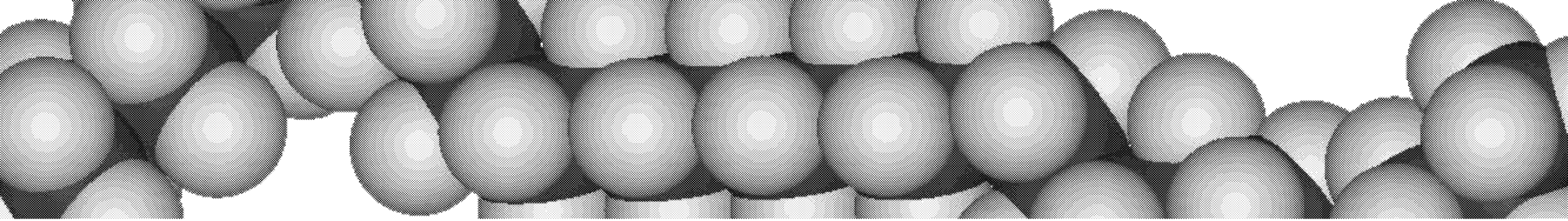

Measurement, occurrence and applications of GenX (HFPO-DA), a replacement for PFOA

Bharat Chandramouli 05-Nov-2018 SETAC NA Sacramento
bharat.chandramouli@sgs.com

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PHASE-OUT: PFOA

EPA United States Environmental Protection Agency

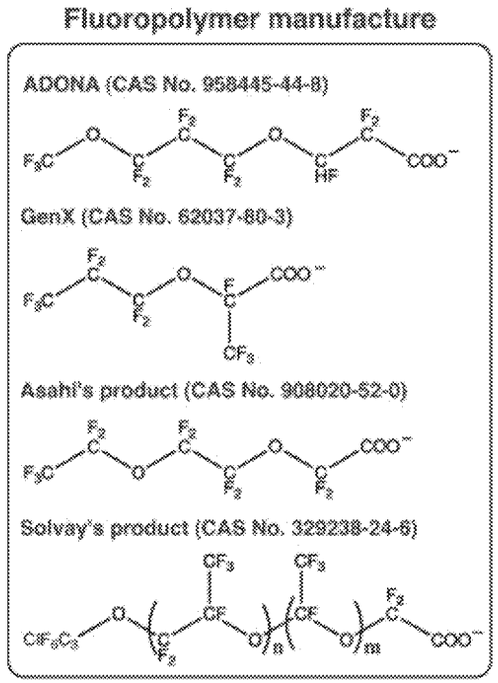
Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) under TSCA

Why is EPA concerned about Long-chain PFASs?

EPA is particularly concerned about so-called long-chain PFAS chemicals. These are persistent in the environment, bioaccumulative in wildlife and humans, and are toxic to laboratory animals and wildlife, producing reproductive, developmental, and systemic effects in laboratory tests.

- PFOA used as dispersion aid in polymer/other industries
- Worldwide presence measured by early 2000s, both from direct emissions and transformation of “precursors”
- EPA phase out in 2006, complete worldwide in 2014
- Alternatives in place, and implemented

PFOA ALTERNATIVES IN FLUORINATED POLYMERS



Wang et al. Environment International 60 (2013) 242–248

- Incomplete list
- Other PFAS, e.g. PFHxA, 6:2 fluorotelomer acid may also be used
- Confidential business information may protect some structures

Chemours
Daikin
Arkema
Asahi Glass
Solvay Solexis
Dyneon- 3M
Constructive Bureau Russia
Tarnowie-Moscicach, S.A.
Kureha
Honeywell
Gujarat Fluorochemicals
Hindustan Fluoropolymer
Shanghai 3F
Fuxin Hengtong
Jiangsu Meilan
Jinan 3F
Zhejian Jusheng
Zhonghao Chenguang
Shandong Dongyue

Fluoropolymer manufacturers

Ebnesajjad, S. (2011).. In Applied Plastics Engineering Handbook, pp. 49–60.

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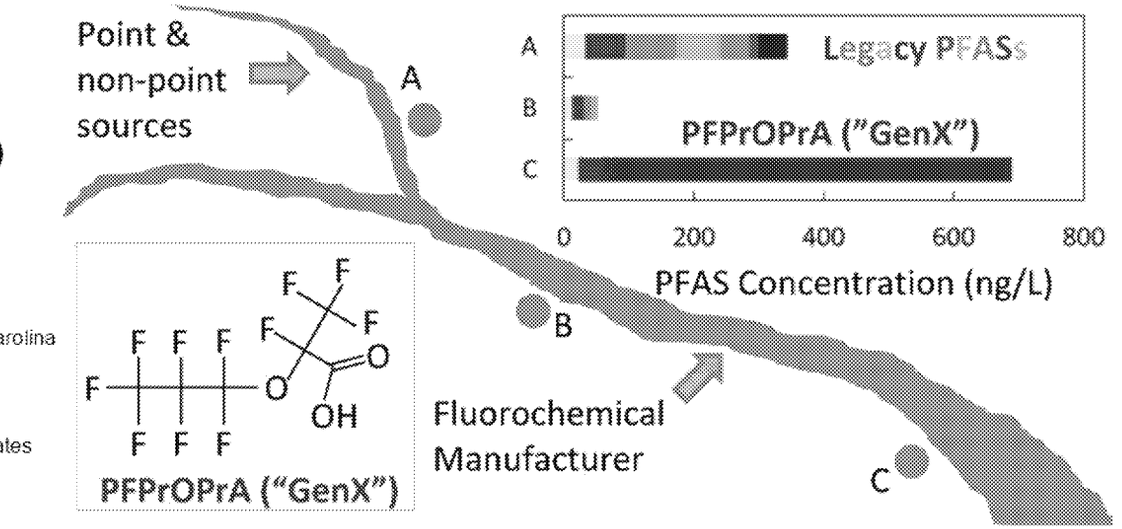
"DISCOVERY" OF HFPO-DA (GenX)

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

Mark Strynar*†, Sonia Dagnino†‡, Rebecca McMahen†‡, Shuang Liang†‡, Andrew Lindstrom†, Erik Andersen†, Larry McMillan§, Michael Thurman‖, Imma Ferrer‖, and Carol Ball⊥
† National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, United States
‡ Oak Ridge Institute for Science and Education, Oak Ridge, Tennessee 37831 United States
§ National Caucus and Center on Black Aged, Inc., Durham, North Carolina 27713, United States
‖ Center for Environmental Mass Spectrometry, University of Colorado Boulder, Boulder, Colorado 80309, United States
⊥ Agilent Technologies Inc., Wilmington, Delaware 19808, United States

Strynar et al. 2015



Sun, M. et al. 2016

- Several structures identified in this study
- Perfluoro-2-propoxy-propanoic acid (PFPrOPrA or HFPO-DA) initial source of focus

