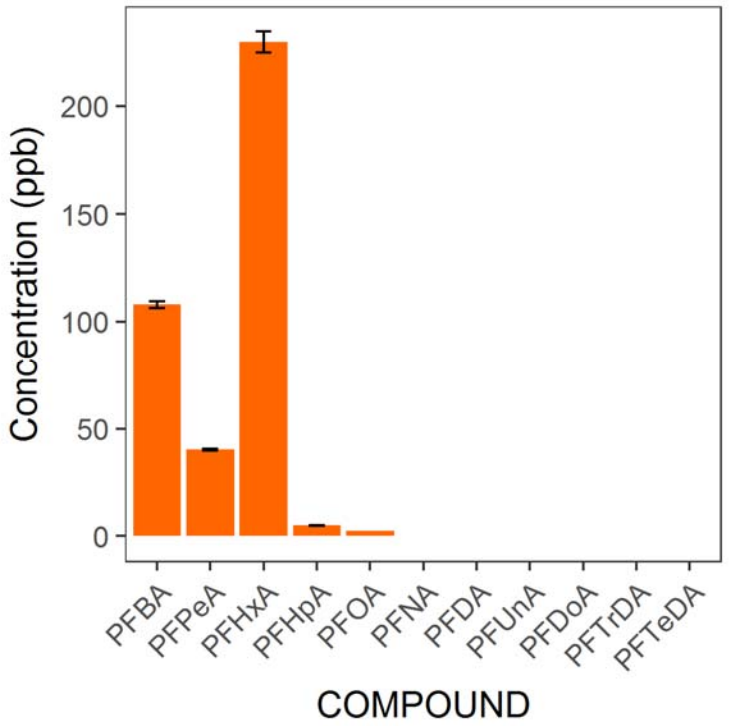


PFOS based

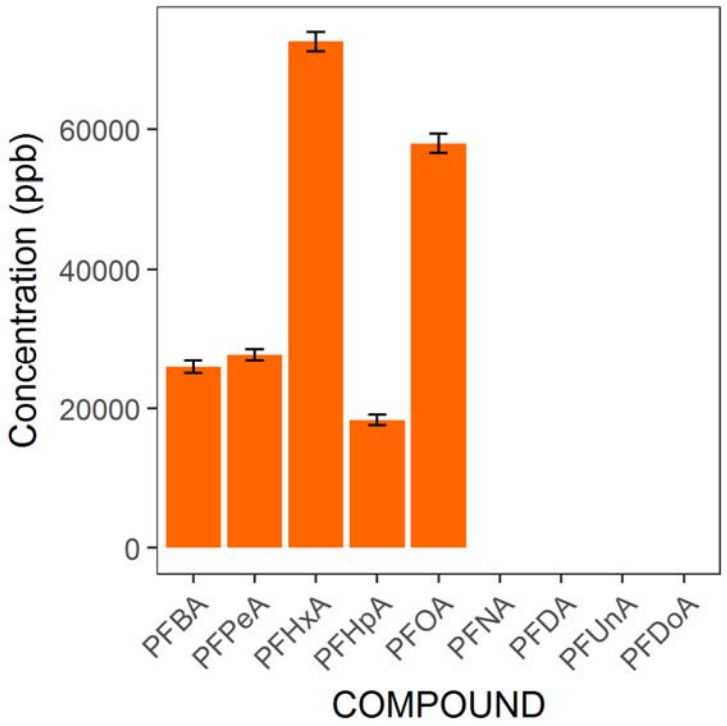


PRODUCT DATA - CARBOXYLATES

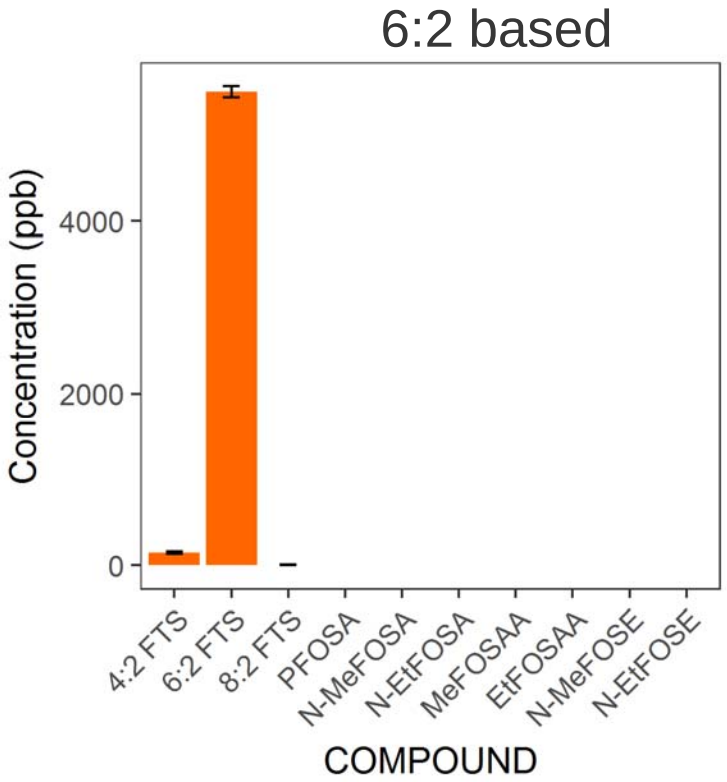
6:2 based



PFOS based

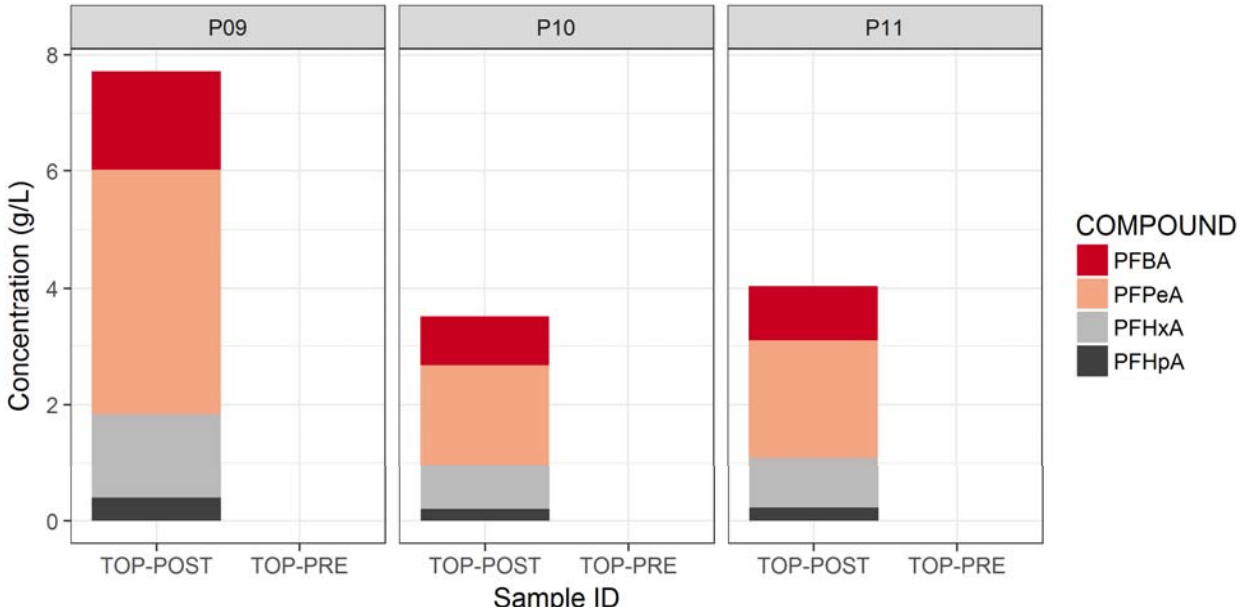


PRODUCT DATA – MEASURED PRECURSORS



- New formulations have other 6:2 active ingredients (varies by manufacturer), e.g 6:2 fluorotelomer sulfonamide betaine
- 6:2 FTS most likely impurity at ppm level or degradation product

TOP – TYPICAL AFFF FORMULATIONS



- These products show exclusively 6:2 fluorotelomer chemistry signatures
- No presence of PFOS/PFOA precursors at a 100 ppb level (sample size selected for TOP)

MASS BALANCE (6:2 PRODUCT POST TOP)

Analyte	Concentration (g/L)	Concentration (moles/L)
PFBA	1.7	0.008
PFPeA	4.18	0.016
PFHxA	1.44	0.005
PFHpA	0.398	0.001
Total Moles		**0.030**
6:2 FTS conversion rate (molar)		0.74
Moles of product		0.037
Assuming example product 6:2 FTAB MW = 571		
g of product per litre		21.2
% of product		**2.1**

