Per- and Polyfluoroalkyl Substances (PFAS)

Charles D. Hertz, Ph.D.

AQUA

Schuylkill Water Utility Forum

Albright College, Reading, PA

September 12, 2018

PFAS in Water: outline

- Introduction
- What are PFAS?
    - History and use
    - Chemistry, nomenclature: per and poly
- Analysis
- Environmental fate
- Occurrence results…*after UCMR3*
- Health Advisory
    - Regulation of unregulated contaminants
- Risk Communication
- Treatment

Introduction to PFAS

- What are PFAS?
  - Synthetic organic compounds
  - Used in many consumer products
- Where do PFAS come from?
  - Fire-fighting foams
  - Stain-resistant materials
  - Clothing, upholstery, rugs

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Major Sources of PFAS

1. Fire fighting foam/ training & response sites
2. Industrial sites
    - textile, leather processing
    - metal finishers, wire manufacturing
    - plating and semiconductor facilities
    - paper mills
3. Landfills
4. Wastewater plants / biosolids

History & Use

History and Use of Per- and Polyfluoroalkyl Substances (PFAS)

PFAS[1]	Development Time Period							
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics			
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS[2])
PFOA		Initial Production		Protective Coatings				
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)

Per- and Polyfluoroalkyl Substances (PFAS) Team Contacts

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March 2018

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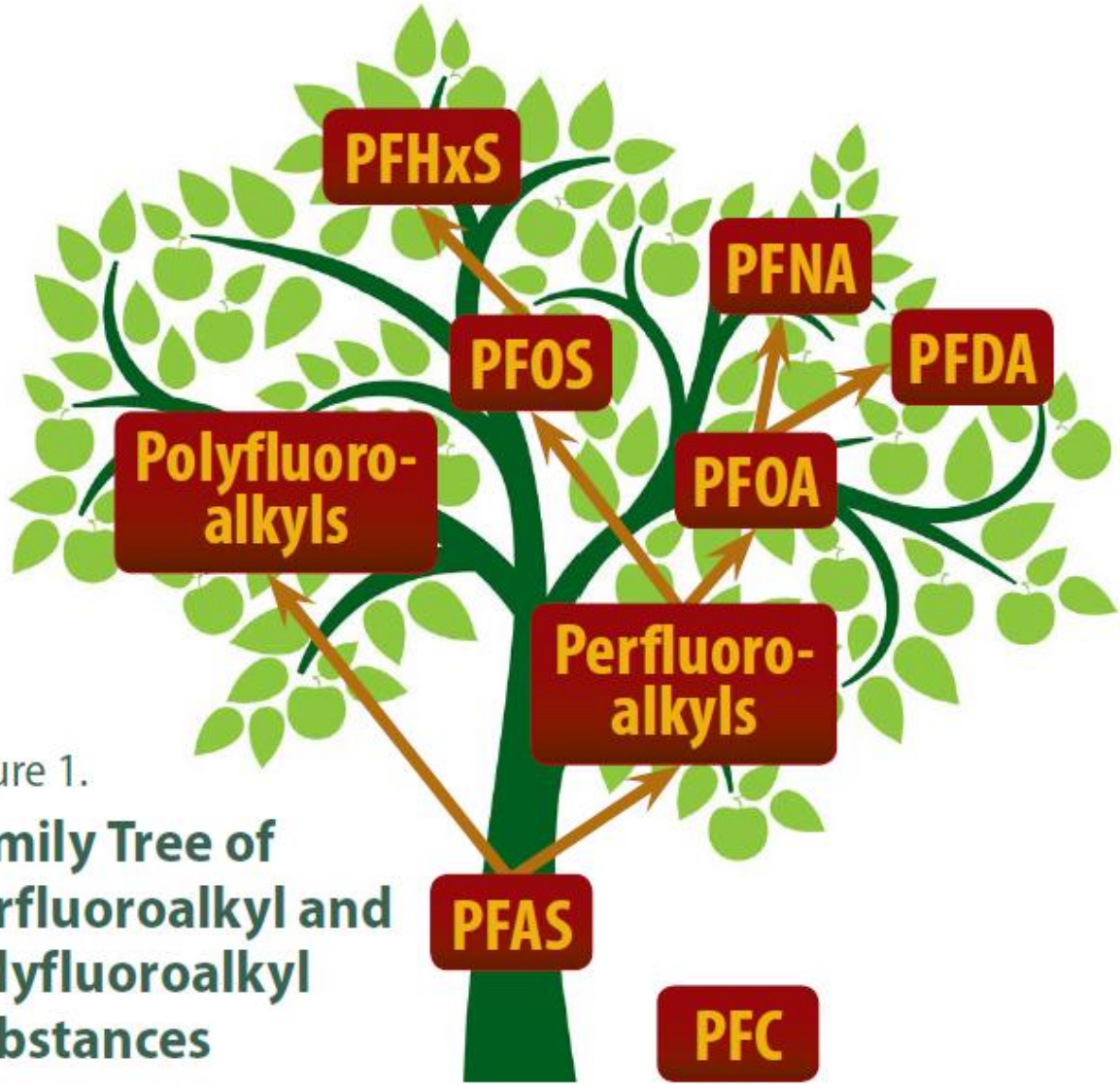

Figure 1.

Family Tree of Perfluoroalkyl and Polyfluoroalkyl Substances

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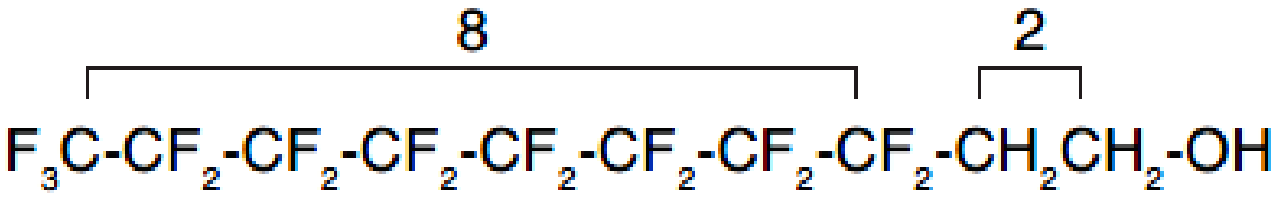
Agency for Toxic Substances and Disease Registry
Division of Community Health Investigations

ATSDR

Perfluorooctane sulfonate (PFOS)

Perfluorooctane carboxylate (PFOA)

Polyfluorinated Substances



8:2 FTOH (8:2 fluorotelomer alcohol)

Analysis of PFAS

- Sampling and precautions
- Multi-step, multi-day laboratory analysis
    - Sample preparation: longest part of analysis
    - Instrumental analysis: LC/MS/MS

- EPA Method 537
    - only approved method for water analysis
- Method 537 modified
    - *anything goes*

Occurrence depends on sensitivity of testing methods

- UCMR3
  - EPA Method 537
  - Mandated sensitivity: Minimum Reporting Levels
  - Low occurrence

- Monitoring outside of UCMR3 program
  - "More sensitive" version of method
  - Lower MRLs…higher occurrence
- ***If you look harder…you will find more***

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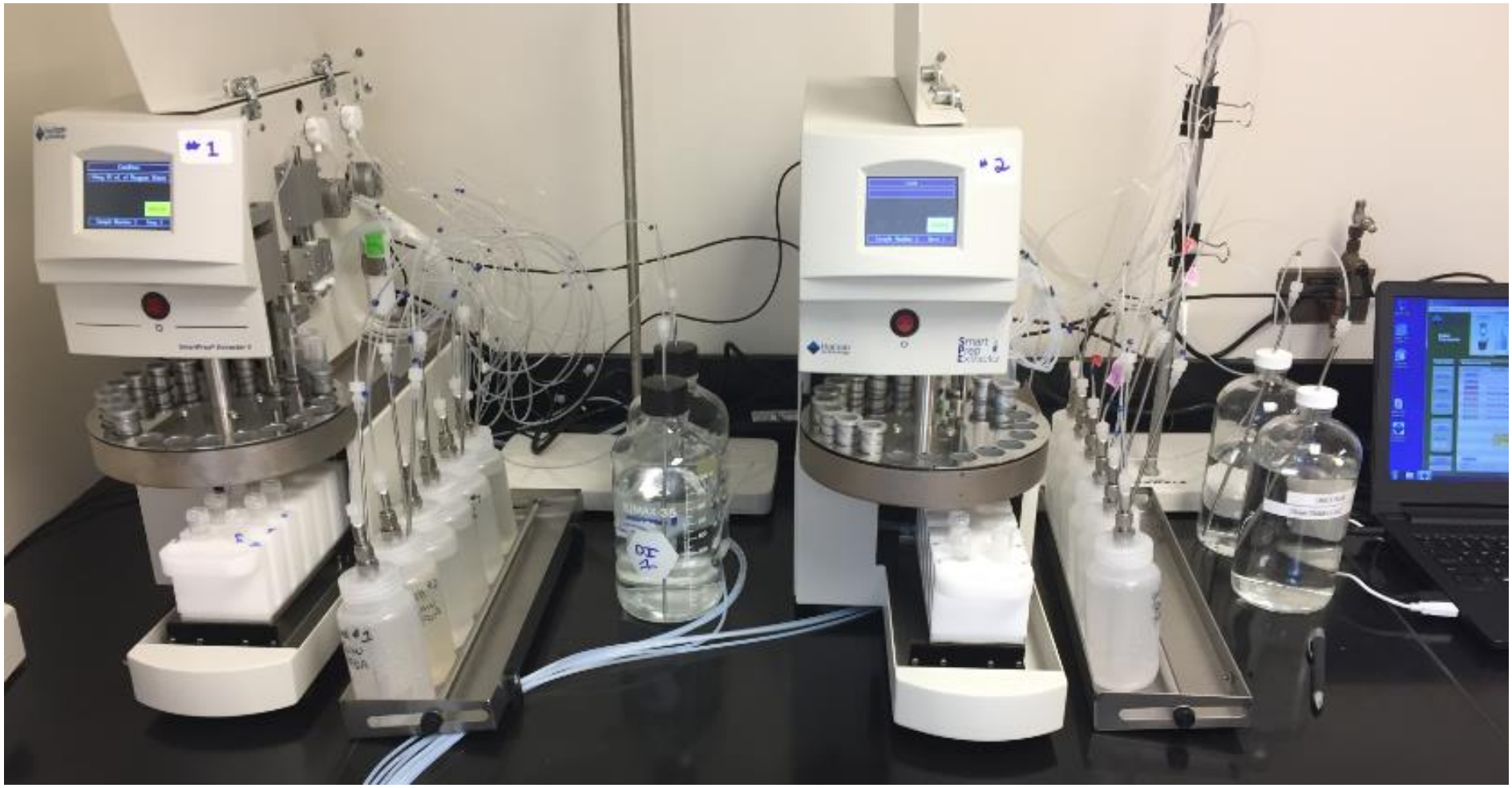
PFAS Analysis: sample preparation