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THE GenX FAMILY

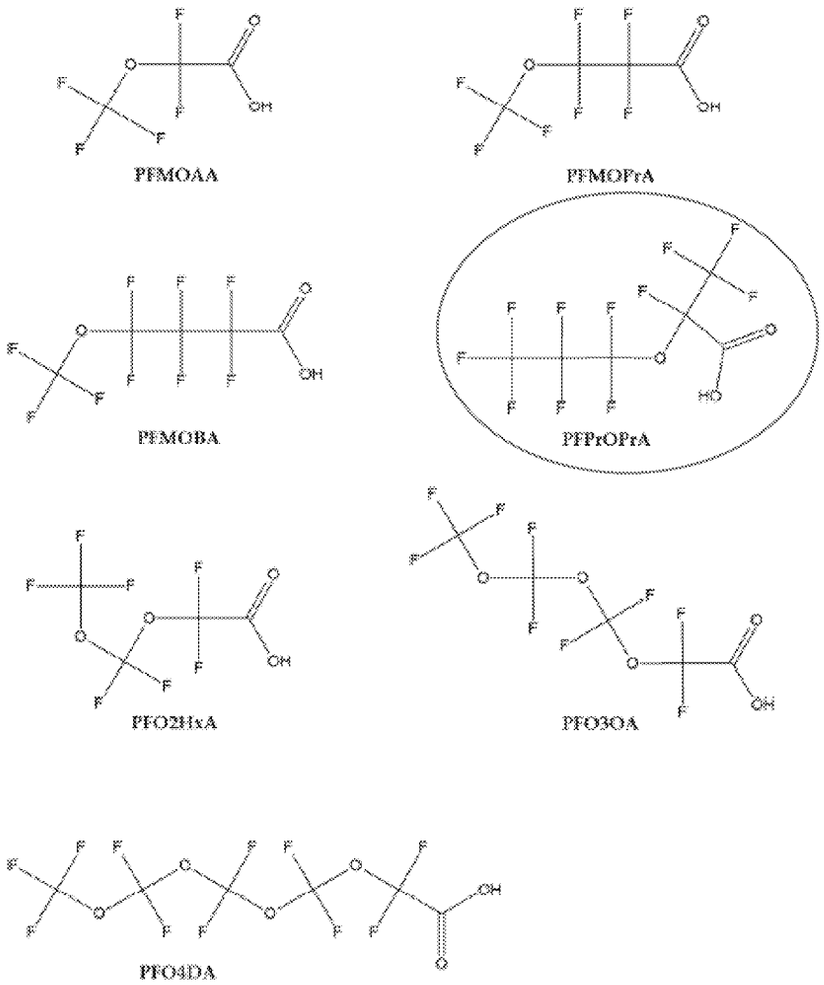


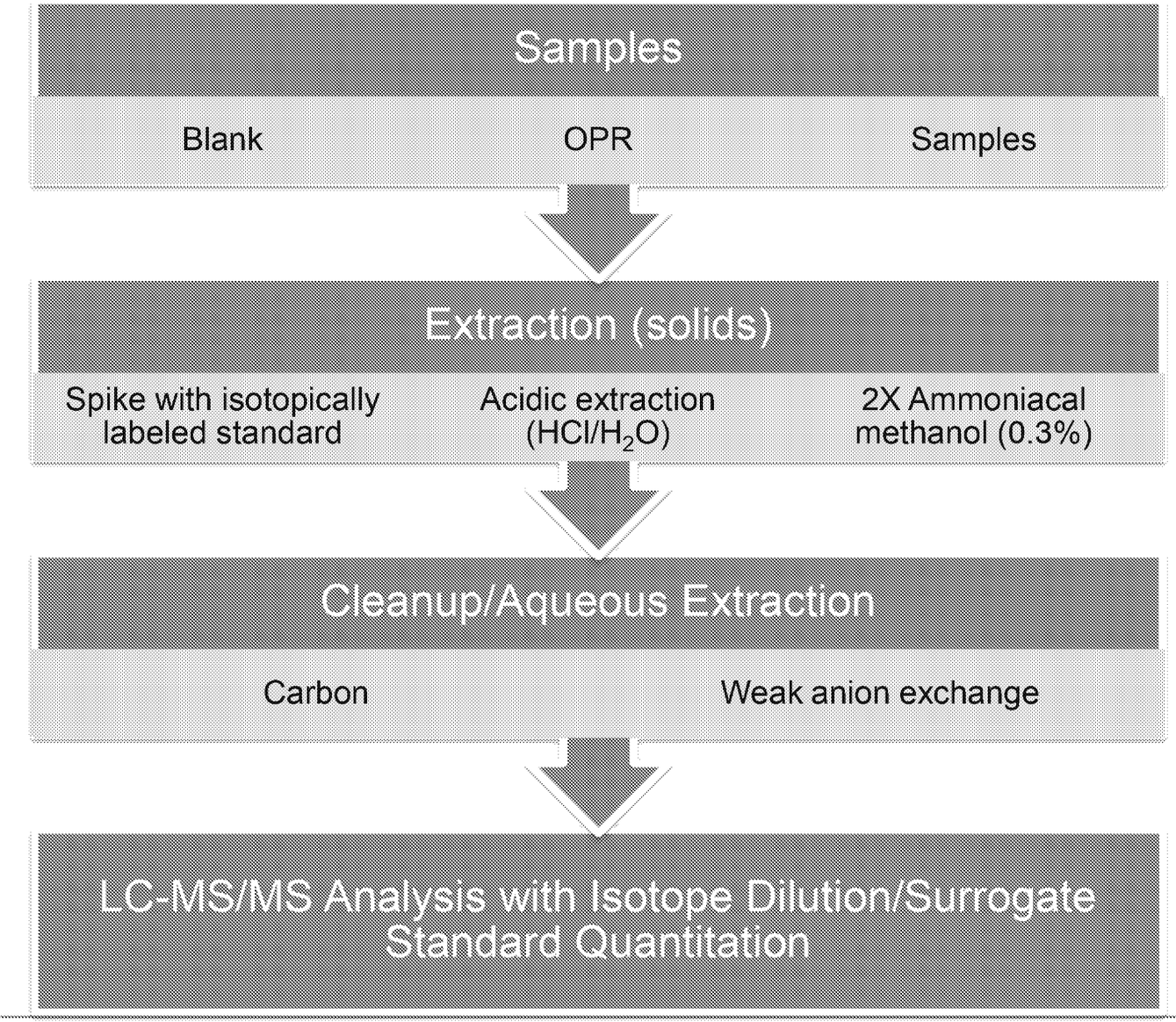
Figure S1. Molecular structures of PFECAs evaluated in this study

- Perfluoro-2-propoxy-propanoic acid (PFPrOPrA/HFPO-DA) one of many
- Multiple other mono-, di- and poly- ethers detected
- Standards not available for some of constituents
- Understanding what to measure will be challenging

Sun, M. et al. Environ. Sci. Technol. Lett. 3, 415–419 (2016).

