A Technique for Determining Total Oxidizable Precursors (TOP) of Perfluoroalkyl Compounds

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Polyfluorinated Compounds

- Polyfluorinated Alkyl Substances (PFAS) are a class of compounds that have been in use since the late 1940's, early 1950's.
- PFAS consists of both perfluorinated and polyfluorinated compounds
- Perfluorinated – all carbons in the chain are fully bonded to fluorine
- Polyfluorinated – not all carbons in the chain are only bonded to fluorine

Polyfluorinated Compounds

PFAS compounds have been used in many applications. They have been used as additives in fluoropolymer production and as surfactants for numerous consumer applications;

- Stain resistant coatings for furniture and carpeting
- Coatings for fast food wrappers and boxes
- Breathable waterproof fabrics
- Insecticides
- Lubricants
- Chromium Plating (mist suppression)

Polyfluorinated Compounds

PFASs were also used in Aqueous Film Forming Foams (AFFF). Developed by 3M and US Navy in the 1960's. The low surface tension and positive spreading coefficient enabled film formation on top of lighter, less dense fuels.

AFFF is a complex, proprietary mix that has been used in large volumes for decades;

- Military
- Airports
- Fire Training Installations
- Oil and Gas Industry
- Chemical Manufacturing

Polyfluorinated Compounds

ENVIRONMENTAL Science & Technology LETTERS

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Letter

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Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

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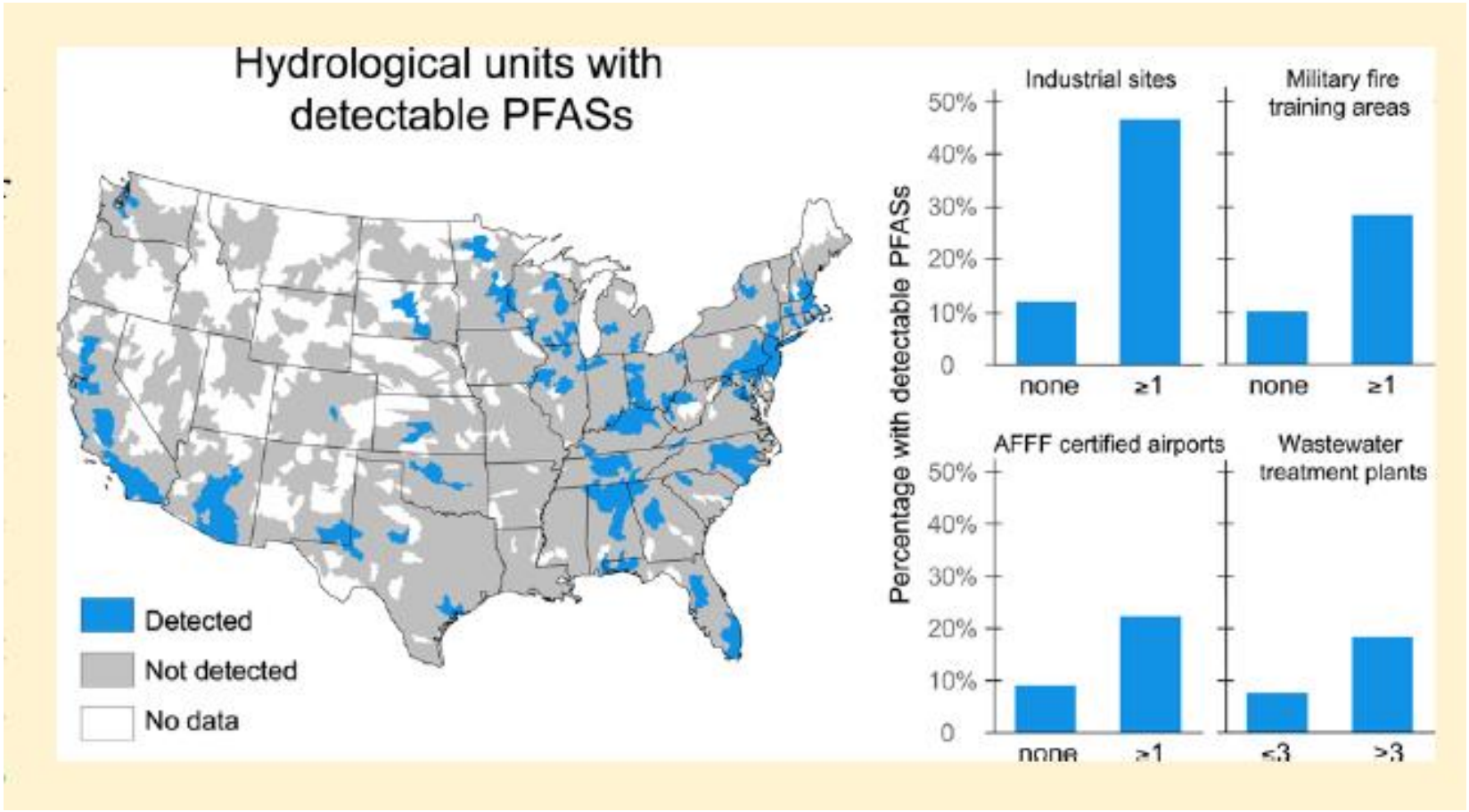
Polyfluorinated Compounds