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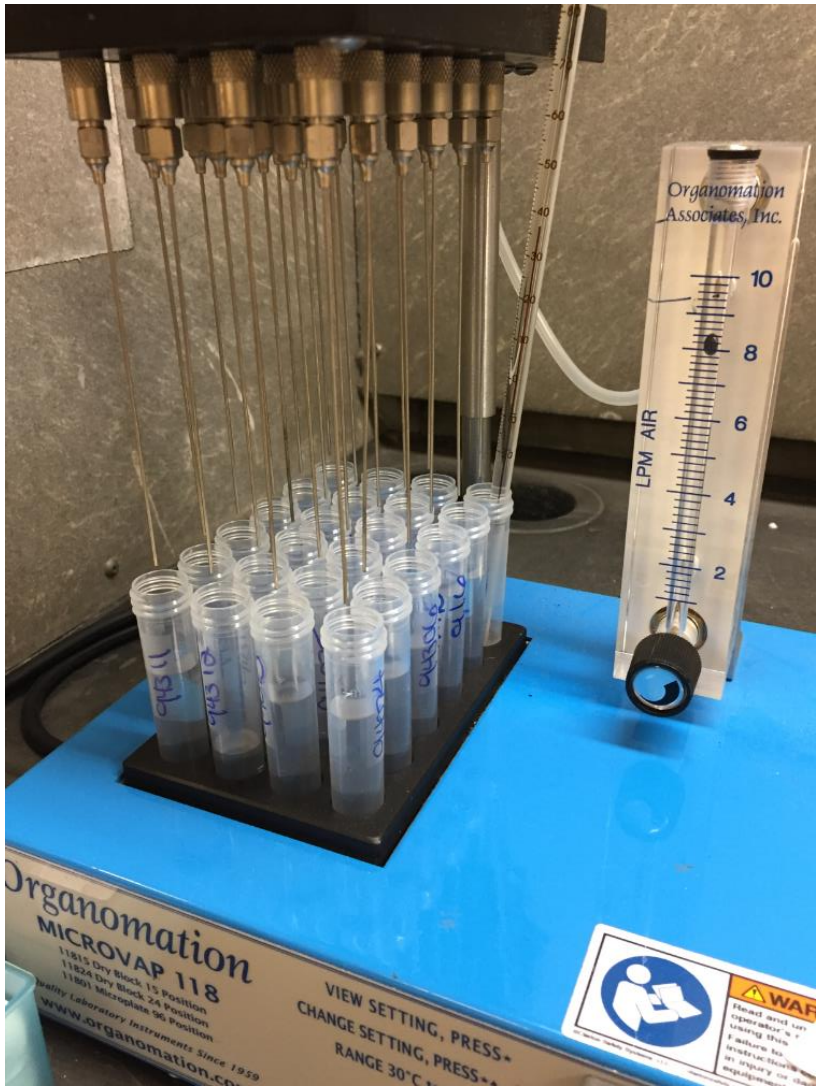
Solid Phase Extraction units

PFAS Analysis: sample preparation



evaporative concentration

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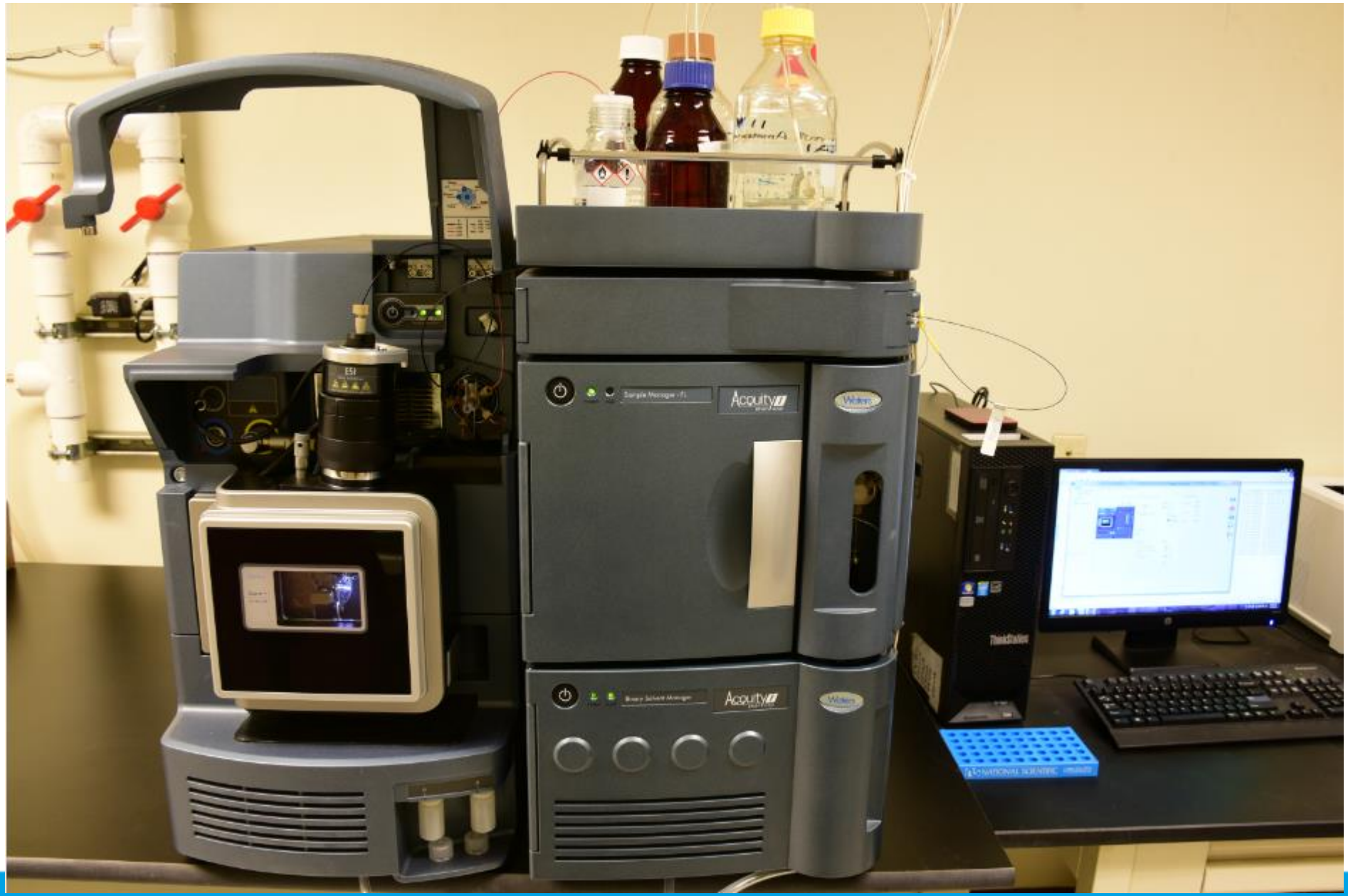
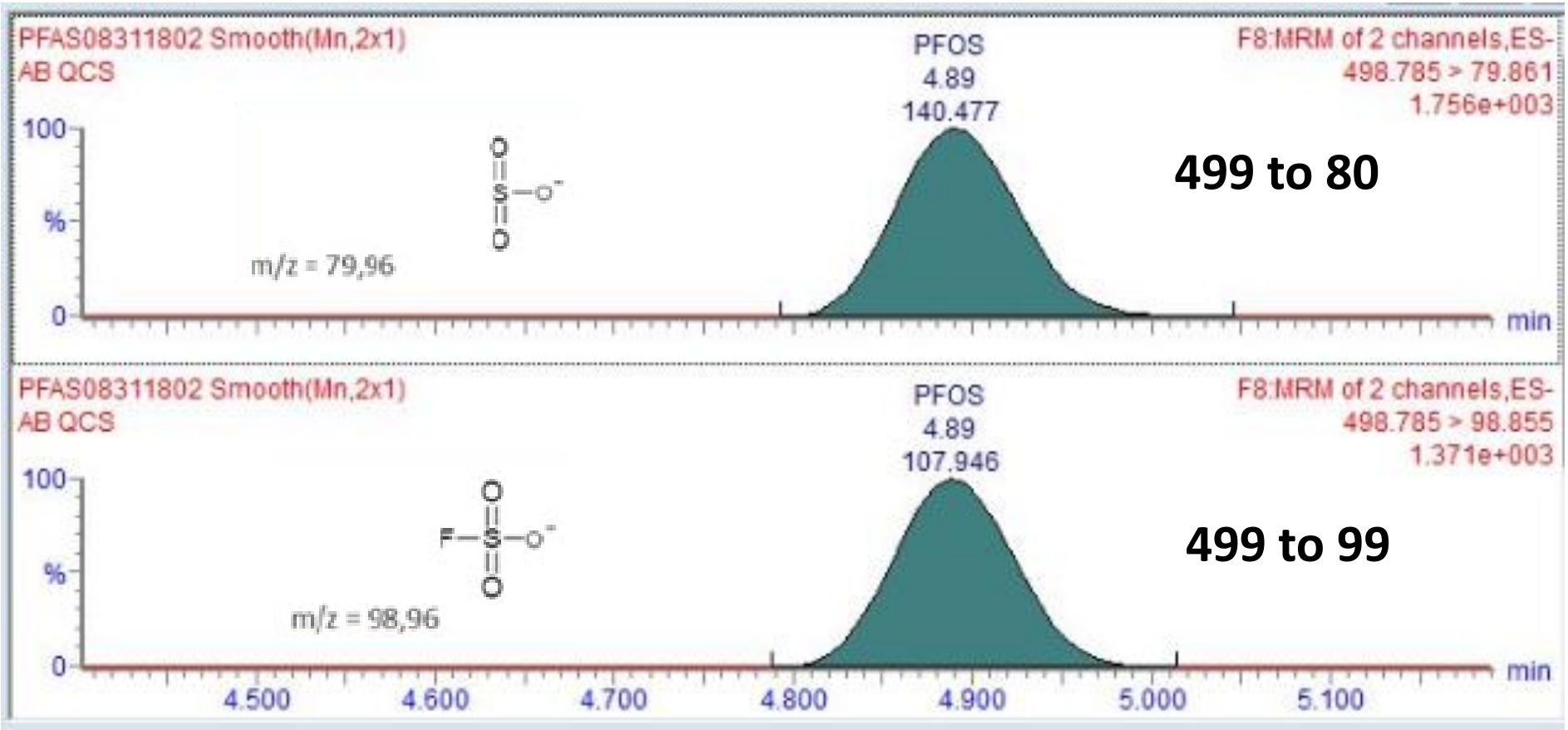
Instrumental Analysis of PFAS: LC/MS/MS