METHODS

ANALYTICAL PROTOCOL



- Isotopically labeled standard available for HFPO-DA
- Method will work for other ether carboxylates, as demonstrated by similar approach (McCord et al., 2018)

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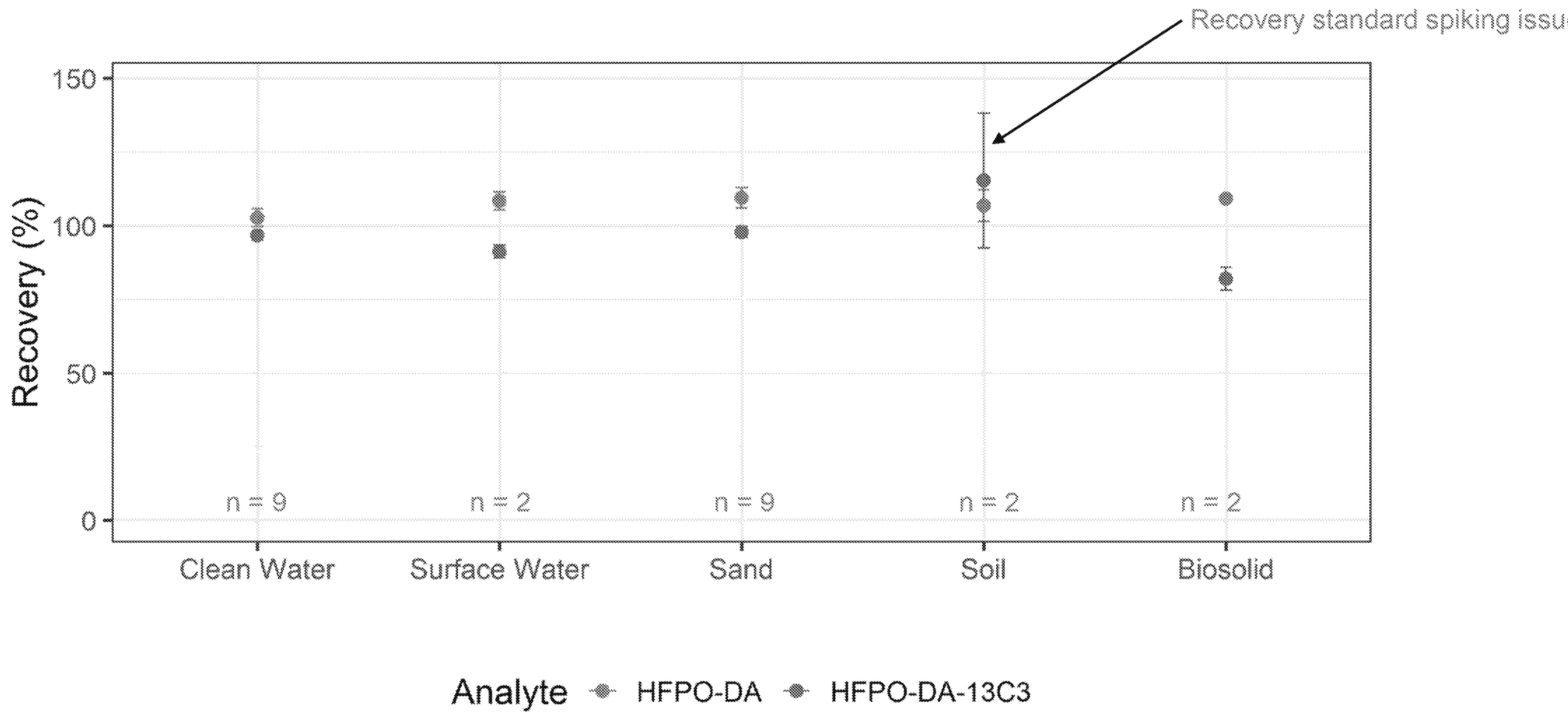
METHOD VALIDATION (TWO LABS CONSOLIDATED)



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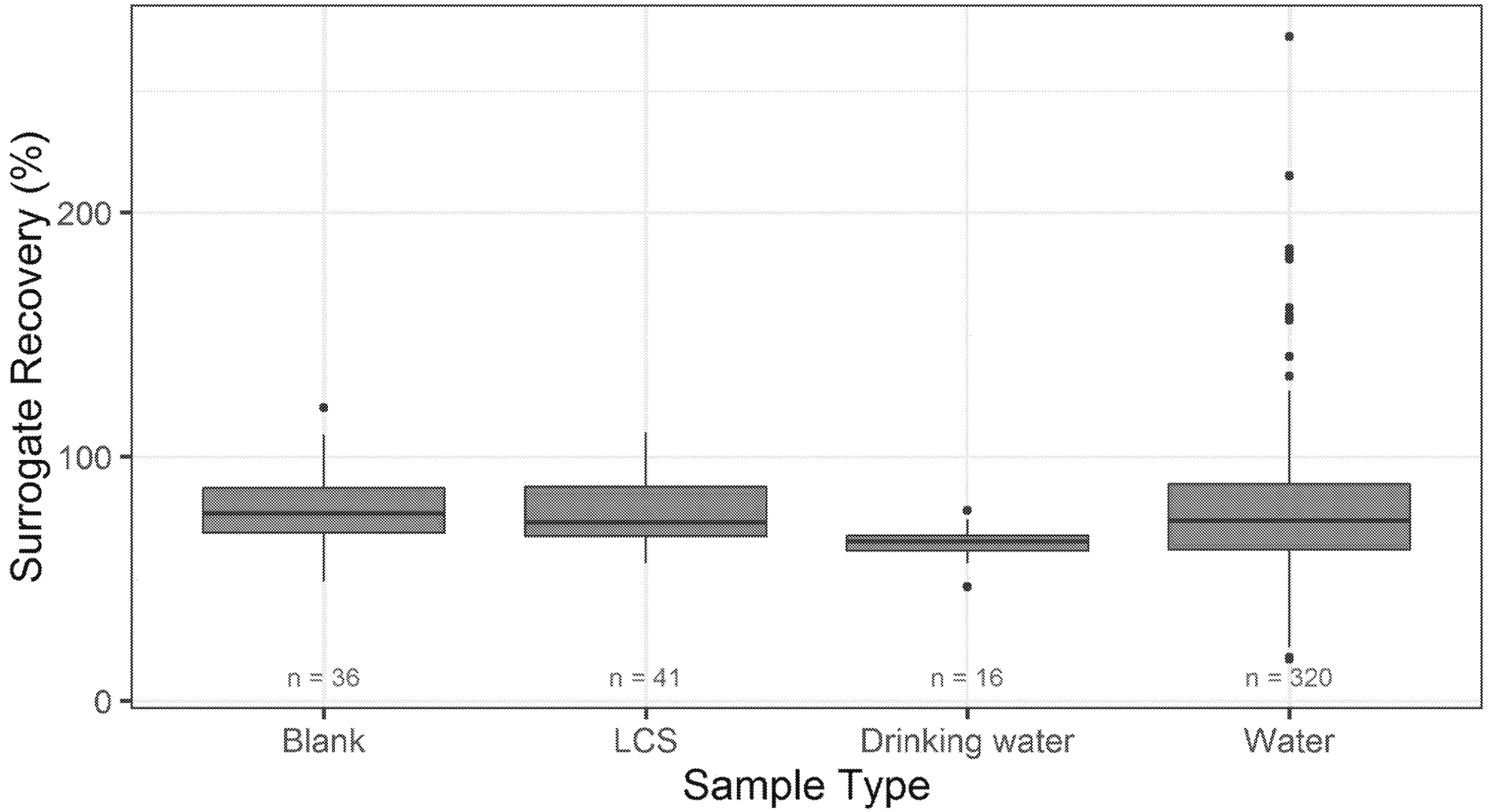
PERFORMANCE DATA



