2019 Sediments Conference

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Closing the PFAS Mass Balance in Sediments and Tissues: The TOP Assay

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TOP Assay - Outline

Introduction to PFAS

What are PFAS?

Nomenclature

Formation/Toxicity/Risk

The TOP Assay

What are precursors?

What is the TOP assay

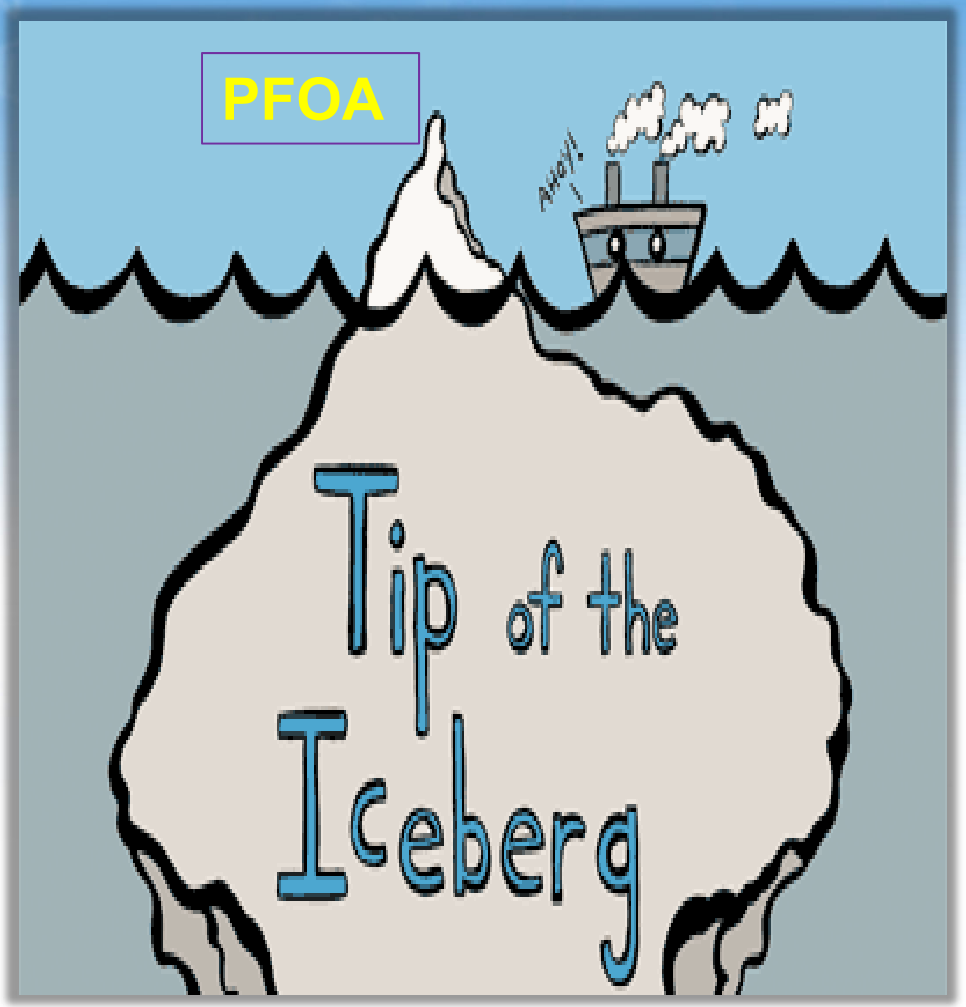
How does it work?

The chemical reaction

Challenges of complex samples

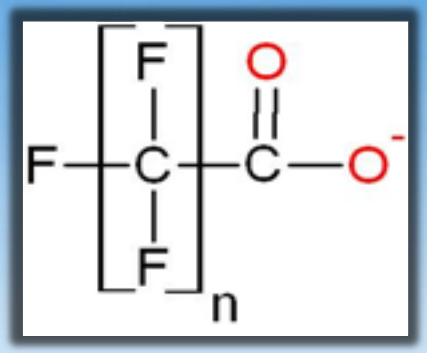
Best Practices for complexity

Conclusions



Briefly - What are PFAS?