Polyfluorinated Compounds

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[*,#]

- Hundreds to thousands of polyfluorinated compounds may be present in environment
- Approximately 240 of those have been specifically identified in AFFF formulations
- Only 40 to maybe 50 of those have standards that are commercially available

Polyfluorinated Compounds

PFCAs

Perfluorobutanoic acid
Perfluoropentanoic acid
Perfluorohexanoic acid
Perfluorheptanoic acid
Perfluorooctanoic acid
Perfluorononanoic acid
Perfluorodecanoic acid
Perfluoroundecanoic acid
Perfluorododecanoic acid

PFSAs

Perfluorobutanesulfonate
Perfluorohexansulfonate
Perfluoroheptanesulfonate
Perfluorooctanesulfonate
Perfluorodecanesulfonate

FTOH

4:2 Fluorotelomer alcohol
6:2 Fluorotelomer alcohol
8:2 Fluorotelomer alcohol
10:2 Fluorotelomer alcohol

Sulfonamides

Perfluorooctanesulfonamide
Methylperfluoro-1-octanesulfonamide
Ethylperfluoro-1-octanesulfonamide
N-methylperfluoro-1-octanesulfonamidoacetic acid
N-ethylperfluoro-1-octanesulfonamidoacetic acid
2-(N-methylperfluoro-1-octanesulfamido)-ethanol
2-(N-ethylperfluoro-1-octanesulfamido)-ethanol

PAP/DiPAP

Perfluorooctyl phosphate
Bis(perfluorooctyl) phosphate

FTS

4:2 Fluorotelomer sulfonate
6:2 Fluorotelomer sulfonate
8:2 Fluorotelomer sulfonate
10:2 Fluorotelomer sulfonate

PFPA/PFPiA

Perfluorohexylphosphonic acid
Perfluorooctylphosphonic acid
Bis(perfluorohexyl)phosphonate

Polyfluorinated Compounds

If we wanted to assess the total potential impact of PFAS contamination, how would we approach given the fact that we only have analytical standards available for a small fraction of the potential contaminants present?

Measure total Fluorine content?

a. PIGE – Proton Induced Gamma Emission Spectroscopy
    i. Captures fluorine at surface
    ii. Sensitivity around 2-5 ug/l
b. AOF/CIC – Absorbable Organic Fluorine/Combustion Ion Chromatography
    i. Sensitivity around 1 ug/l

Total Oxidizable Precursors - TOP



Environmental Science & Technology

Article

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Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

Erika F. Houtz and David L. Sedlak*

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Concept is to analyze a sample for perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) and any identified precursors . Then subject a second aliquot of the sample to relatively harsh oxidative conditions. Analyze the oxidized sample for the same perfluoroalkyl acids and precursors. Expect to see;

a. Reduction or elimination of the precursors
b. Increase in concentrations of perfluoroalkyl acids