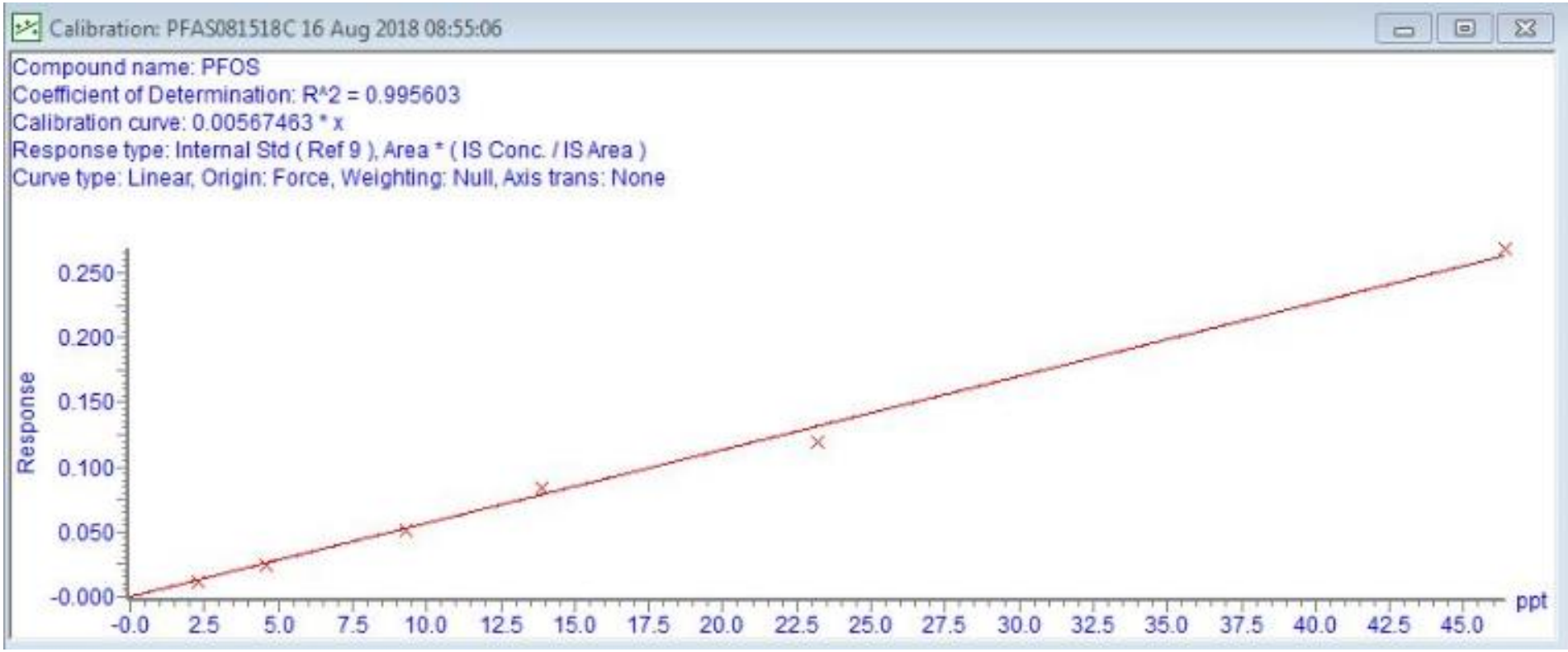


Identification of PFOS: specific masses monitored



MRM chromatograms

PFOS calibration curve: 2.3 ng/L – 46 ng/L



MRL during UCMR3: 40 ng/L

PFAS analysis: summary

- Time-consuming
- Costly
- Expensive instrumentation
- Few certified laboratories
- EPA Method 537: drinking water only
- Method 537, *modified*…wide variations
    - Analyte list
    - Reporting levels

Chemistry determines:

- Solubility
- Adsorption
- Volatility
- Ionization
- **Fate**
- Treatment
- Analysis

Perfluorooctane sulfonate (PFOS)

Perfluorooctane carboxylate (PFOA)

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Compilation of environmental fate parameters
Chemical / physical properties

Environmental Fate and Transport for Per- and Polyfluoroalkyl Substances

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ENVIRONMENTAL SCIENCE FOR THE EUROPEAN REFINING INDUSTRY

Understanding PFAS Fate and Transport

Dave Woodward, AECOM
Erika Houtz, PhD, Arcadis
Jeffrey Burdick, Arcadis
November 30, 2016

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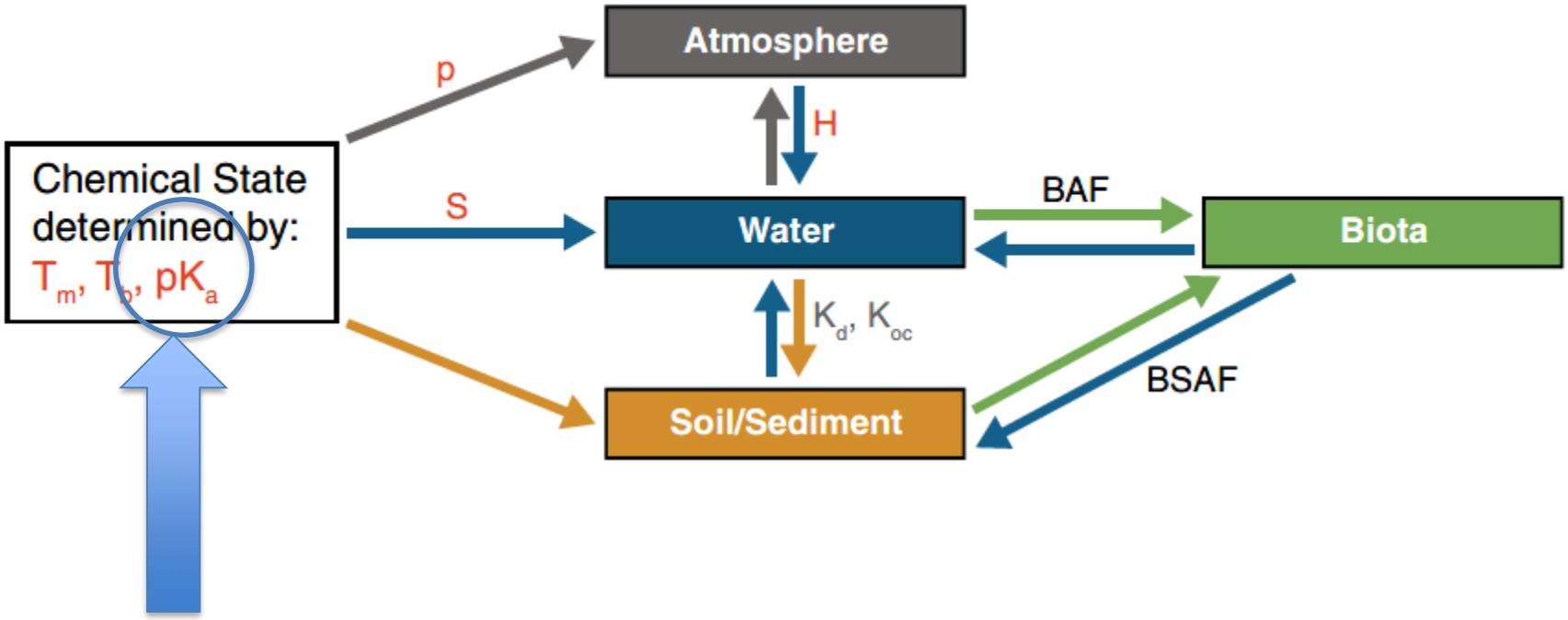
NICOLE
Network for Industrially Contaminated Land in Europe

report no. 8/16

Environmental fate and effects of poly- and perfluoroalkyl substances (PFAS)

Environmental Fate of PFAS



Ionization constant, pK_a

at environmentally relevant pH PFOS is present as the ***anion***

pH > pK_a

protonated sulfonic acid

anion sulfonate

pK_a

Implications on fate & transport

Implications on treatment

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PFOS: pK_a -6 to -2.6

PFOA: pK_a -0.16 to +3.8

Chemical / Physical Data: incomplete and/or wide estimates

Acronym	Water Solubility[b] (20 - 25 °C) [g/L]	Melting Point[a] [°C]	Boiling Point[a] [°C]	Vapor Pressure[b] [Pa]	Henry-Coefficient [Pa·m³·mol⁻¹]	log Kow[b] [-]	log K_{oc} [L/kg]	Kd (pH 7)	Dissociation Constant (pKa)
PFCAs									
PFBA	Miscible	-17.5	121	1307	--	2.82	1.88	--	-0.2 to 0.7
PFPeA	112.6	--	124.4	1057	--	3.43	1.37	--	-0.06
PFHxA	21.7	14	143	457	--	4.06	1.91	--	-0.13
PFHpA	4.2	30	175	158	--	4.67	2.19	0.4 - 1.1	-0.15
PFOA	3.4 - 9.5	37 - 60	188 - 192	4 - 1300	0.04 - 0.09	5.30	1.31 - 2.35	0 - 3.4	-0.16 to 3.8

PFOA: melting point 37 to 60 C

PFOA: pK_a -0.16 to +3.8

Red font indicates parameters estimated with published equations. Calculated parameters are based on the neutral form of the substances (and not the conjugate base, which predominates for some PFAS at neutral pH)

-- No data or not applicable.