- Class of synthetic compounds containing **carbon** chains with **fluorine** attached.
- The **C-F** bond is one of the shortest and strongest bonds in nature.
- PFC – Subset of PFAS completely fluorinated compounds. PFOS and PFOA are PFCs (no hydrogen atoms)
- **PFAAs – Perfluoroalkyl acids – 2 classes PFCAs and PFSAs**
- **PFAS do not degrade BUT they do biotransform**



Perfluoroalkyl Carboxylate

Perfluoroalkyl Sulfonate

Nomenclature

PFAS
Per- and Polyfluoroalkyl Substances

Completely & Incompletely Fluorinated

PFCs
Perfluorinated Compounds

Completely Fluorinated

PFAAs
Perfluoroalkyl Acids

Subset of PFCs

PFSAs
Perfluorinated sulfonic acids

PFCAs
Perfluoroalkylcarboxylic acids

PFOS

PFOA

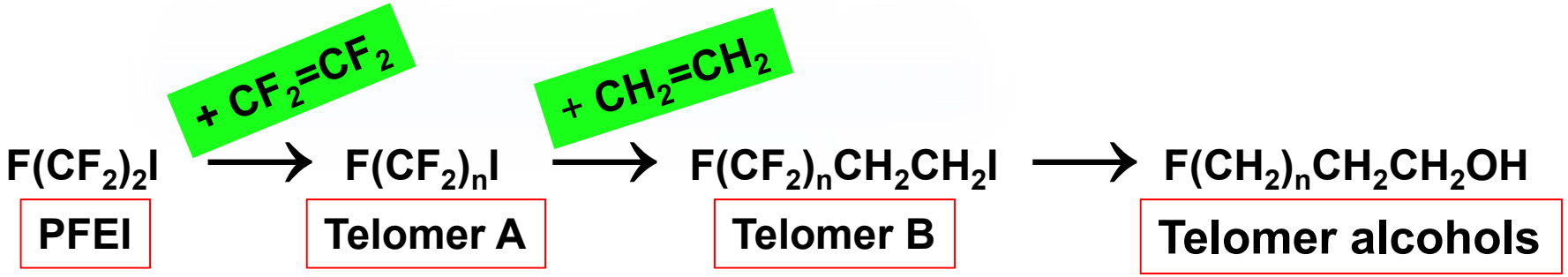
PFAS Formation

- **ECF Reaction:** Process yields a mixture of B/L isomers

$$C_8H_{17}SO_2F + 34HF \rightarrow C_8F_{17}SO_2F + 17H_2 \text{ (POSF)}$$

- **Telomer Reaction:** Process yields 100% linear isomers

(Synthesis of building blocks leading to fluorotelomer alcohols)



Exposure, Toxicity and Risk

Human exposure is primarily from:

- **food (fish) and air**

Exposure continues beyond phase out:

- **due to persistence**

Half-lives in humans:

- **2 to 9 years**

PFOA associated with:

- **liver, pancreatic, testicular, mammary gland tumors in animals.**

PFOS associated with:

- **liver and thyroid cancer in rats.**

PFOA and PFOS associated with:

- **cancers in humans; toxicology still being studied**

What is the Risk?
Why Do We Care About PFOA?

- Risk = one in one million risk of cancer from a lifetime exposure with no adverse effects
- NJ recommended health based MCL based on cancer and non-cancer endpoints = 14 ppt
- Production and use of PFOA in U.S. phased out
- Exposure continues due to persistence, biotransformation of precursor compounds and manufacturing abroad

Polyfluorinated – PFAA Precursors

- Thousands of PFAS are used in industrial and consumer products
- Some biotransform to make PFAAs
- Some are fluorotelomers
- Most are ionic either positive, negative or both
- Fate and transport – complex process

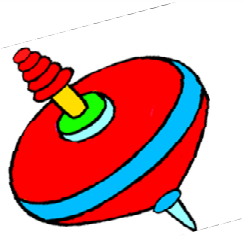
How Do Other PFAS Become PFOA?