Future – TOP Analysis



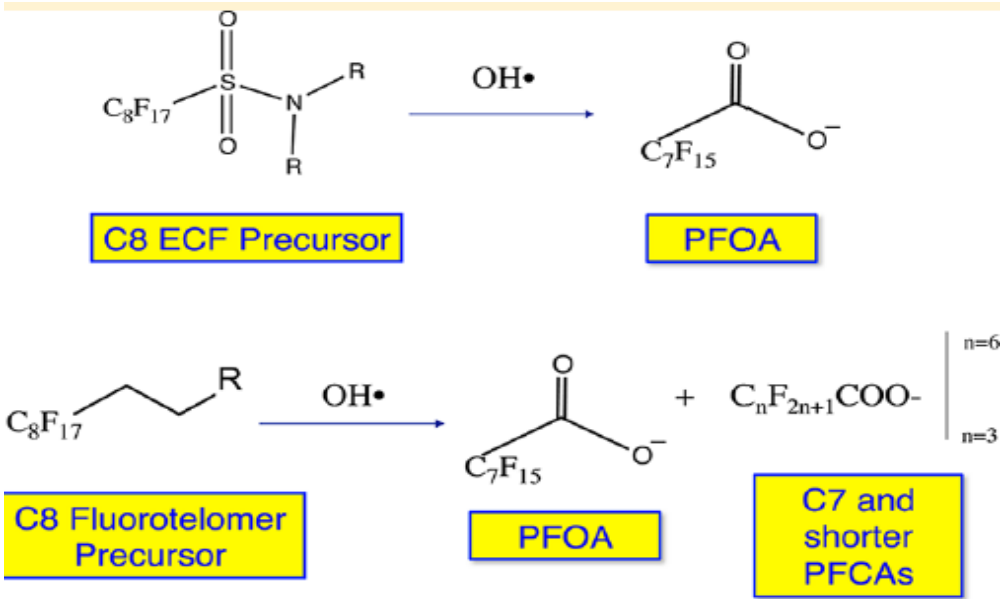
TOP – Total Oxidizable Precursors

Based on paper authored by Erika Houtz and David Sedlak (ES&T, 2012, 46, 9342-9349)

Concept is to analyze a sample for perfluorinated acids and precursors (such as telomer sulfonates). Then subject a second aliquot of the sample to relatively harsh oxidative conditions. Analyze the oxidized sample for the same perfluorinated acids and precursors. Expect to see;

a. Reduction or elimination of the precursors
b. Increase in concentrations of perfluorinated acids

TOP Assay



Houtz & Sedlak (2012), ES&T, 9342-9349

- Compounds like fluorotelomer sulfonates, alcohols and sulfonamides considered precursors
- Precursors have some part of organic structure that is susceptible to oxidation, i.e. C-H bond

TOP Assay – Advantage?

- Oxidation process for TOP Assay addresses those compounds that can be converted to PFCAs.
- Would appear to be little or no influence from other organofluorine compounds.
- Able to take advantage of LC/MS/MS analysis technique that uses isotope dilution.
- Sensitivity better that observed with PIGE and AOF/CIC. Limits in the low ng/l range.

TOP Assay – Oxidation

- After analysis sample(s) by normal LC/MS/MS isotope dilution procedure, take second aliquot
- Spike sample with TOP oxidation appropriate QC
- Add potassium persulfate and NaOH solutions to aliquot of sample until potassium persulfate at 60mM and NaOH at 125 mM. Resulting pH should be approximately 13.
- 85C bath for 6 hours
- Quench with HCl, adjust pH to approximately neutral

TOP Assay - QC

Isotopically labeled compounds that are used with extraction for LC/MS/MS monitor the extraction efficiency for the PFAS analysis, but what about the TOP Assay?