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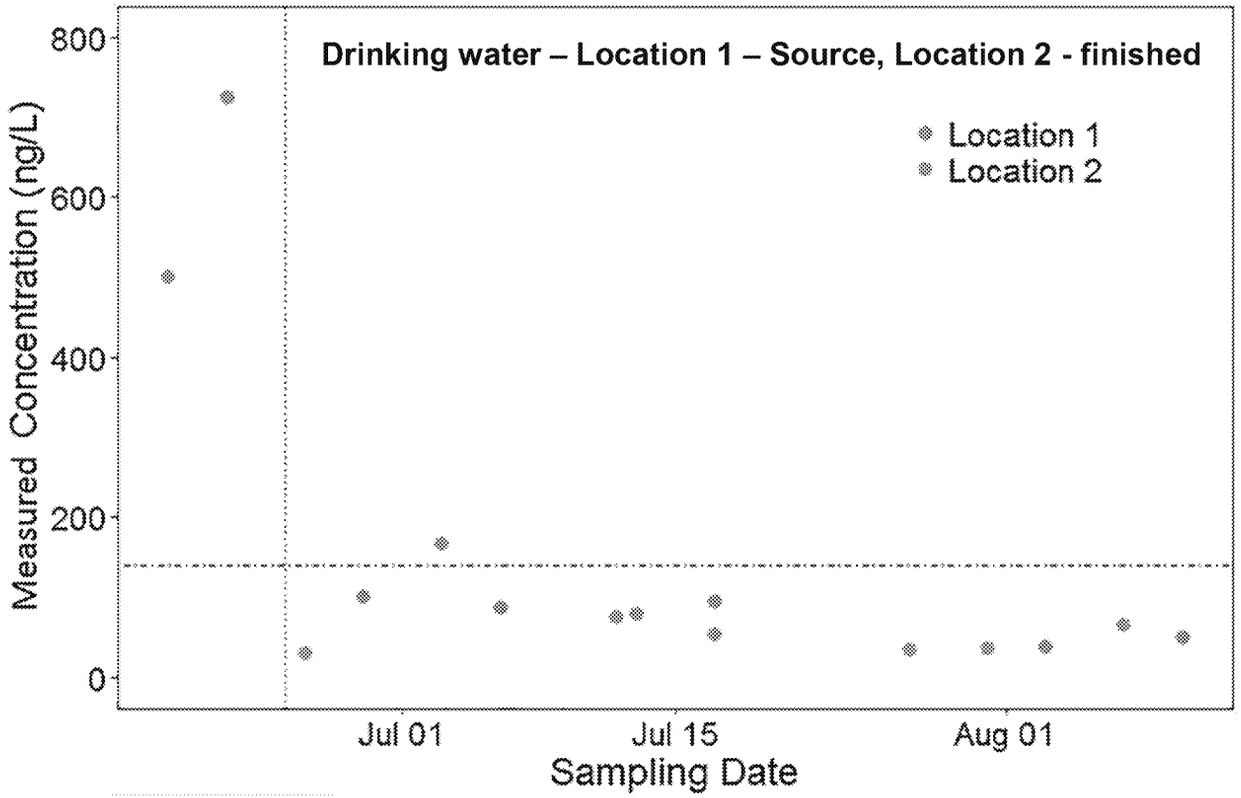
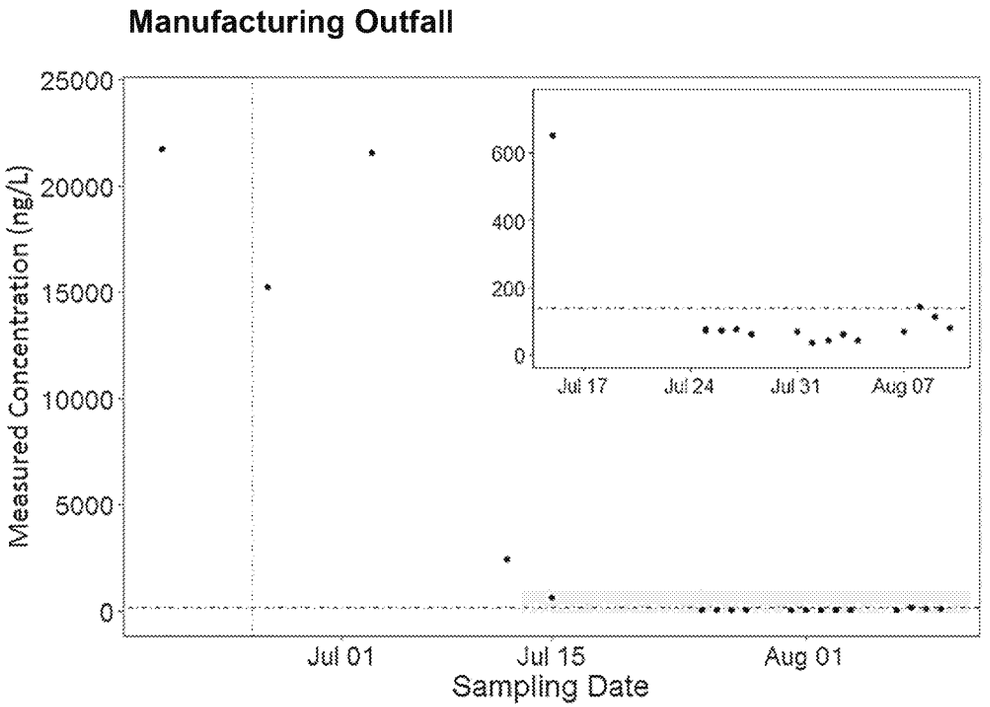
OCCURRENCE

SGS AXYS PUBLISHED RESULTS FROM NORTH CAROLINA (2017)