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Chemical / Physical Data: incomplete and/or wide estimates

Acronym	Water Solubility[b] (20 - 25 °C) [g/L]	Melting Point[a] [°C]	Boiling Point[a] [°C]	Vapor Pressure[a] [Pa]	Henry-Coefficient [Pa·m³·mol⁻¹]	log Kow[b] [-]	log K_{oc} [L/kg]	Kd (pH 7)	Dissociation Constant (pKa)
PFSAs									
PFBS	46.2 - 56.6	76 - 84	211	631	--	3.90	1.00	--	-6.0 to -5.0
PFHxS	2.3	--	--	58.9	--	5.17	1.78	0.6 - 3.2	-6.0 to -5.0
PFHpS	--	--	--	--	--	--	--	--	--
PFOS	0.52 - 0.57	54	> 400	6.7	<2e-6 to 3e-4	6.43	2.5 - 3.1	0.1 - 97	-6.0 to -2.6

PFOS: Henry's Law <2E-6 to 3E-4

PFOS: pK_a -6 to -2.6

Red font indicates parameters estimated with published equations. Calculated parameters are based on the neutral form of the substances (and not the conjugate base, which predominates for some PFAS at neutral pH)

-- No data or not applicable.

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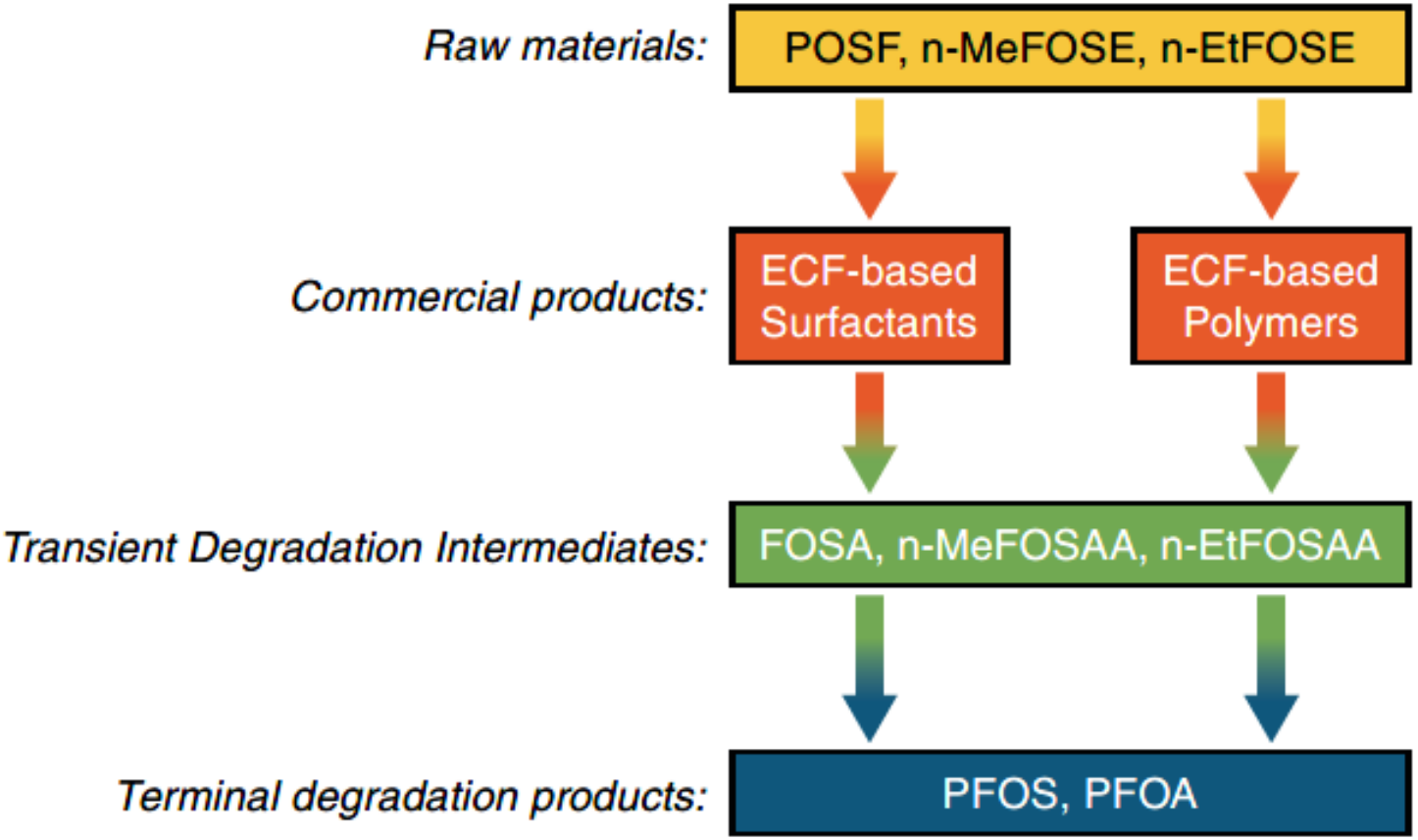
ECF Degradation Pathway Overview

Example for perfluorooctane sulfonyl homologue



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March 2018

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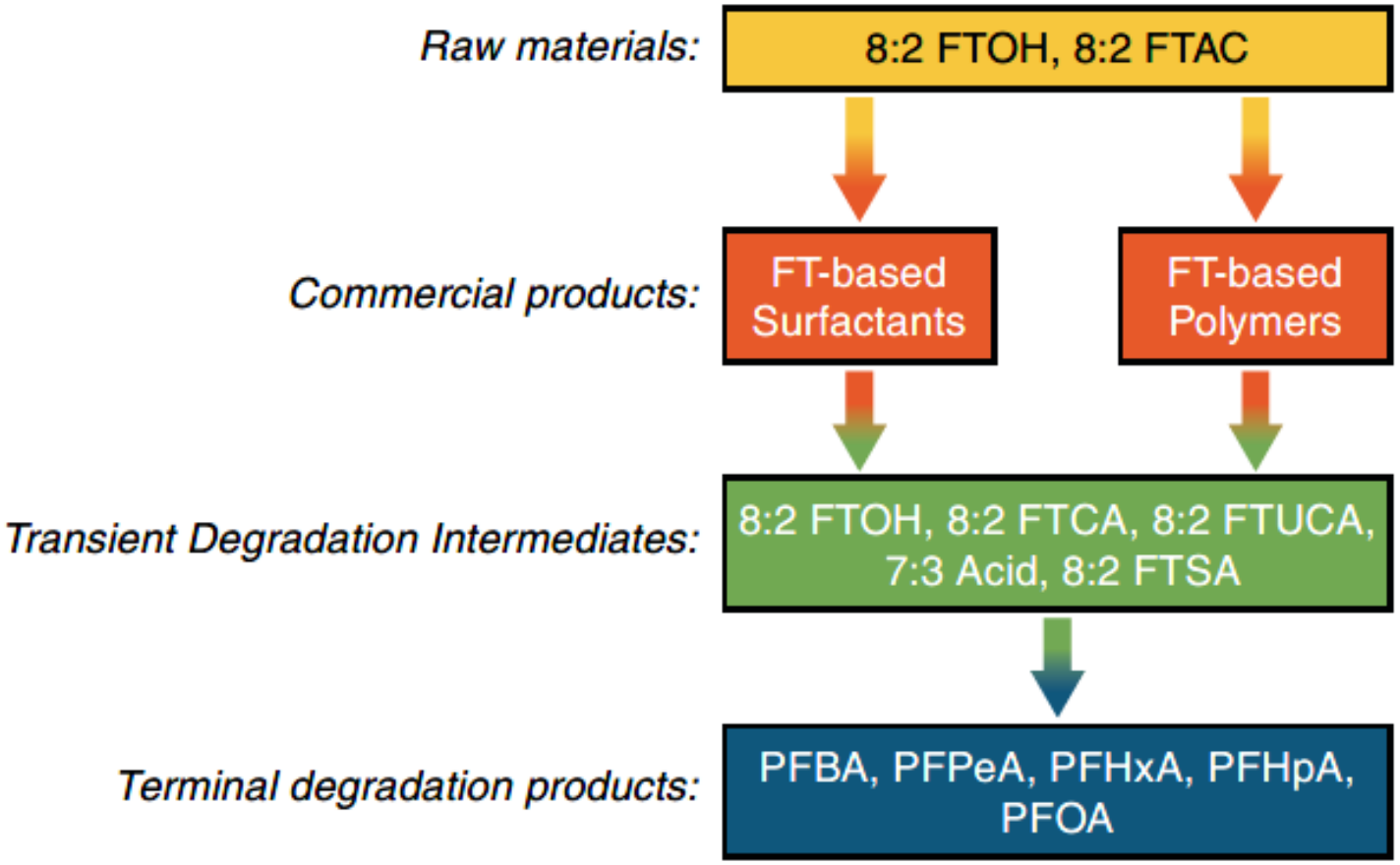
ECOS

Fluorotelomer Degradation Pathway Overview

Example for 8:2 fluorotelomer homologue



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Schuylkill watershed map: UCMR3 and beyond