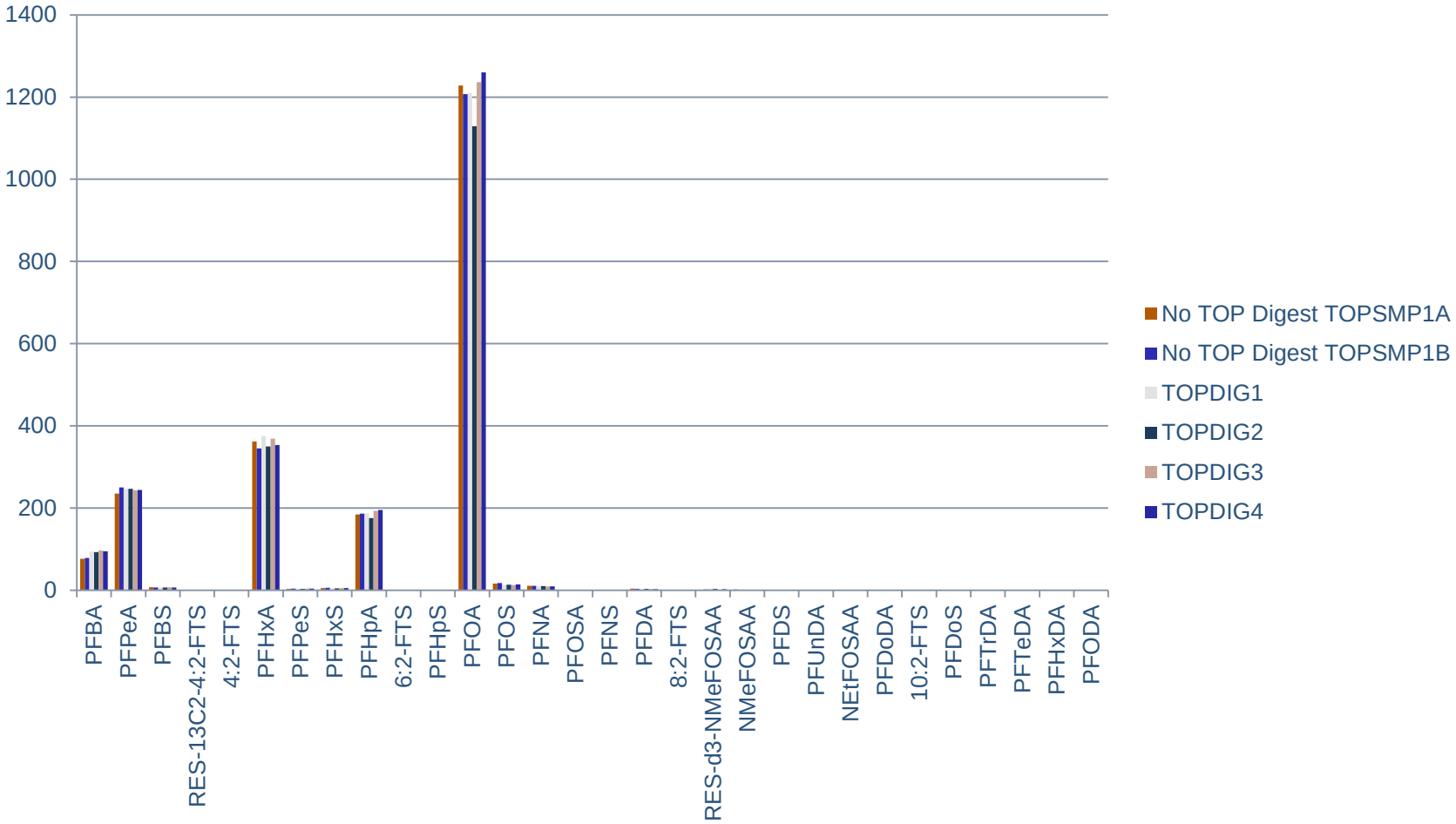
- Procedural recovery standards – labeled PFAAs that are not theoretically reactive to TOP Assay