Primarily 2 mechanisms:

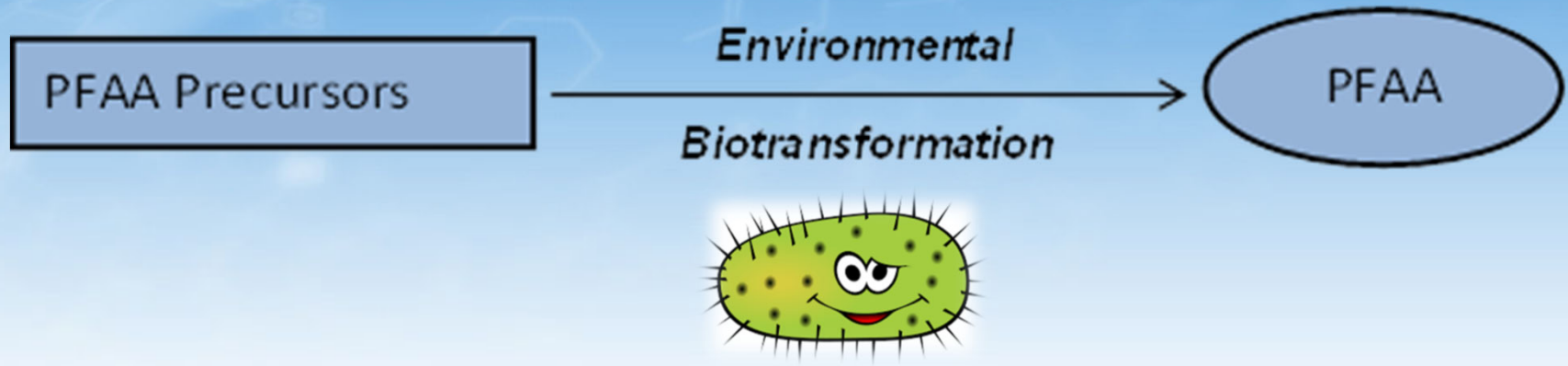
- Abiotic transformation of PFAA precursors sulfonamido and fluorotelomer precursors oxidize to form PFCAs
- Aerobic biotransformation of fluorotelomer precursors to form PFCAs
- Other biological mechanisms exist

What is the TOP Assay?

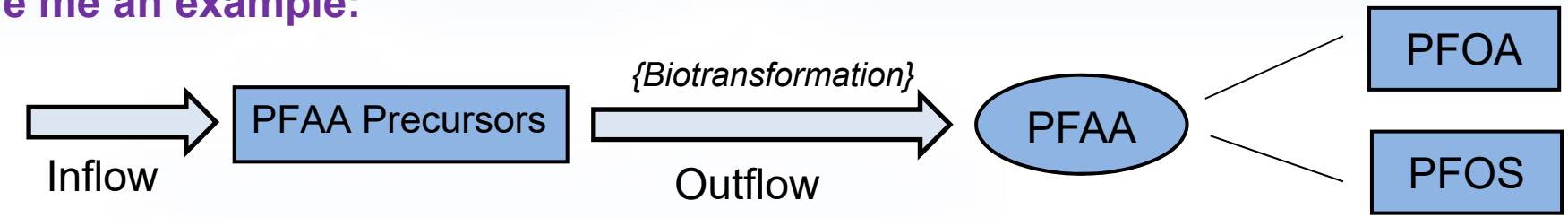
- A new PFAS sample preparation technique
- Conceptually simple chemistry
- Used in conjunction with 537M (Not 537) – combines pre and post oxidation results
- Indicates presence of unidentified PFAS in water, sediment and soil



How Does it Work in the Environment?