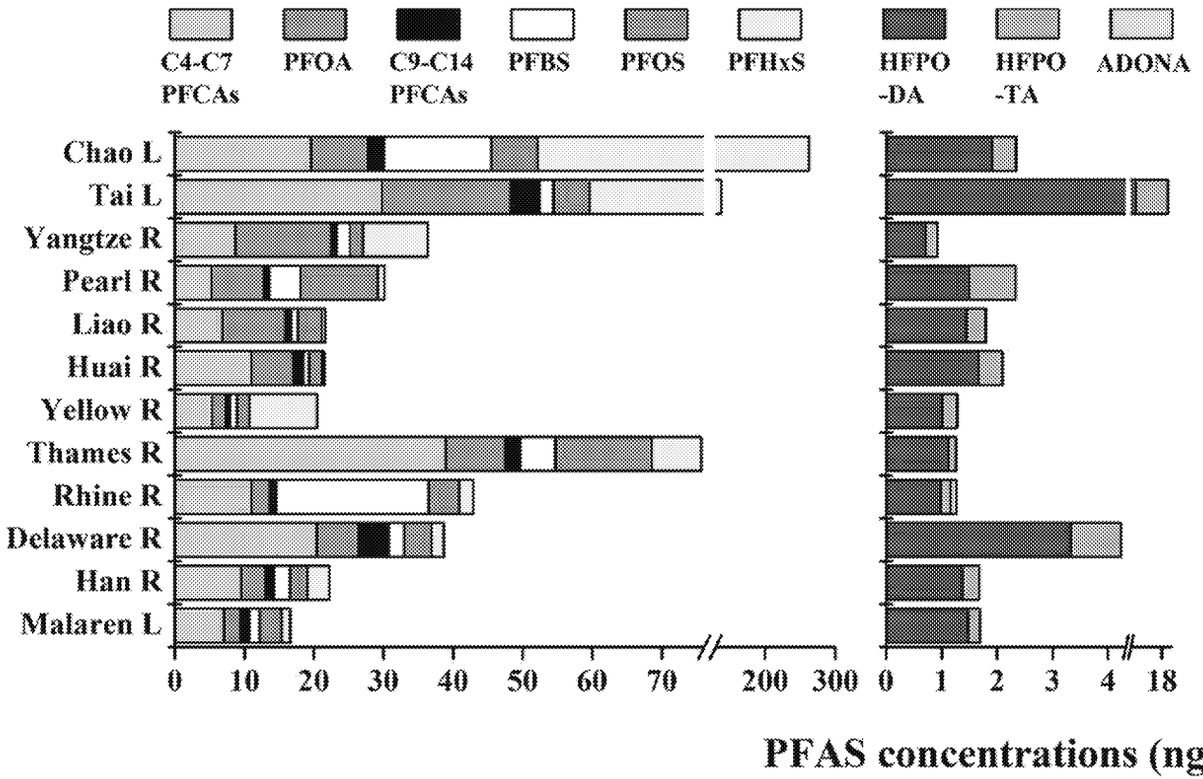


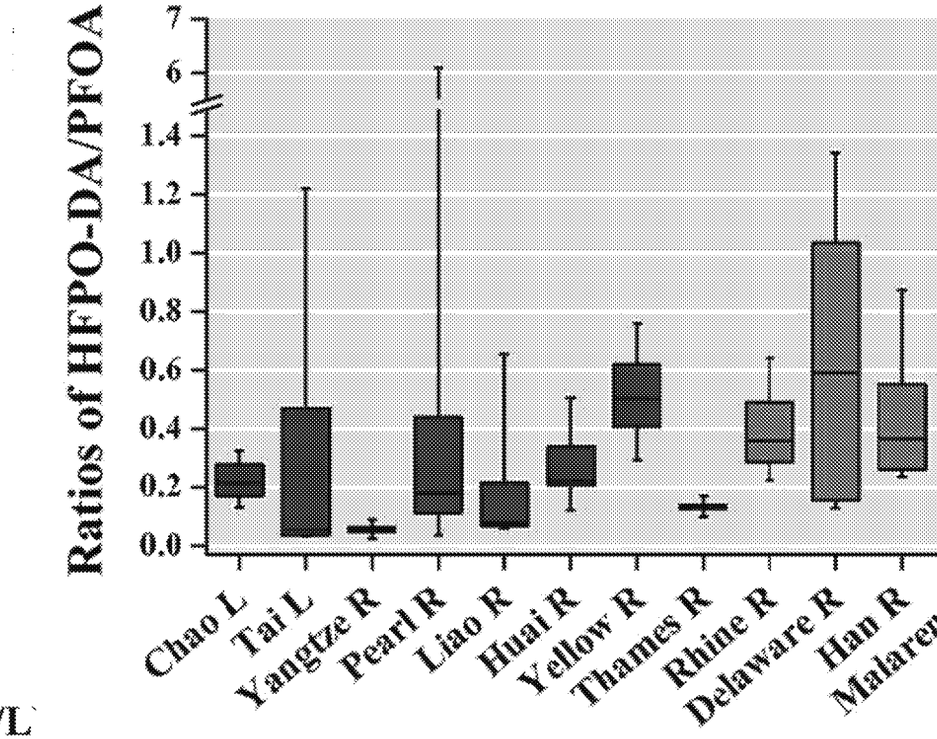


McCord et al. 2018

- Diversion of manufacturing waste stream (vertical line) results in reduction of concentrations to below 140 ng/L DW health guideline

GLOBAL SURVEY DATA (PAN ET AL)