  13C2-PFHxA
  13C2-PFOA
  13C4-PFUnDA

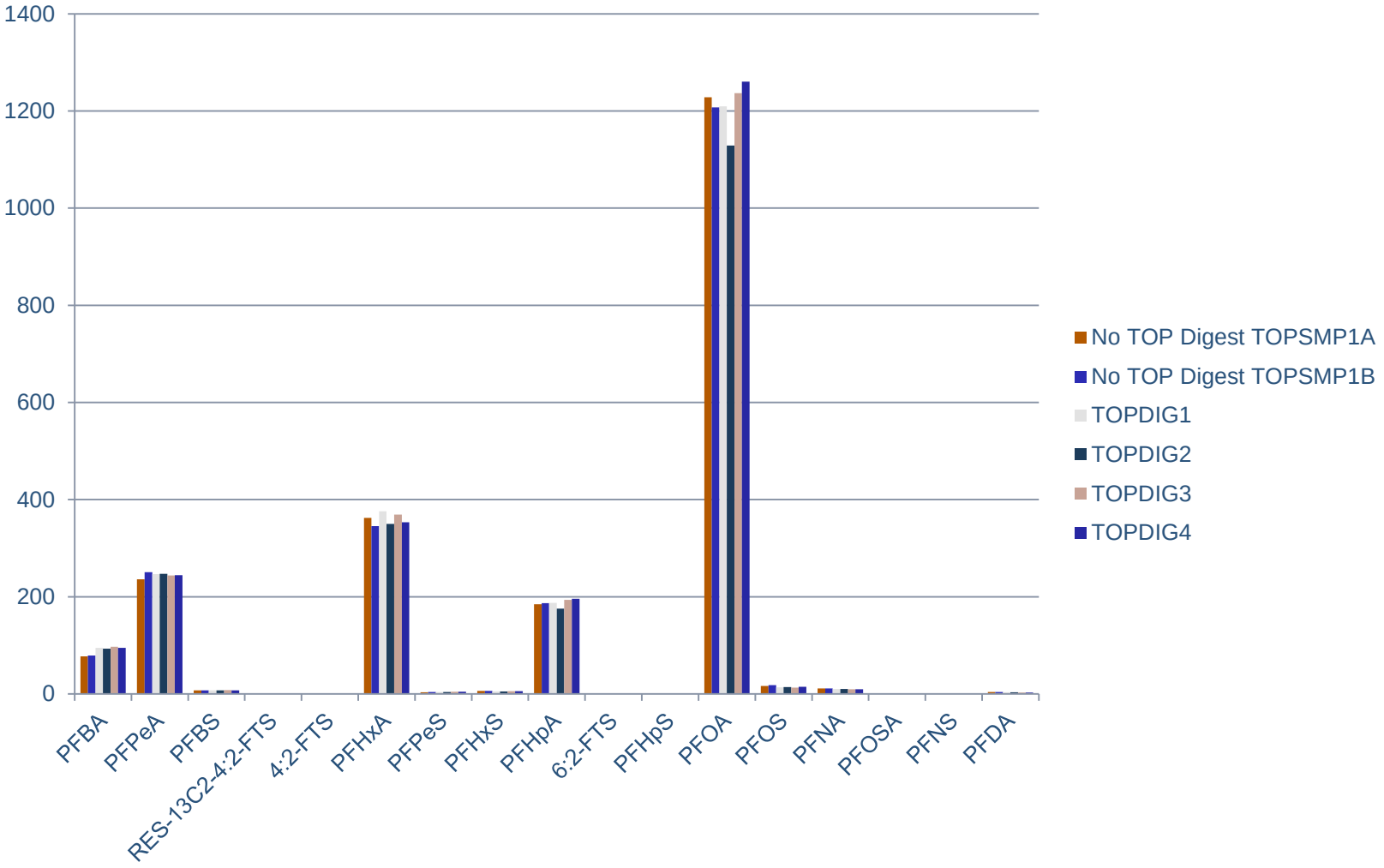
- Reaction Efficiency Standards – labeled PFAA precursor that should completely disappear when subjected to TOP Assay