Give me an example:

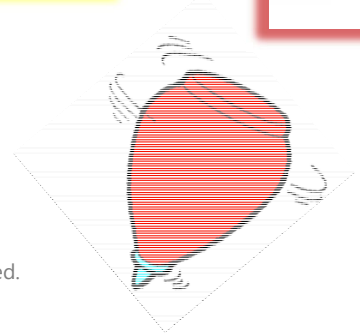


Low levels of discrete compounds are detected

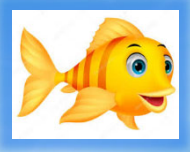
High levels of discrete compounds are detected, which can include PFOA and PFOS

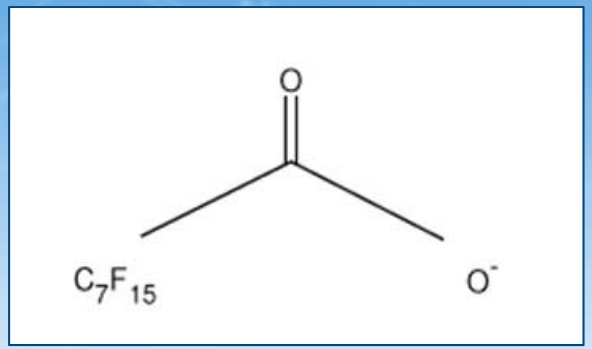
TOP – How it Works in the Laboratory

PFAA Precursors + OH• OH• OH• 85°C = PFOA + other PFCAs