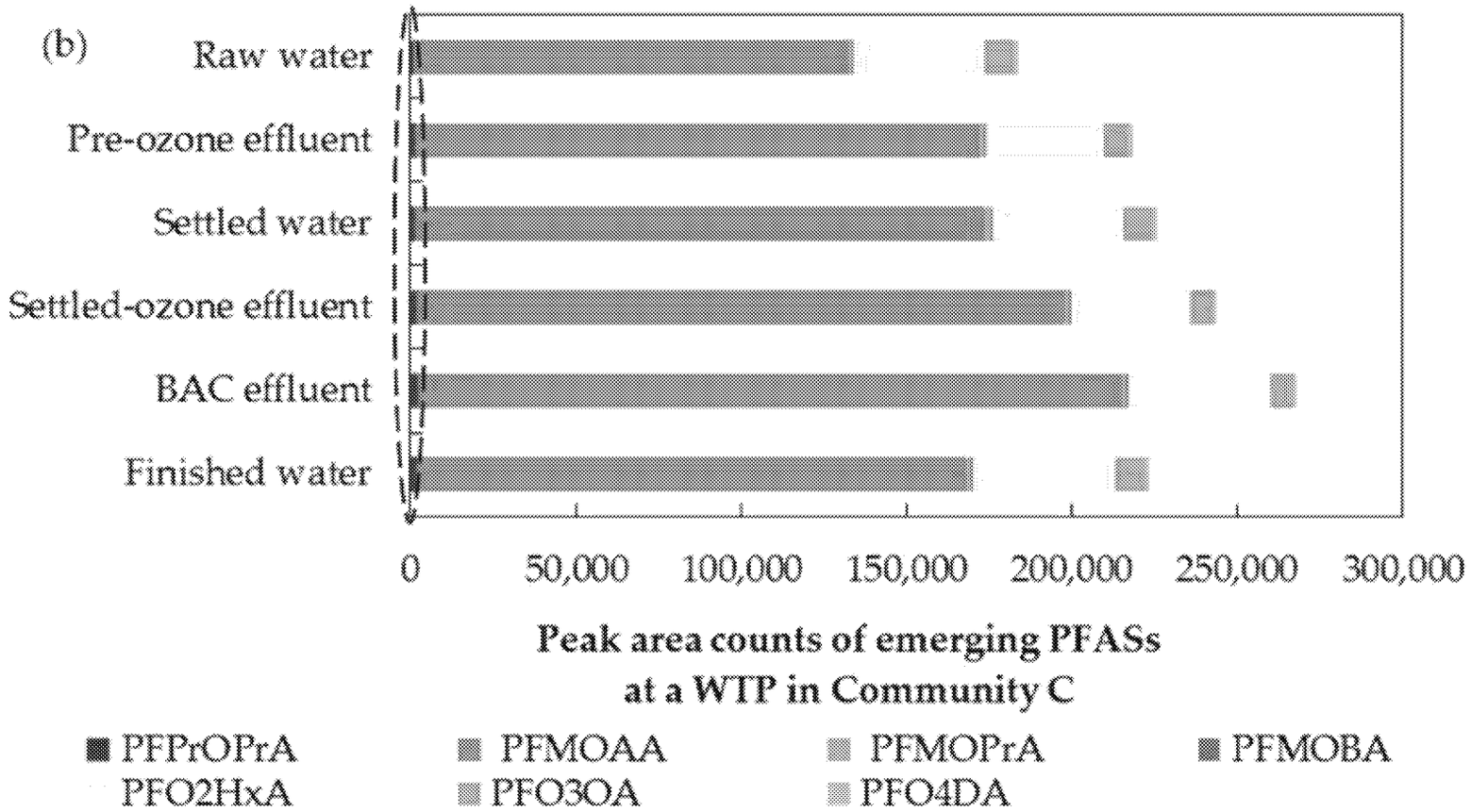


- HFPO-DA widespread, detected at all locations (96% > LOQ)
- Concentrations approaching those of PFOA in some locations

Pan, et al.(2018). Environmental Science & Technology.

HFPO-DA MAYBE A MINOR COMPONENT OF GenX

Sun et al. 2016



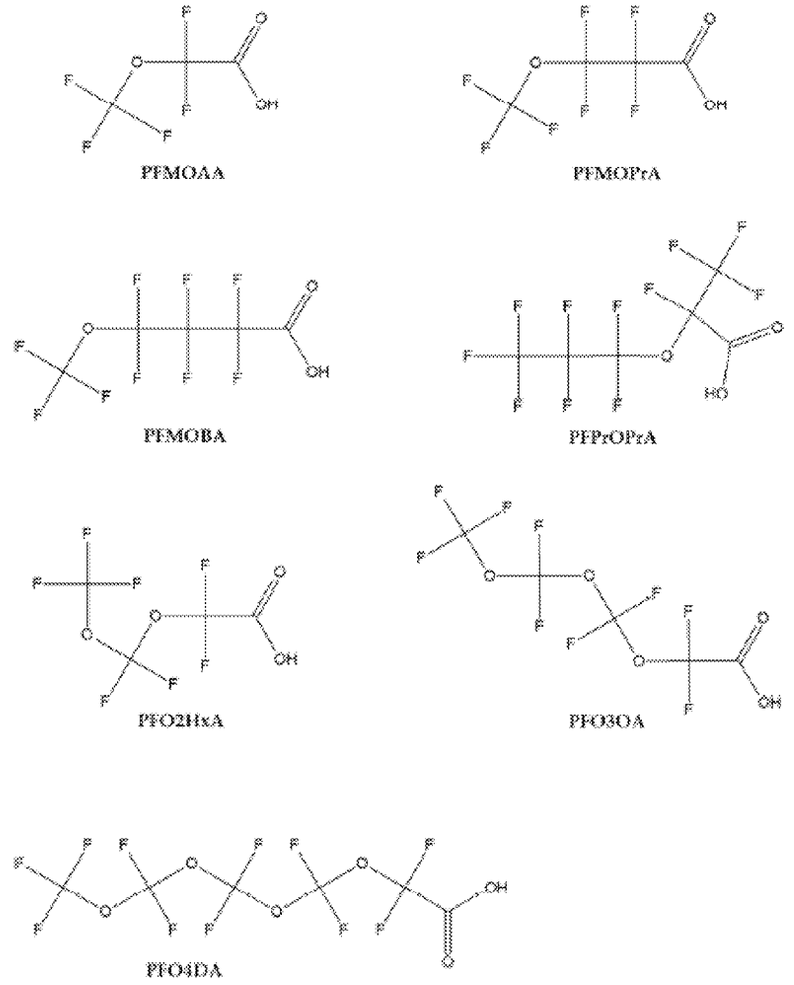


Figure S1. Molecular structures of PFECAs evaluated in this study

- Short chain PFMOAA largest area count
- Is HFPO-DA the only GenX component to measure?

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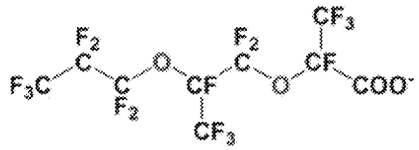
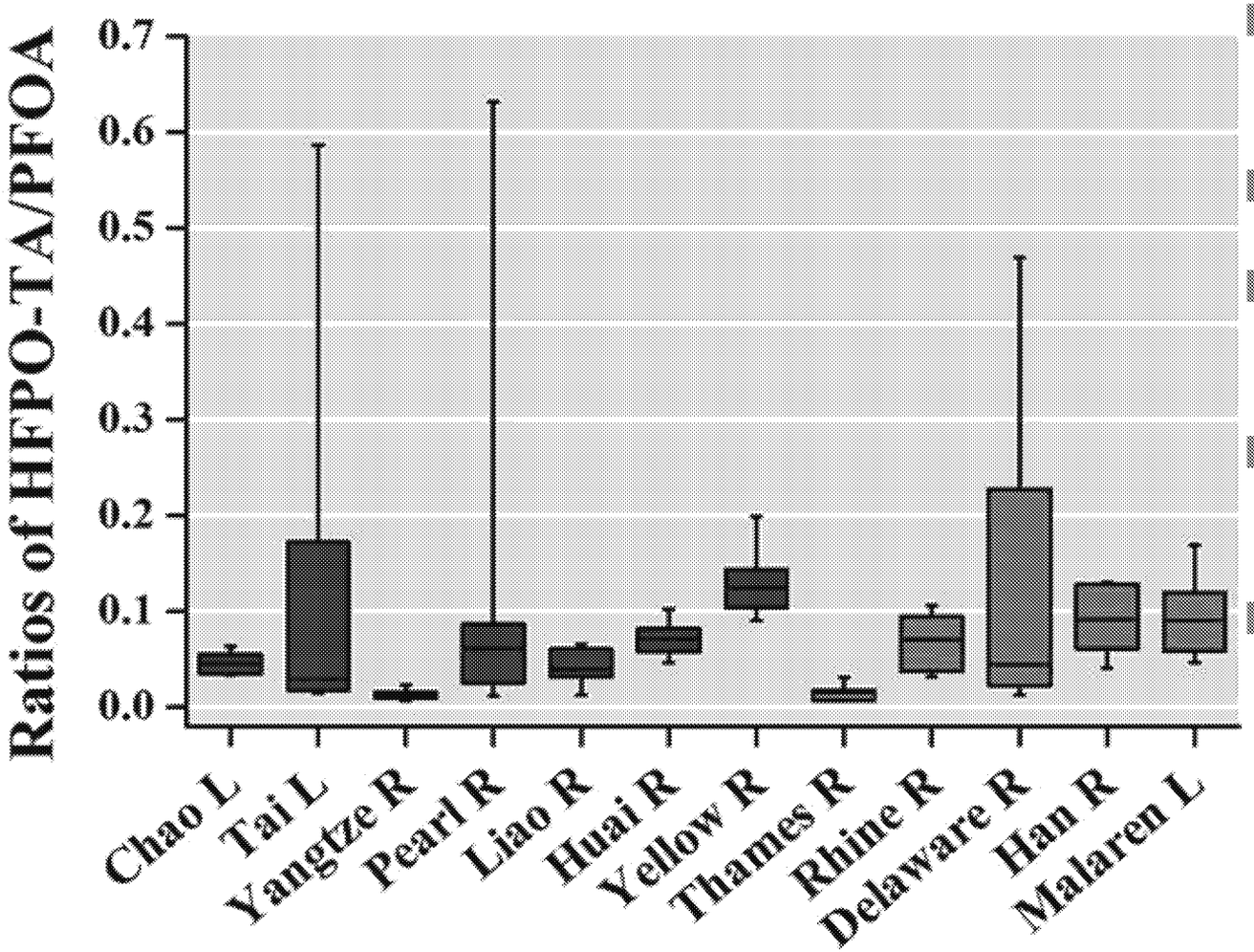
HFPO-TA