  13C2-4:2-FTS
  d3-NMeFOSAA

Results – TOP Assay



Results – TOP Assay

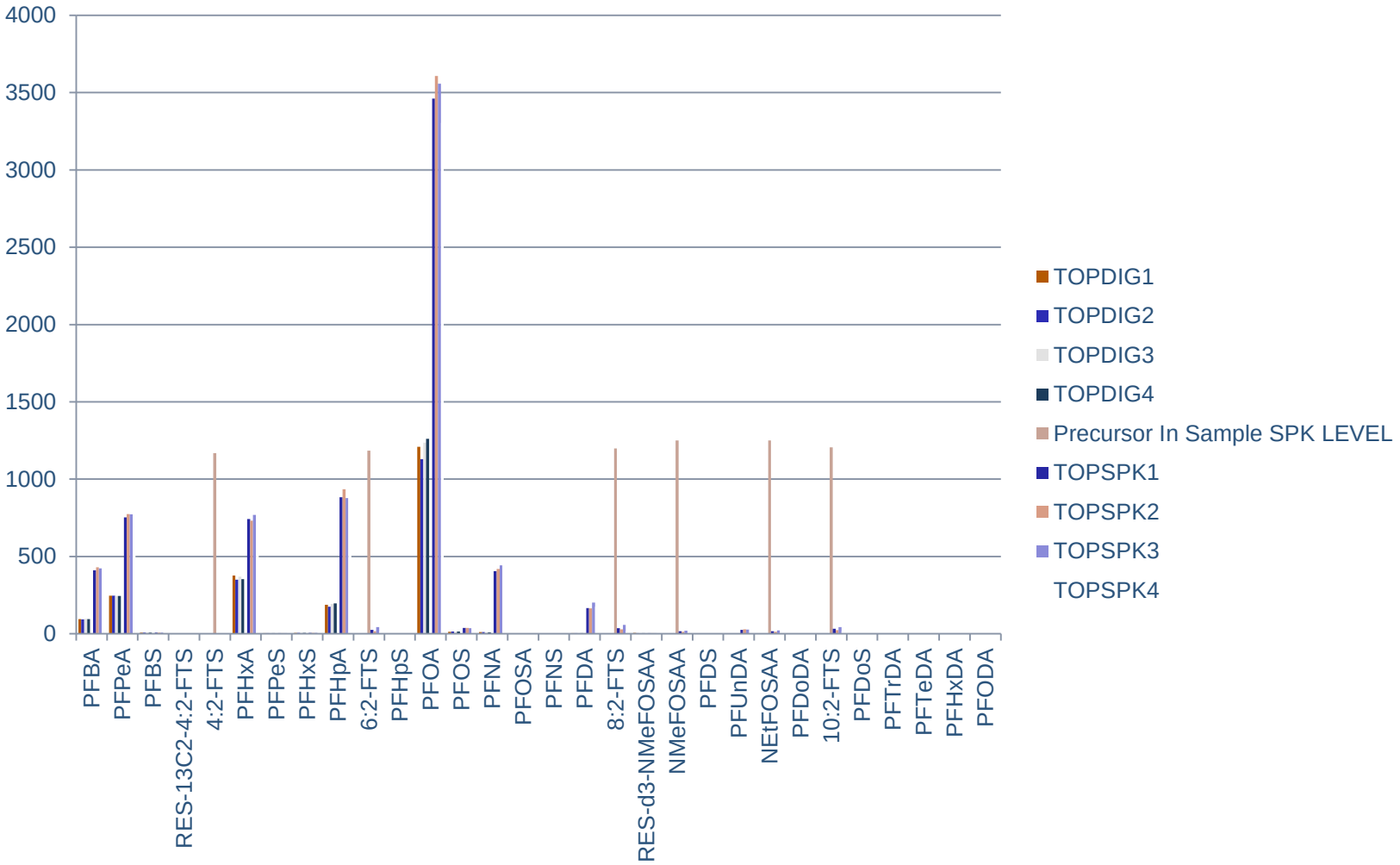


Preliminary Conclusions

- Comparison of sample results from Pre-TOP versus Post-TOP when no precursors determined to be present indicates no artifacts added to sample
- Recoveries of procedural recovery standards acceptable - > 75% recovery
- Reaction efficiency standard recoveries are zero, indicating effective oxidation of precursor content
- No new precursors were observed through the oxidation process