A Closer Look at the Chemistry



C_8F_{17} — OH• → 

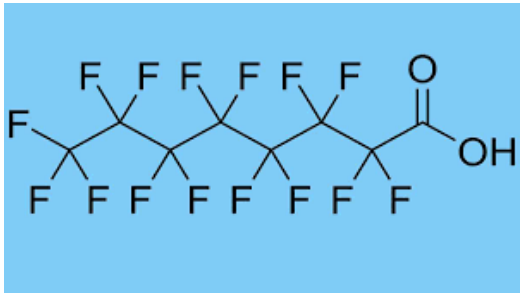
+ $C_nF_{2n+1}COO$ n=3 - 6

C_8 Fluorotelomer Precursor

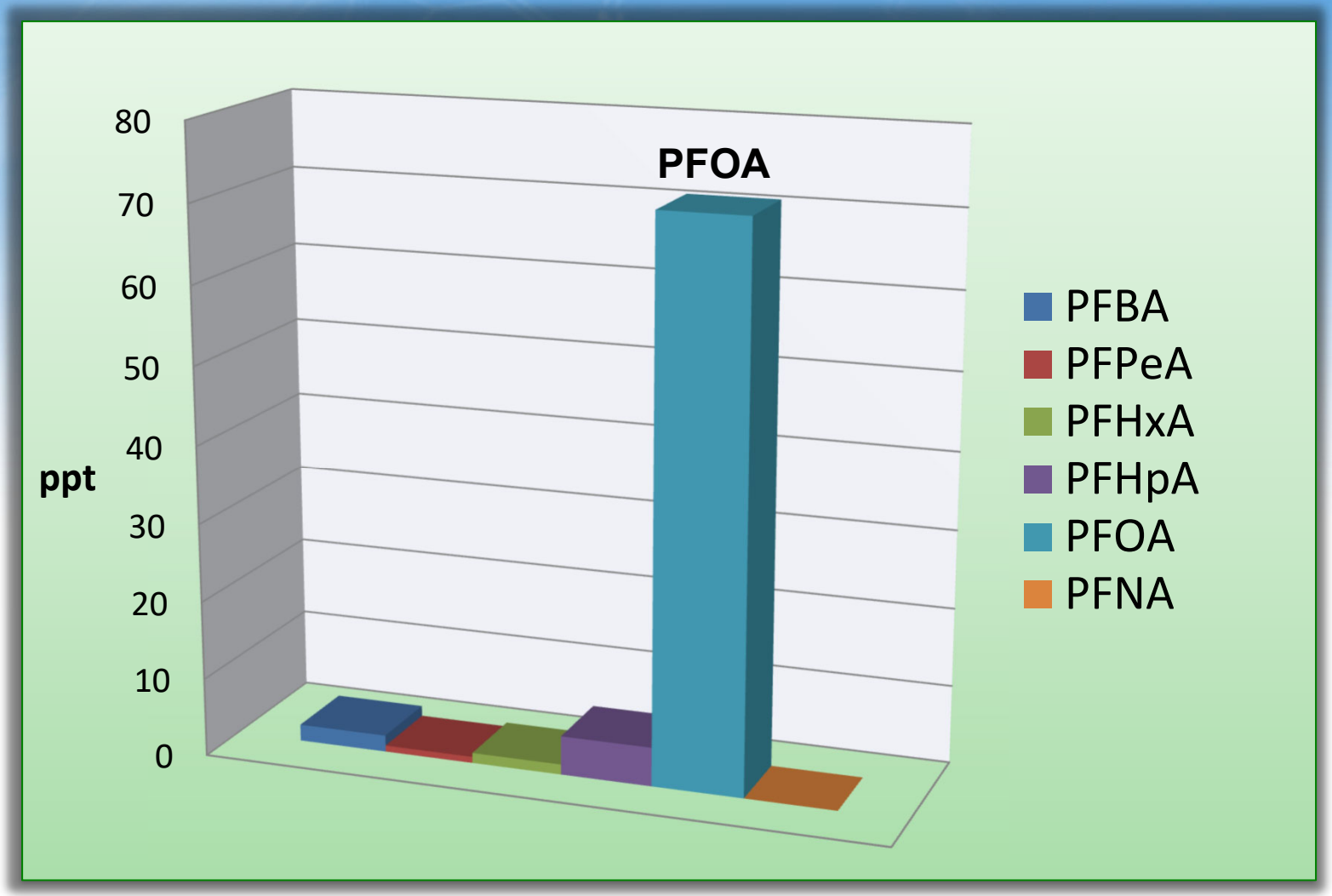
PFOA

C7 and shorter PFCAs

+ 

= 

PFCA Pattern – Me-FOSA Precursor



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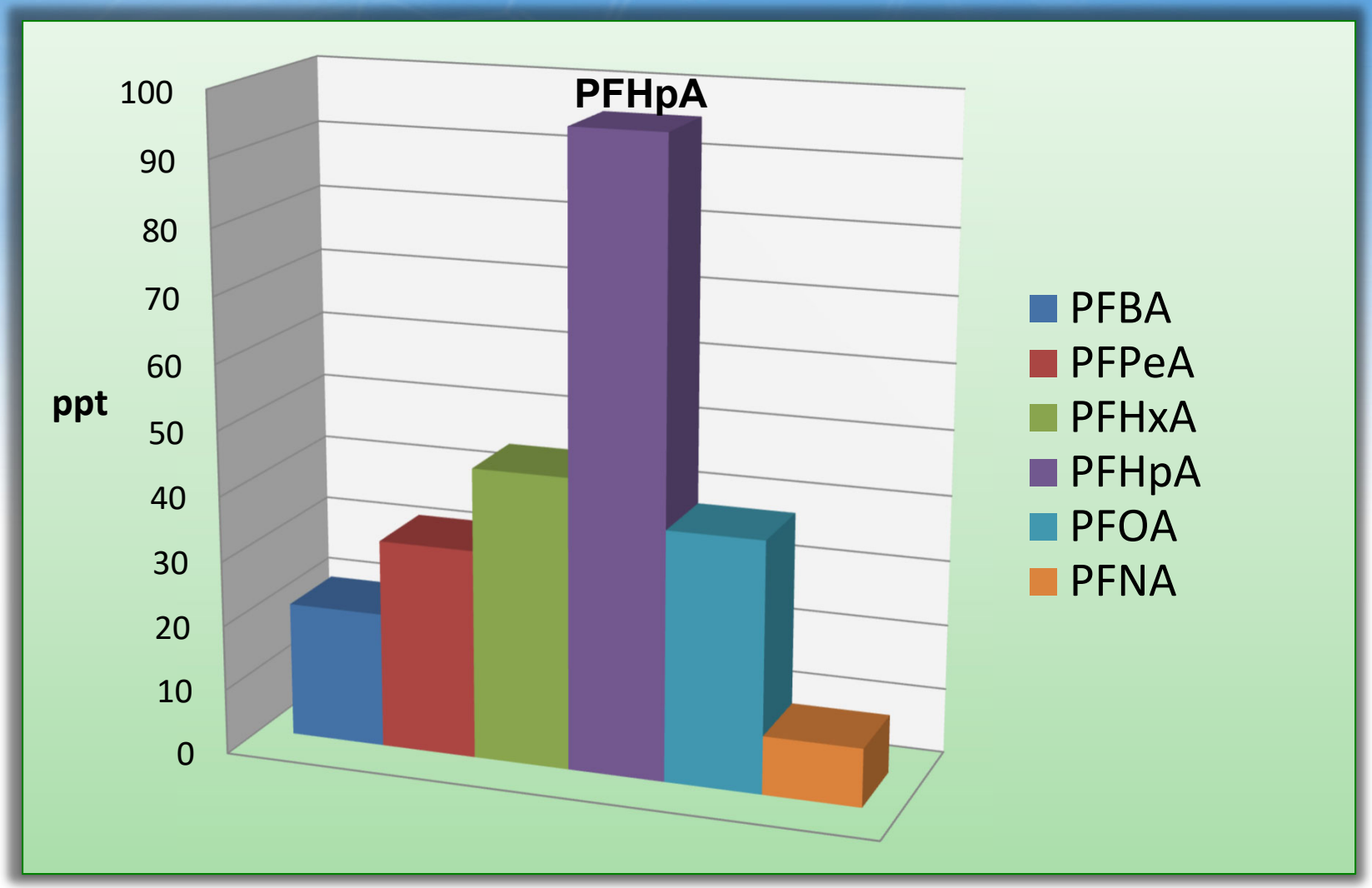
PFCA Pattern – 8:2 FTS