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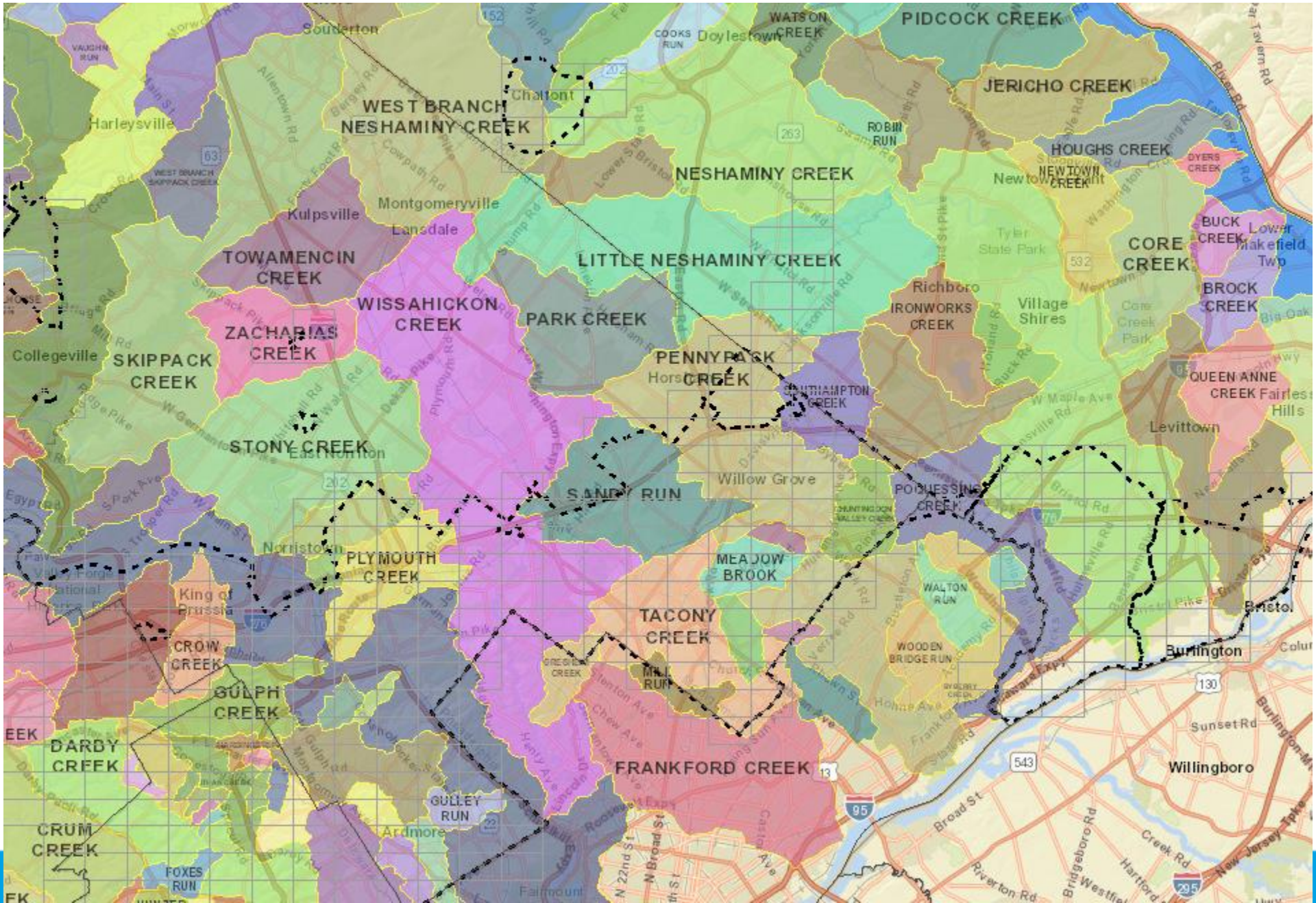
Schuylkill Action Network

Occurrence in SEPA

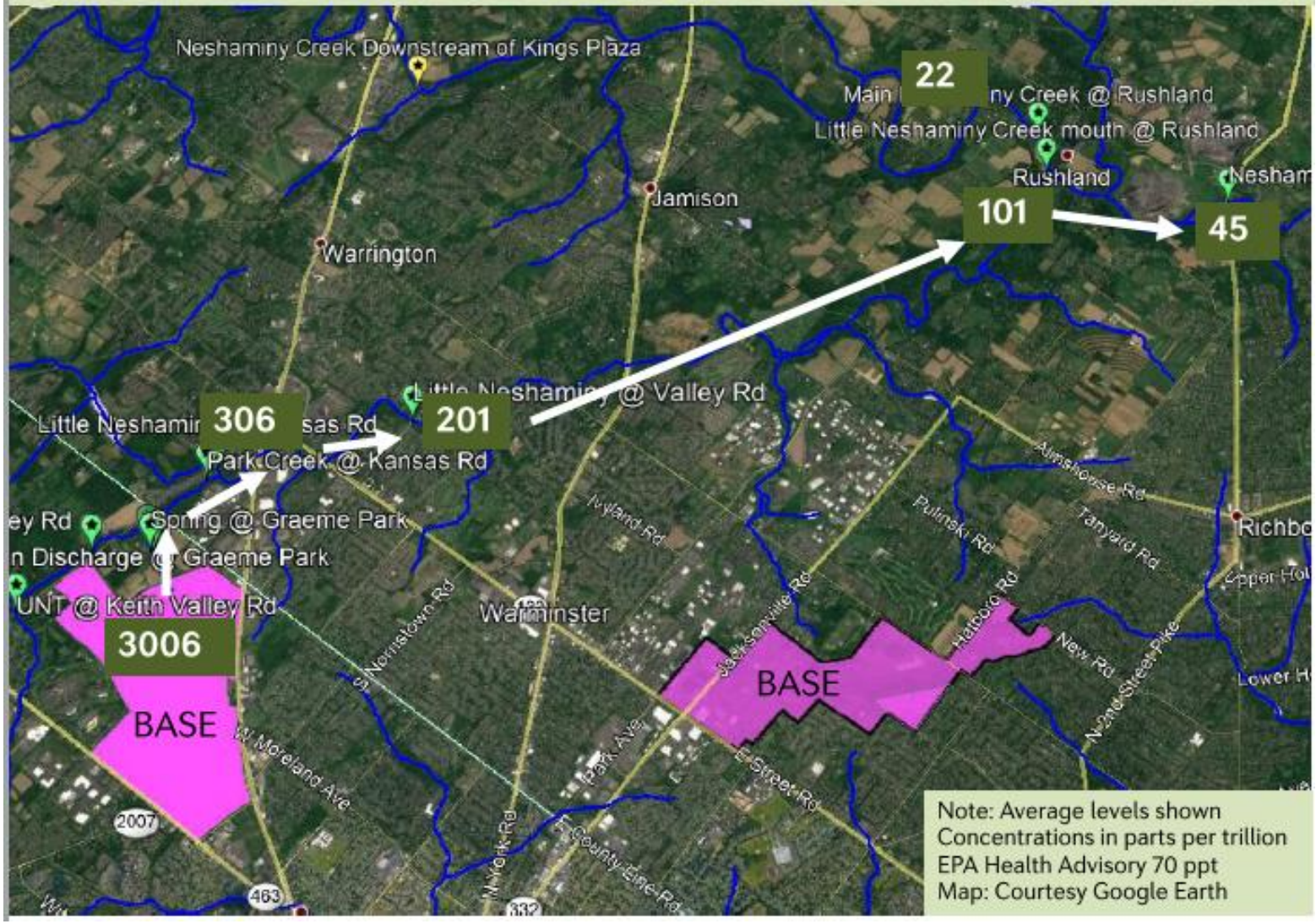
- UCMR3 data, detections at selected sites
- Post-UCMR3 monitoring, frequent detections
- Some obvious and known sources
- Widespread occurrence at low ng/L levels
    - Less obvious sources

Significance?
Our ability to detect
has far outpaced
our ability to understand the significance

PFAS Case Study: watershed map



The Impact of Willow Grove Base Daily Discharges on PFOA + PFOS Levels in the Neshaminy, Little Neshaminy, and Park Creeks



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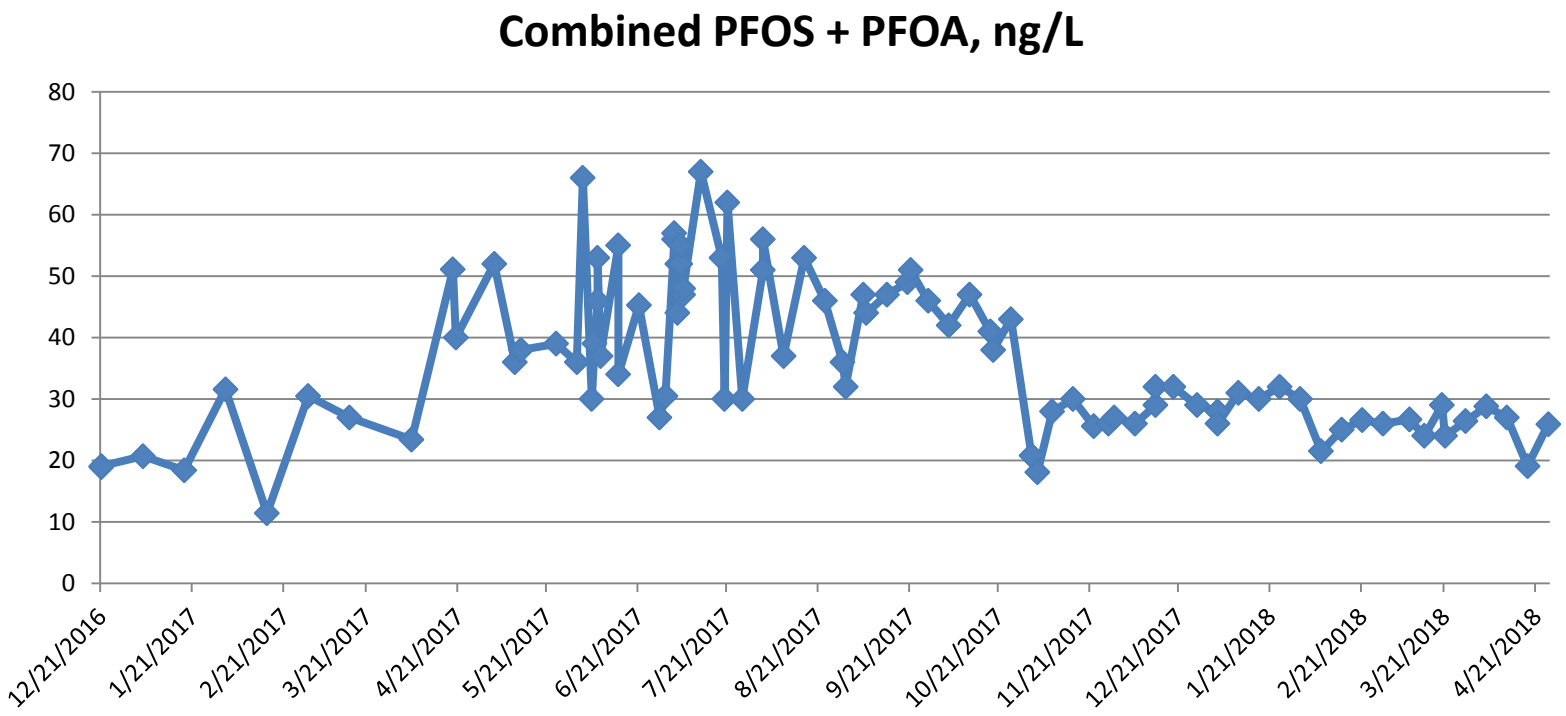
PFAS Monitoring, Neshaminy raw