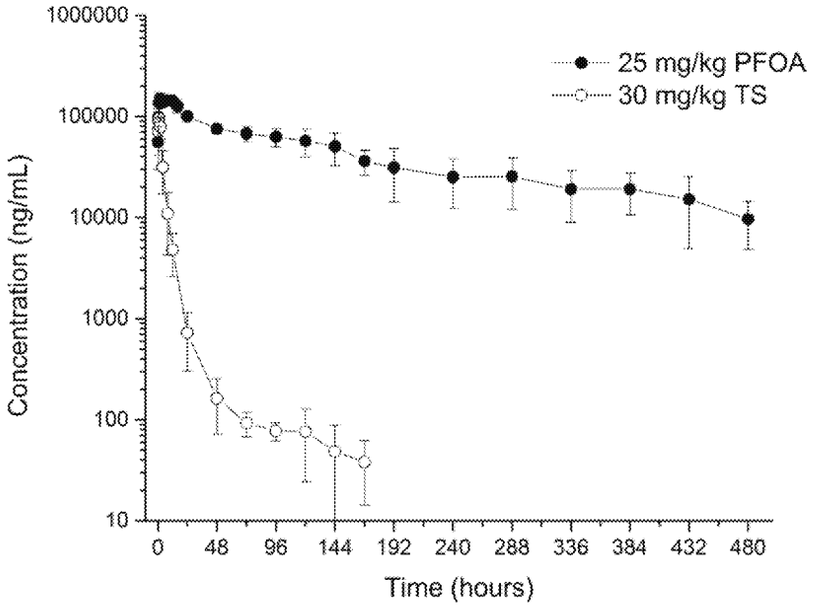




- HFPO-TA processing aid first detected in China
- Bioaccumulative
- Sheng et al. 2018 reports on genotoxicity > PFOA
- Pan et al. global survey detects HFPO-TA up to 20% of PFOA
- Spearman's rank correlation coefficients in 160 samples from Pan et al. 2018 between HFPO-DA and HFPO-TA is 0.7, suggests similar source and usage

FATE AND TREATMENT

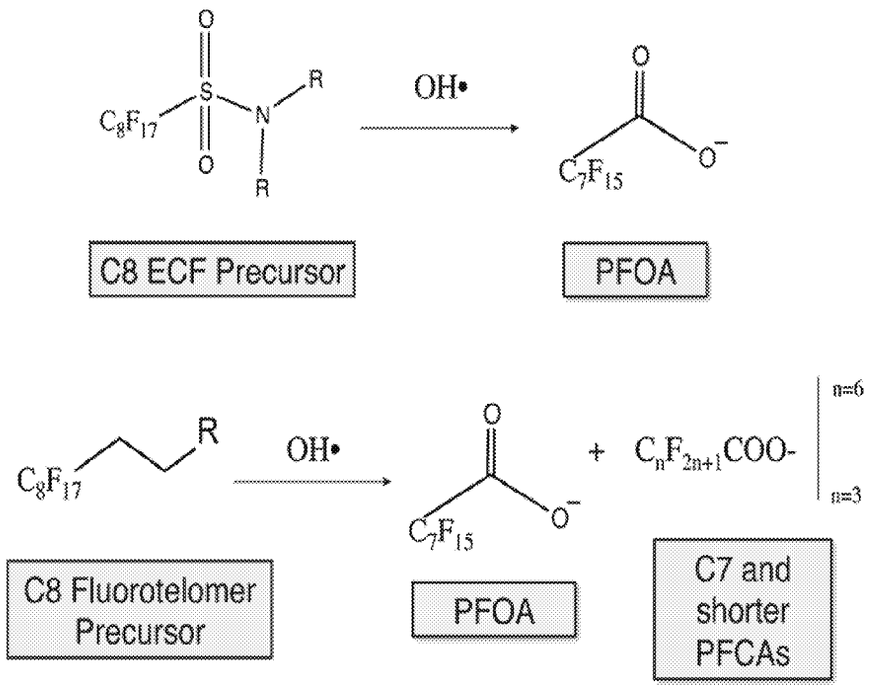
SGS AXYS HFPO-DA IS PERSISTENT. BIOACCUMULATIVE? TOXIC?



Comparison of plasma concentration (ng/mL) of test substance (30 mg/kg) and PFOA (25 mg/kg) in male rats
S.A. Gannon et al. / Toxicology 340 (2016)

Property	Results	Ref
Photolysis	?	
Hydrolysis	Stable	ECHA (REACH) 2014
Biodegradation	0% (28 days)	ECHA (REACH) 2014
Typical WWTP	Increase?	Sun et al. 2016
Carbon filtration removal	40-90%	Multiple
Hydroxyl/persulfate Oxidation	Not likely	Multiple
UV/Persulfite reduction	2h	Bao et al. 2018
Half life	<12h (rats) Humans? Renal resorption not likely?	Gannon et al. 2016, Shea 2018
Human data	ND in 50 paired human/serum. Compare PFOA/PFOS 98% detect	Kato et al. 2018