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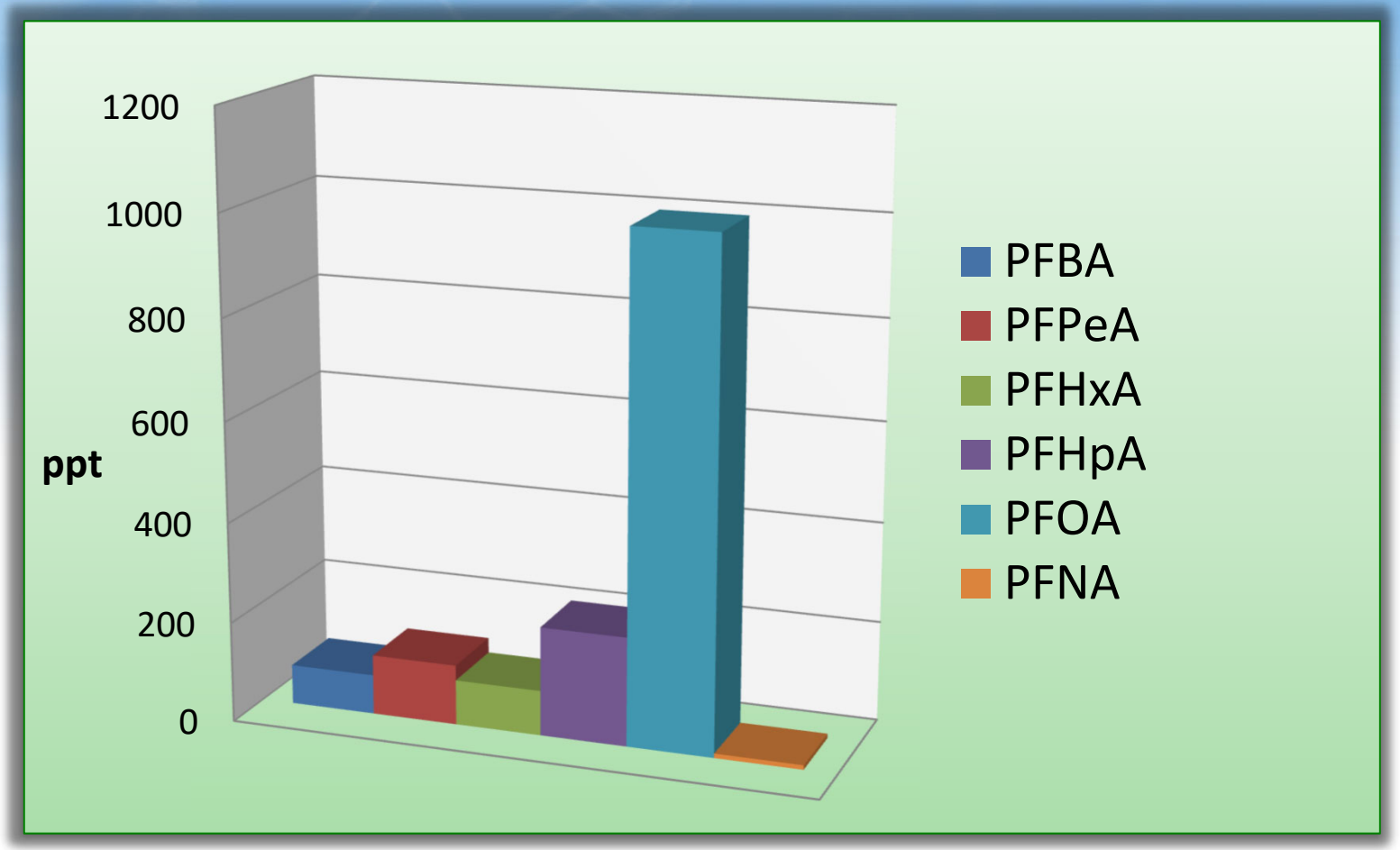
PFCA Pattern, 8 Precursors:

FOSA, MeFOSA, EtFOSA, 4:2FTS, 6:2FTS, 8:2FTS, MeFOSAA, and EtFOSAA



Complex Sample Challenges

- **Poor or variable IDA/Surrogate Recoveries**
- **Incomplete oxidation** – native precursors are not completely converted
  - Consumption of oxidation potential by non-PFAS
  - Consumption of oxidation potential by PFAS
  - Poisoning of reagent chemistry
- **Chromatographic Disturbances**
  - Low molecular weight early eluters are problematic – split peaks
  - Unresolved mass
  - Interferences – lots of extra peaks

Example of Complex Sample (Results in ppb)

Precursor	Pre - TOP	Post - TOP	Oxidation
FOSA	350	9.5	Incomplete
MeFOSAA	ND	ND	Complete
EtFOSAA	5.9	ND	Complete
6:2 FTS	48	57	Incomplete
8:2 FTS	690	270	Incomplete

Total PFCA Pre = 150 ppb

Total PFCA Post = 16,000 ppb

Repeat with Best Practices Applied

Precursor	Pre - TOP	Post - TOP	Oxidation
FOSA	350	ND	Complete
MeFOSAA	ND	ND	Complete
EtFOSAA	5.9	ND	Complete
6:2 FTS	48	ND	Complete
8:2 FTS	690	ND	Complete