	Ratio of PFOS to Combined
Average	0.64
Median	0.64
Minimum	0.46
Maximum	0.85

Regulatory Response: regulation of *unregulated* contaminants

- Evolving regulatory response since UCMR3
  - *de facto* Maximum Contaminant Level for PFOS and PFOA
    - Provisional Health Advisory: 200 + 400 parts per trillion
    - Lifetime Health Advisory: **70 parts per trillion**

- Potential standards / guidelines / MCLs
  - Uncertainty for water utilities, potential impacts
    - Treatment
    - Financial
    - Outreach to consumers

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2018 Edition of the Drinking Water Standards and Health Advisories Tables

	Health Advisories						
	10-kg Child						
	One-day (mg/L)	Ten-day (mg/L)	RfD (mg/kg/day)	DWEL (mg/L)	Life-time (mg/L)	mg/L at 10^{-4} Cancer Risk	Cancer Descriptor
PFOA	-	-	2×10^{-5}	3.7×10^{-4}	7×10^{-5}	5×10^{-2}	S
PFOS	-	-	2×10^{-5}	3.7×10^{-4}	7×10^{-5}	-	S

RfD 20 ng/kg/day

DWEL 370 ng/L

10^{-4} cancer risk
PFOA
50,000 ng/L

Life-time Health Advisory 70 ng/L

Regulatory Response: implications of Health Advisory

- Inconsistent implementation (nationally)
  → ***confusion***
- Certain EPA regions and states
  - Health Advisory ~ acute MCL
  - Actions & expectations from regulatory agencies

HA → ***de facto* MCL**

effectively by-passing regulatory process

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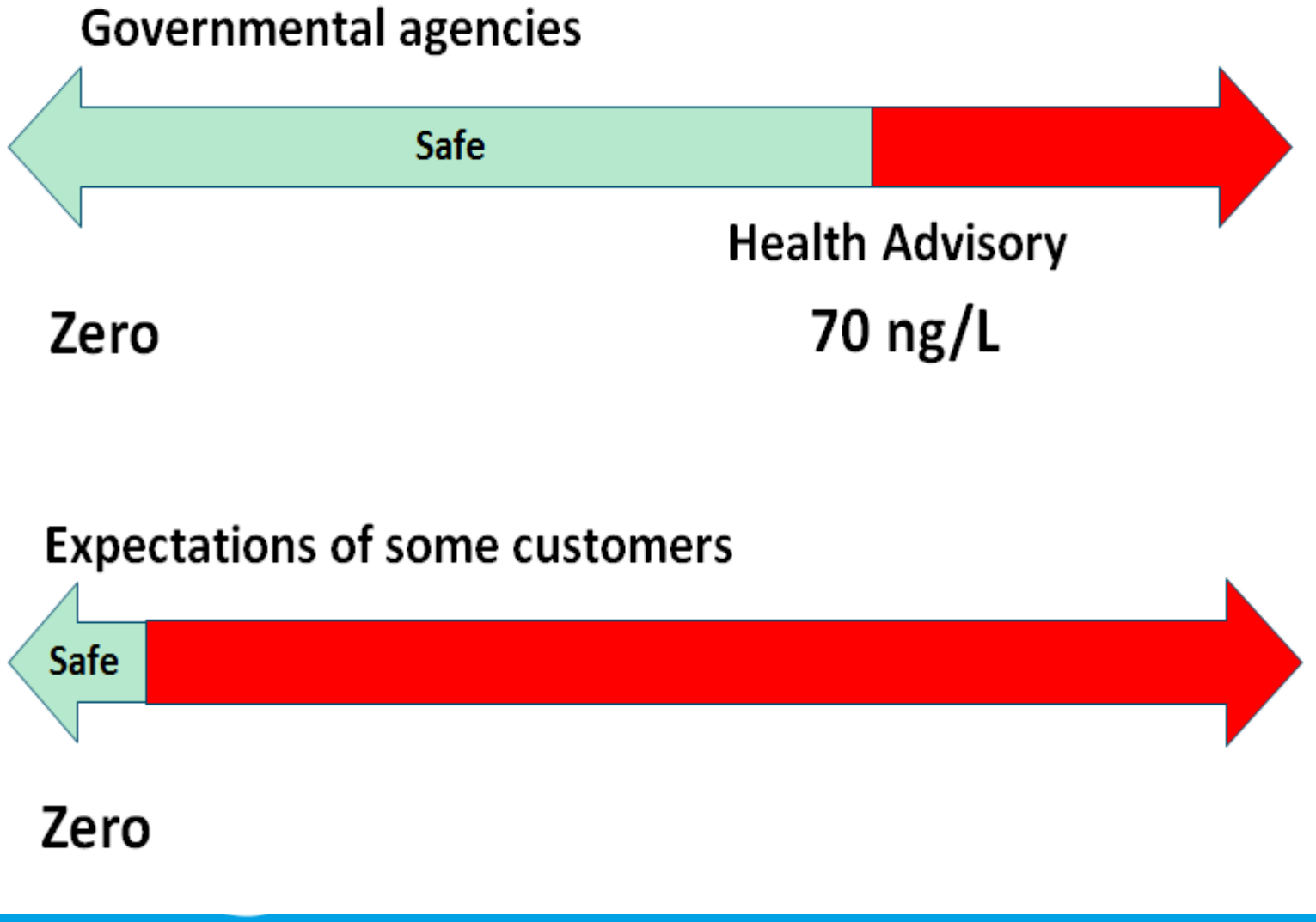
Perceived Risk. *What is safe?*



Key Challenge for Utilities

Risk Communication / Outreach

- Risk Communication
  - Explanation and clarification of HA

  Challenge of explaining topics not well understood by scientific community

  - Being perceived as
    - Hero or villain?
    - Victim or perpetrator?
- Challenge of social media

Risk = Hazard + Outrage

Unregulated just means no MCL

No relationship to:

- media attention
- controversy
- public expectations

Risk = Hazard + Outrage

The Peter M. Sandman
Risk Communication Website

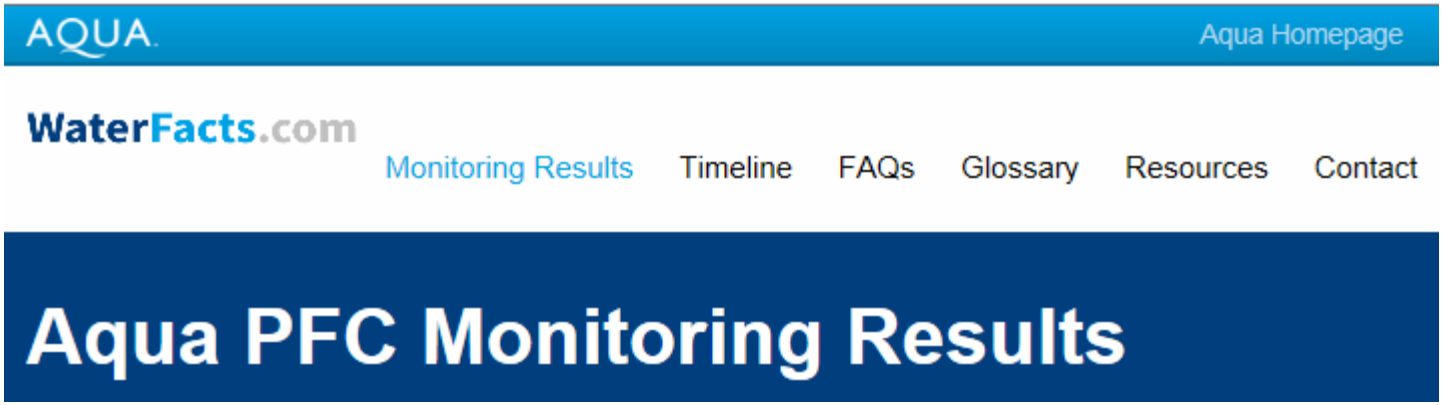
Risk = Hazard + Outrage

Home Page Contents

- What's New On Site
- Most Recent Columns
- About Peter M. Sandman
- By Peter M. Sandman
- In Other People's Words
- Topical Indexes
- Seminar Handouts
- For More Help
- Comments and Questions
- Contact Information

(Photo courtesy of the NSW Minerals Council, Australia)

Outreach to Customers: website



WaterFacts.com

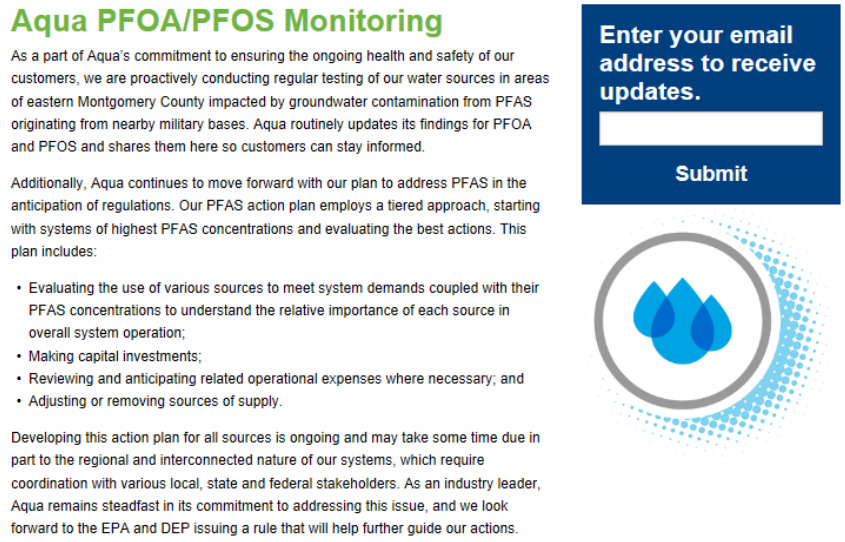
Purpose: to communicate

- PFAS information
- results of PFAS monitoring

How many PFAS are important?