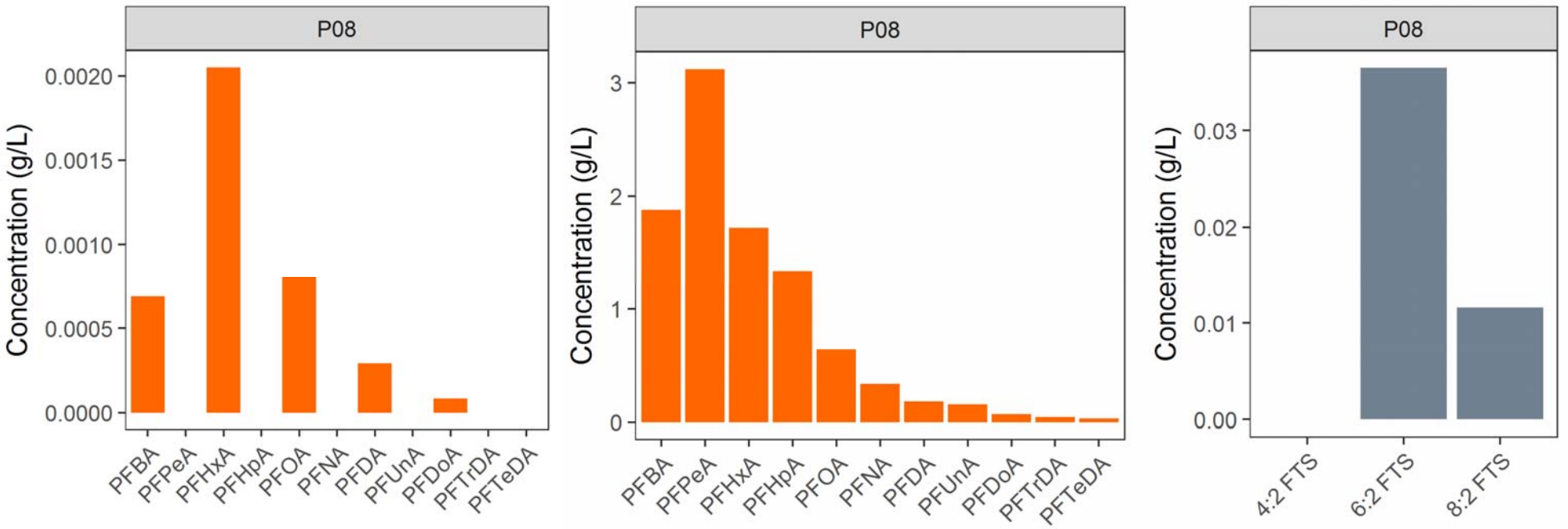
- Targeted analysis tiny fraction of product
- Post-TOP mass balance explains significant fraction of fluorine
- Not a reflection of environmental fate, only source accounting

MASS BALANCE – PFOS PRODUCT – NO TOP

COMPOUND	Concentration (g/L)
PFBA	0.03
PFPeA	0.03
PFHxA	0.07
PFHpA	0.02
PFOA	0.06
PFBS	0.09
PFHxS	0.34
PFOS	2.79
Total g/L in product	3.42
% of Product (caveat: We did not get pure product, so, lower bound)	0.34%

- Direct targeted analysis gets a significant fraction of the expected amount
- Contrast with new products where TOP is needed to explain mass in absence of analysis of specific active ingredient

DETECTING LONG CHAIN PRESENCE



- TOP showed high (0.5 g/L) formation of PFOA (approx. 100 ppb pre)
- Other long chain compounds seen as well
- Precursor product results cannot explain bulk of mass balance

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CONCLUSIONS

- Products analysis for residual terminal acids is possible at low detection limits
- Lower detection limit methods can reveal residual long chain presence at lower levels
- TOP works well in products, use in detection of unknown precursor, especially longer chain
- Interpretation of TOP data: Identifying risks, focusing remediation, not indicator of fate, or mass balance

ACKNOWLEDGEMENTS AND QUESTIONS

- My co-authors, especially Million Woudneh
- SGS AXYS lab staff Eileen Zhang, Lei Chen, Natasha Hoover and others for their high quality lab work and troubleshooting

- Questions? Bharat.Chandramouli@sgs.com