Total PFCA Pre = 150 ppb

Total PFCA Post = 13,000 ppb

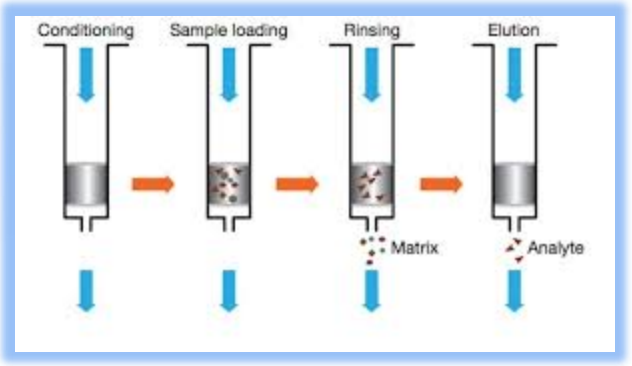
Best Practice Steps

Step 1

Step 3

Step 2

Step 4



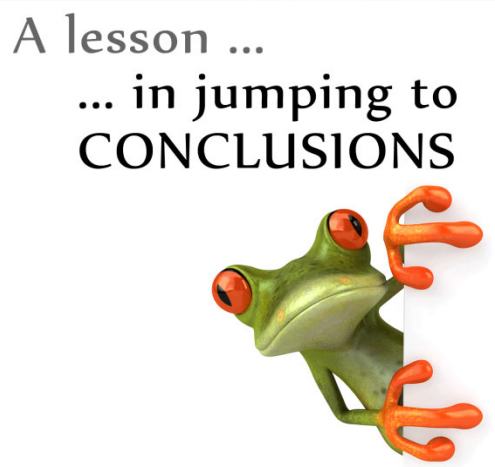
Fish Study - IDA/Surrogate Ave Recoveries

	1g Pre	1g Post	% Imp	0.1g Pre	0.1g Post	% Imp	1g Pre	1g Post	% Imp	0.1g Pre	0.1g Post	% Imp
	No EnviCarb			No EnviCarb			With EnviCarb			With EnviCarb		
13C4 PFBA	16	65	49	22	74	52	43	72	29	40	74	35
13C5 PFPeA	31	62	31	53	72	20	51	71	20	52	72	20
13C2 PFHxA	32	65	32	54	73	19	52	72	20	54	73	19
13C4 PFHpA	32	65	33	55	74	19	52	73	21	54	77	23
13C4 PFOA	37	65	28	56	77	21	61	72	12	55	76	20
13C3 PFBS	36	59	23	50	69	19	54	65	11	50	66	16
18O2 PFHxS	37	63	26	51	70	19	53	67	14	50	67	17
13C4 PFOS	37	63	27	53	72	18	57	71	14	52	71	19
13C8 FOSA	31	50	18	50	59	9	48	54	6	50	62	12
d3-NMeFOSAA	41	60	19	53	70	17	61	67	6	55	69	14
d5-NEtFOSAA	51	61	10	59	72	13	77	68	-8	56	71	16

Fish Study Matrix Spikes

	1g MS Pre	1g MS Post	1g MS Pre	1g MS Post	1g MS Pre	1g MS Post	1g MS Pre	1g MS Post
	No EnviCarb				With EnviCarb			
PFBA	10.68	12.51	10.99	12.05	10.47	12.91	10.45	12.74
PFPeA	10.44	11.69	9.79	11.89	9.91	11.79	10.10	11.98
PFHxA	10.60	11.87	9.20	11.17	9.76	11.10	10.35	11.97
PFHpA	11.30	12.17	10.78	12.20	13.95	13.01	14.92	11.78
★ PFOA	10.49	17.96	10.41	17.84	10.50	19.65	10.78	19.91
PFBS	8.99	9.26	8.94	8.88	9.08	9.27	9.10	9.24
PFHxS	9.02	8.34	9.31	8.61	9.12	8.83	9.60	8.81
PFHpS	10.06	9.43	10.61	9.46	10.27	9.21	10.52	9.30
★ PFOS	14.27	14.24	14.02	14.03	13.68	13.11	13.33	12.63
FOSA	11.56	ND	11.41	ND	10.85	ND	11.09	ND
NMeFOSAA	10.74	ND	11.92	ND	10.58	ND	10.39	ND
NEtFOSAA	10.65	ND	9.79	ND	10.59	ND	9.79	ND
6:2 FTS	10.10	ND	8.72	ND	9.45	ND	9.45	ND
8:2 FTS	9.23	ND	9.63	ND	9.85	ND	9.69	ND

What Conclusions Can We Draw?



- The TOP Assay can be performed on complex matrices
- Best practices include:
  - Mass reductions
  - EnviCarb
  - Optimized SPE cleanups
- IDA/Surrogate recoveries improve
- More effective oxidation has little impact on total PFCA concentration
- Might be useful for fish advisories

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Thank you for attending

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If you have any additional questions you may submit them directly to:

http://testamericainc.com/services-we-offer/ask-the-expert/karla-buechler/