- Aqua chose to focus on PFOS & PFOA
  - as per EPA Health Advisory
  - as per focus from PADEP
    - operating permits for GAC treatment
    - performance monitoring requirements

- Data posted to WaterFacts.com



Aqua PFOA/PFOS Monitoring

As a part of Aqua's commitment to ensuring the ongoing health and safety of our customers, we are proactively conducting regular testing of our water sources in areas of eastern Montgomery County impacted by groundwater contamination from PFAS originating from nearby military bases. Aqua routinely updates its findings for PFOA and PFOS and shares them here so customers can stay informed.

Additionally, Aqua continues to move forward with our plan to address PFAS in the anticipation of regulations. Our PFAS action plan employs a tiered approach, starting with systems of highest PFAS concentrations and evaluating the best actions. This plan includes:

- Evaluating the use of various sources to meet system demands coupled with their PFAS concentrations to understand the relative importance of each source in overall system operation;
- Making capital investments;
- Reviewing and anticipating related operational expenses where necessary; and
- Adjusting or removing sources of supply.

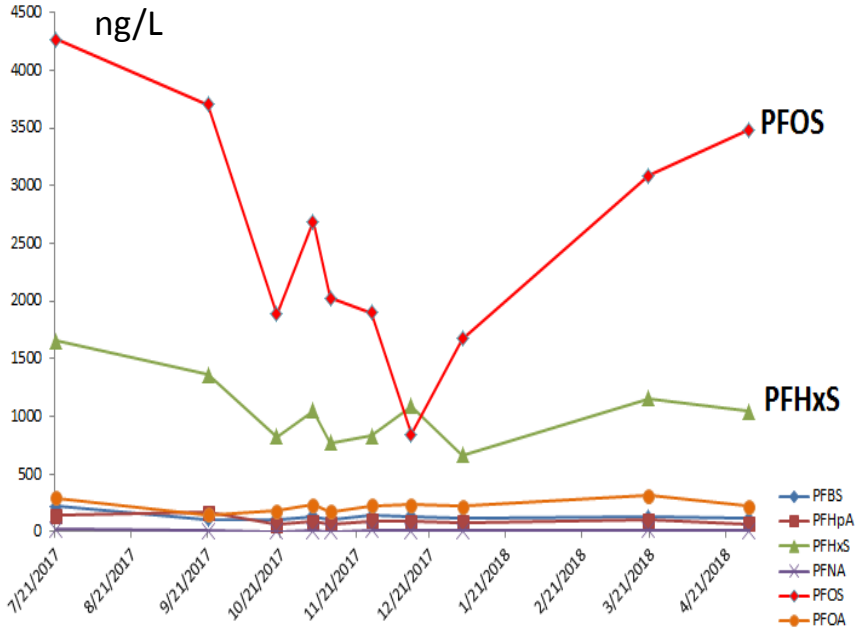
Developing this action plan for all sources is ongoing and may take some time due in part to the regional and interconnected nature of our systems, which require coordination with various local, state and federal stakeholders. As an industry leader, Aqua remains steadfast in its commitment to addressing this issue, and we look forward to the EPA and DEP issuing a rule that will help further guide our actions.

Comparison of watershed site and groundwater supply

PFOS and PFHxS as portion of PFAS $_6$

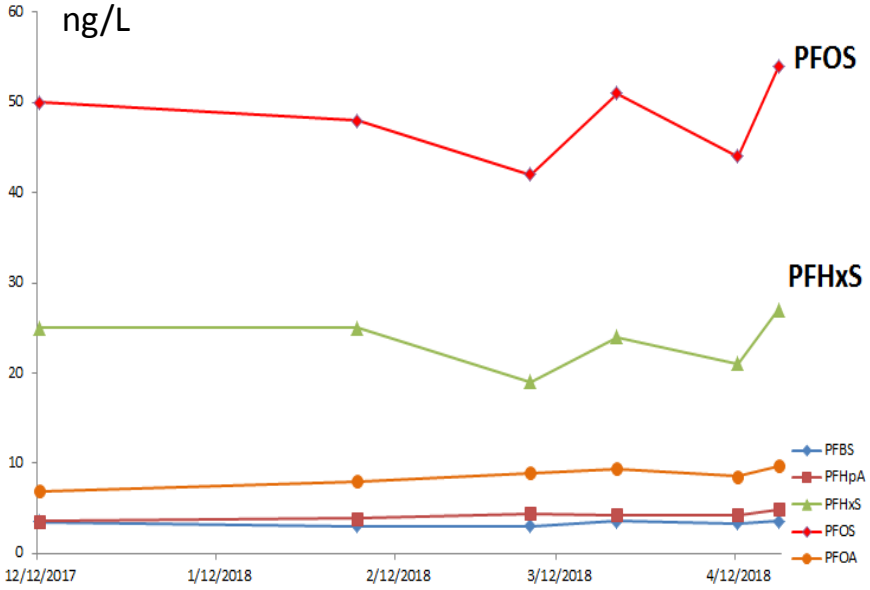
61% PFOS; 27% PFHxS as portion of PFAS $_6$

Surface water near source



55% PFOS; 27% PFHxS as portion of PFAS $_6$

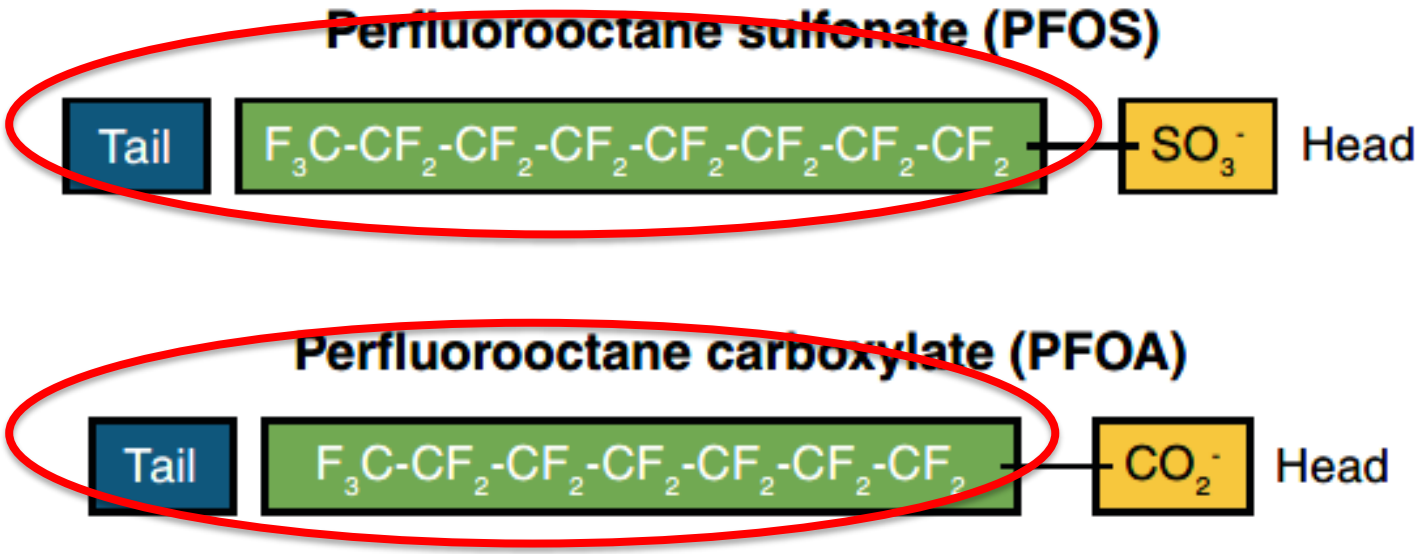
Groundwater site



Environmental Fate and Treatment

Chemistry determines:

- Solubility
- Adsorption
- Volatility
- Ionization



Treatment

Adsorption on Granular Activated Carbon

EPA Water Treatability Database

- GAC
- Biologically active GAC
- PAC
- Ion-exchange
- Membranes

Drinking Water Treatability Database

Contact Us

Search EPA: Go

- You are here: EPA Home
- Drinking Water Treatability Database
- Per- and Polyfluoroalkyl Substances / Granular Activated Carbon

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Per- and Polyfluoroalkyl Substances / Granular Activated Carbon

Treatment

		Removal:	<10%	10-90%	> 90%					
		M.W. (g/mol)	AER	COAG/ DAF	COAG/ FLOC/ SED/ G- or M-FIL	AIX	GAC	NF	RO	MnO_4, O_3 ClO_2, Cl_2, CLM, UV, UV-AOP
Compound	PFBA	214	assumed	assumed						
	PFPeA	264								
	PFHxA	314								
	PFHpA	364								
	PFOA	414								
	PFNA	464		unknown		assumed	assumed			
	PFDA	514		unknown		assumed	assumed			
	PFBS	300								
	PFHxS	400								
	PFOS	500								
	FOSA	499	unknown	unknown		unknown	assumed	unknown	assumed	unknown
	N-MeFOSAA	571	assumed	unknown		assumed	assumed	assumed		unknown
	N-EtFOSAA	585		unknown		assumed	assumed	assumed		unknown[a]