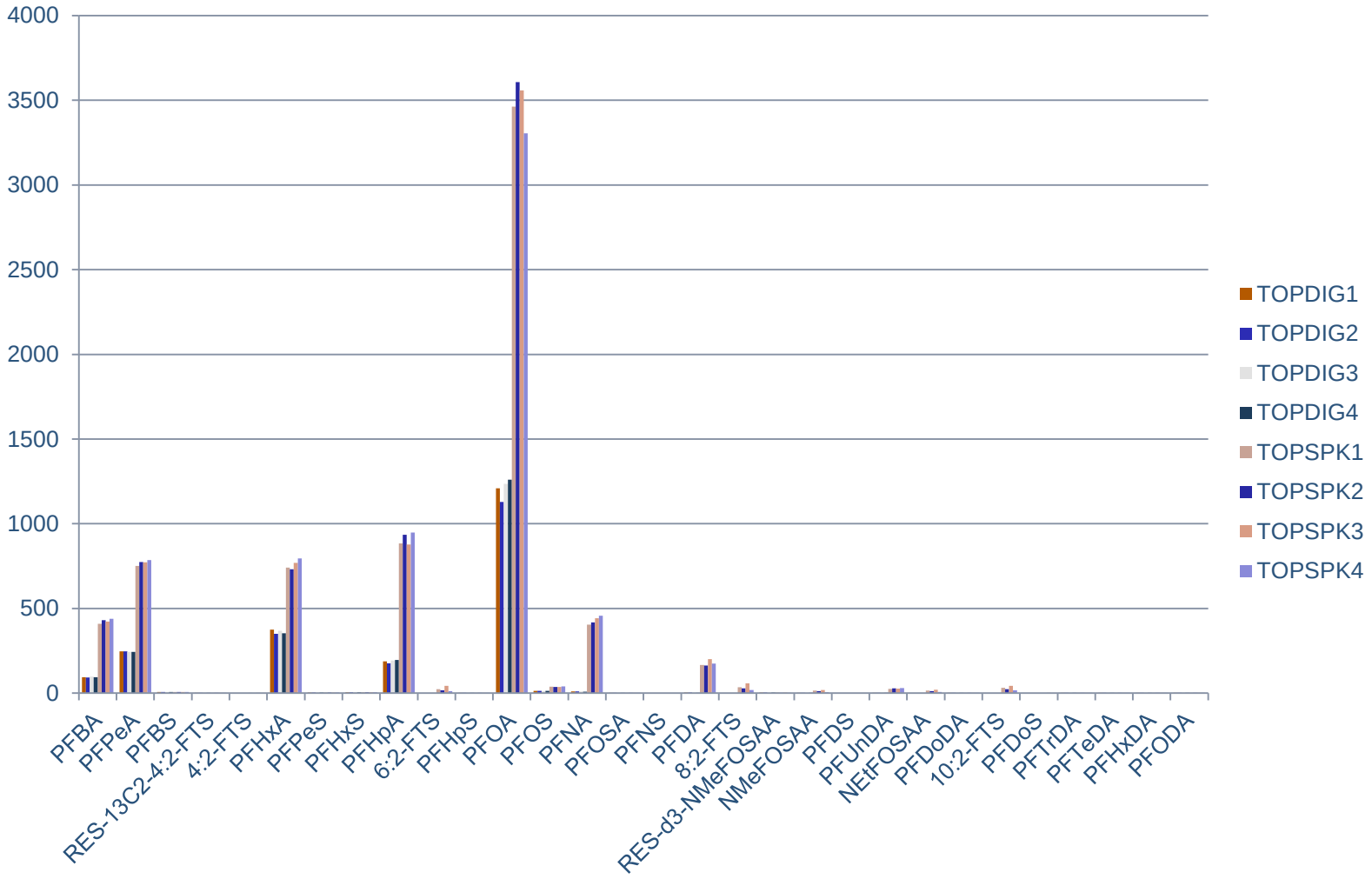
Results – Spiked w/Precursors





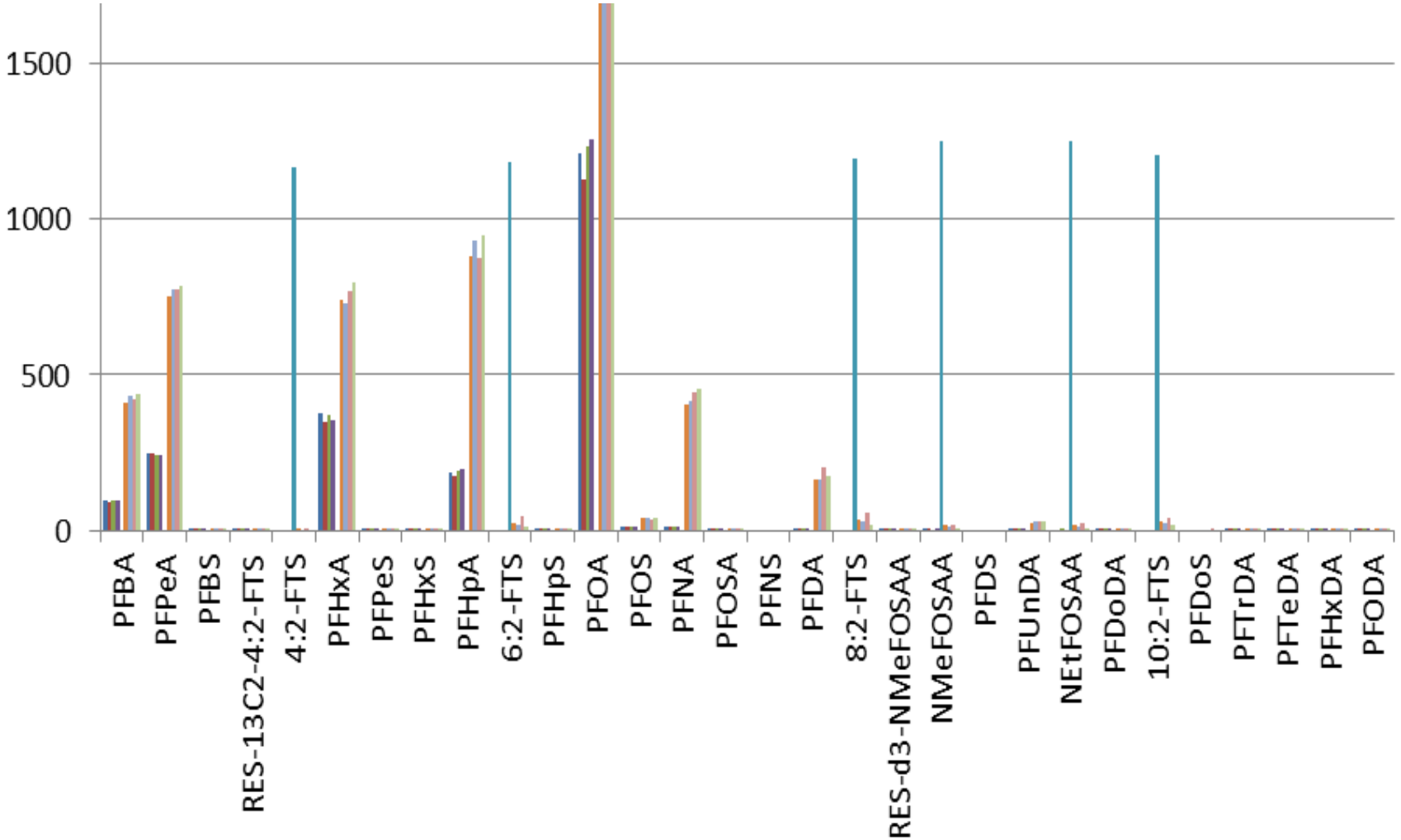
Results – Spiked w/Precursors





Results – Spiked w/Precursors





Conclusions

- Reaction conditions do not negatively impact the recoveries of perfluorinated acids
- Reaction conditions are sufficient to consume majority of (known) precursors. By extension, assume similar results for unknown precursors
- Results compare well with literature results
- Use of labeled isotopes to monitor reaction and analytical improves overall quality

Conclusions

- TOP Assay useful tool for assessing total potential impact on site from PFAS contamination
- Potentially useful, also, in determining that only impact on site is from perfluorinated alkyl acids (ex. PFOA)
- Uncertain what, if any, regulatory impact might develop out of the application of TOP Assay

Questions