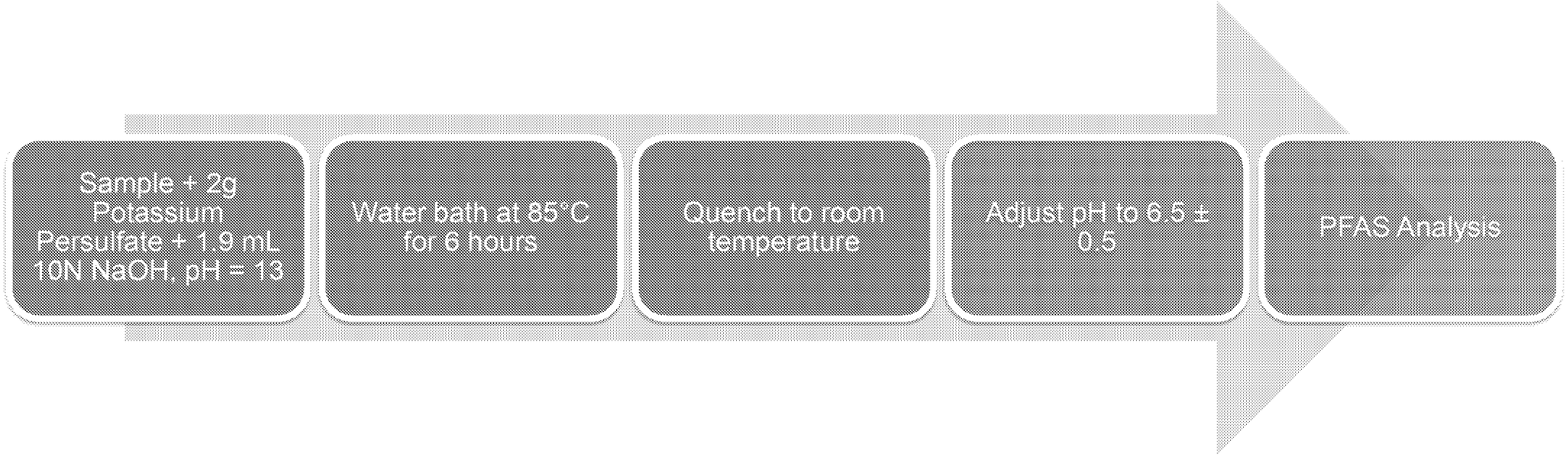
HYDROXYL RADICAL OXIDATION USING TOP



- Total Oxidizable Precursor (TOP) oxidizes PFAA precursors to PFCAs
- Measure PFCAs/PFSAs in sample before and after hydroxyl radical oxidation to report conversion rates
- What happens with HFPO-DA?

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

TOP REACTION PROTOCOL



Treatment	Description	N
Control	Control	3
Heated	Water bath 85°C for 6 hours, no persulfate/base	3
Reacted	Persulfate + base + 85°C for 6 hours	3

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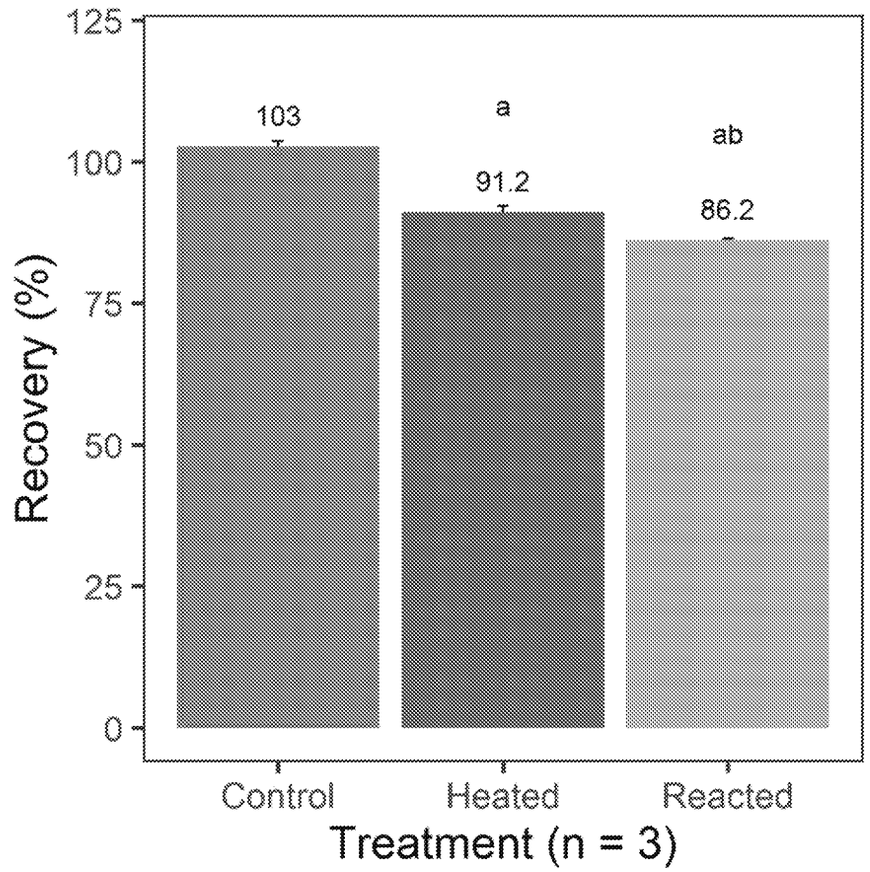
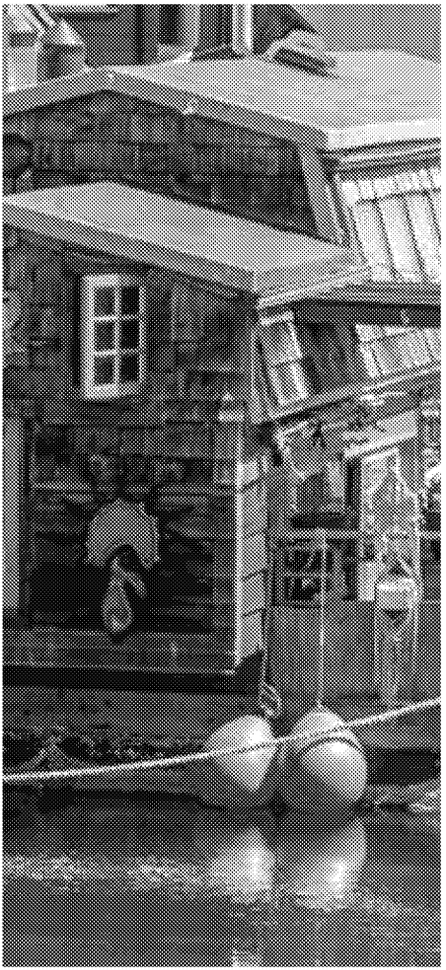
HYDROXYL RADICAL REACTION OF HFPO-DA



- No C4-C14 perfluorinated carboxylates detected
- (a) Significant reduction after 85ºC water bath for 6 hours (Heated)
- (b) Smaller, but significant reduction after heat + hydroxyl reaction (Reacted)
- Statistical change small, need to study product formation to separate effects of processing from reaction effect
- Need to repeat with other ether carboxylates, especially di-, etc. to understand fate

CONCLUSIONS, GAPS AND FURTHER WORK



- HFPO-DA is one of many processing aids that warrant further monitoring
- LC-MS/MS methods likely suitable, but standards availability may limit measurement
- HFPO-DA is mostly resistant to hydroxyl radical attack, but are other ether carboxylates?
- Many gaps in fate, long range transport and health information

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