THE Water Research FOUNDATION

Per- and Polyfluoroalkyl Substances: Background Technical Information

June 2018

Kenan Ozekin, The Water Research Foundation

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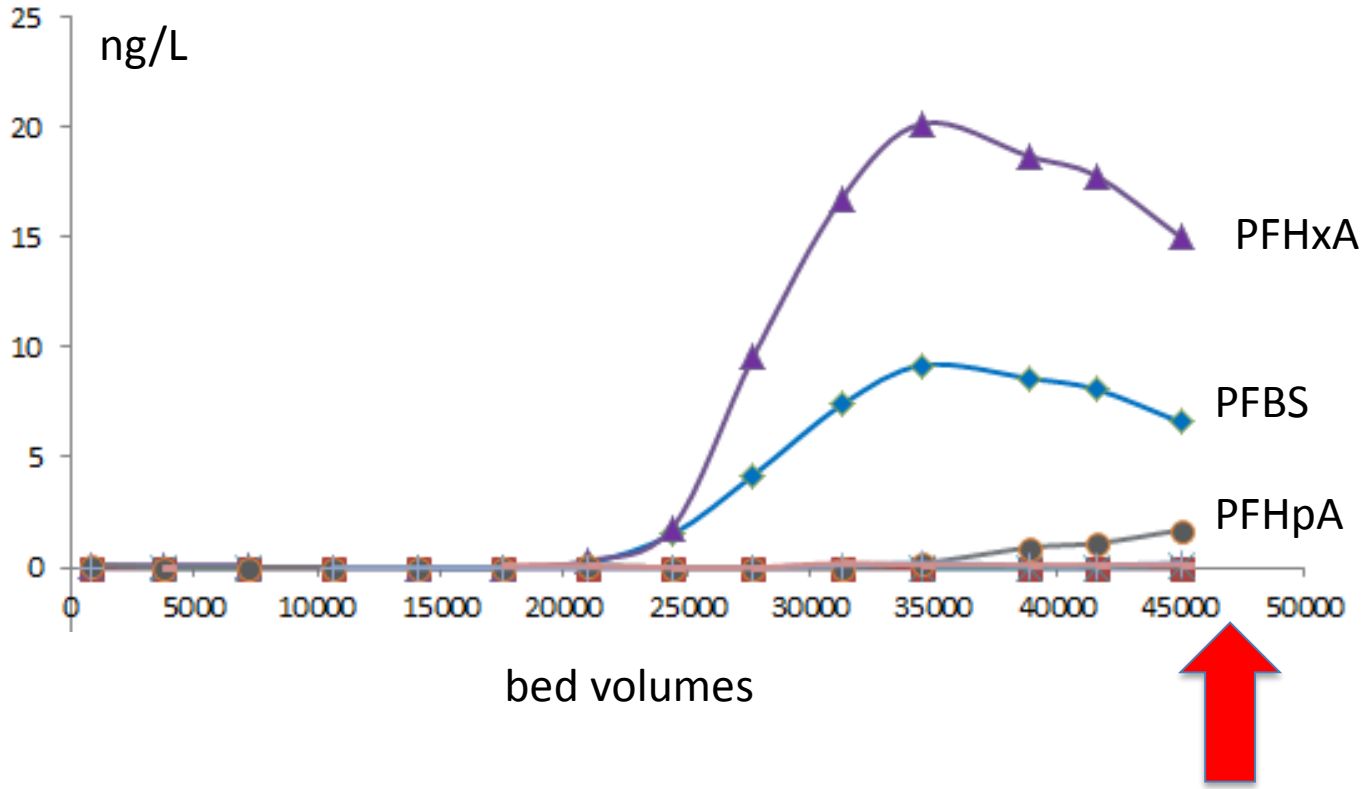
RSSCT, Neshaminy raw breakthrough before PFOA

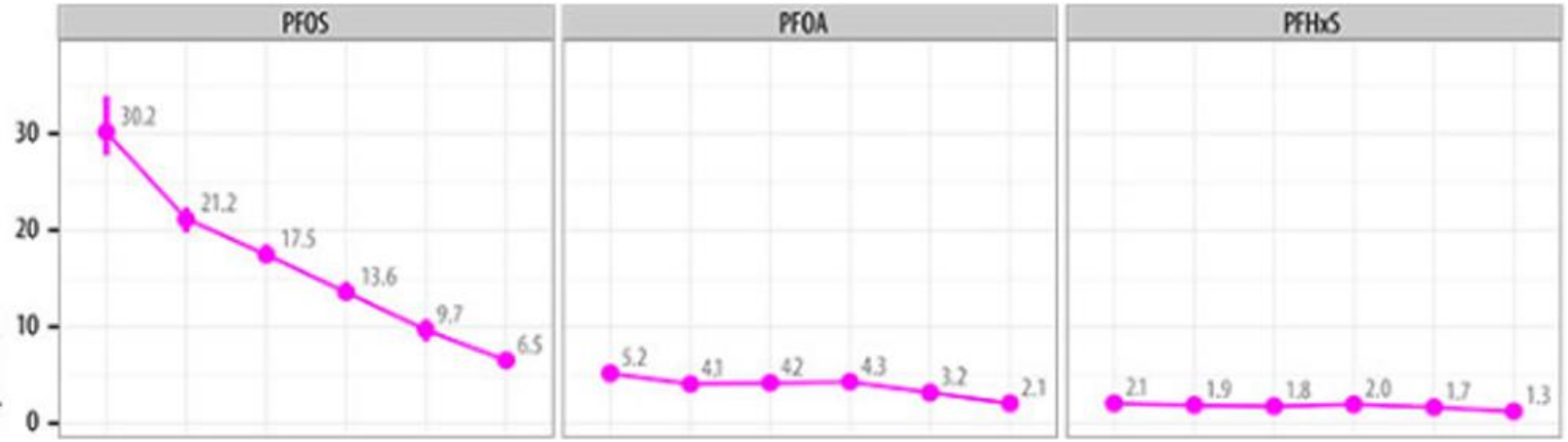


PFOA breakthrough: 48,000 bed volumes

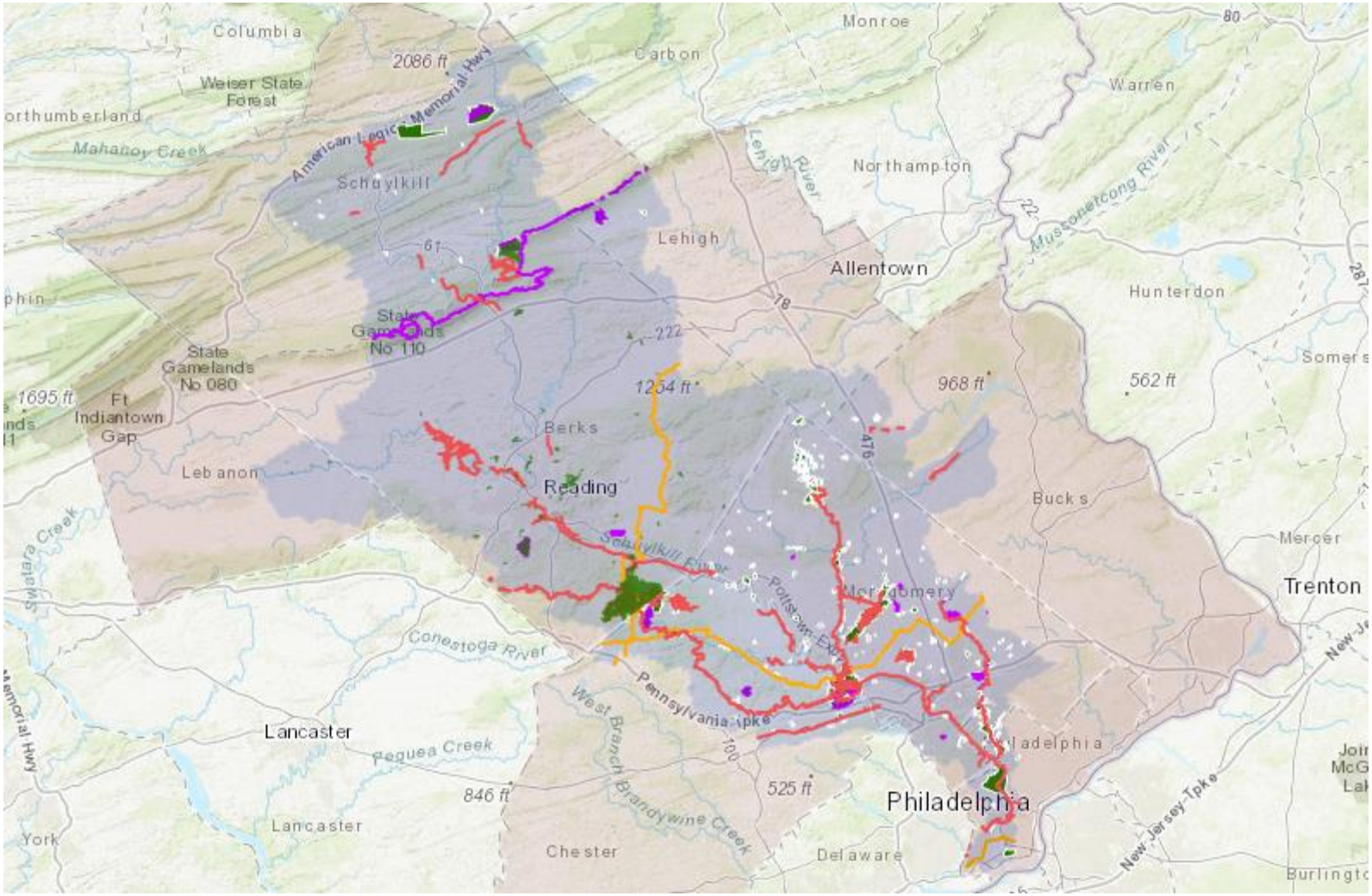
Fate within humans

PFOS in blood serum, ug/L

decrease over time



Considering additional PFAS monitoring? *Have a plan!*



Schuylkill watershed map

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Schuylkill Action Network

Summary

- Chemistry determines…*everything*
  - Analysis
  - Environmental fate
  - Treatment
- Occurrence
- Regulatory uncertainty
- Risk communication and perception

Contact Information

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