THE EMERGING ISSUE

PFAS POLY- AND PERFLUOROALKYL SUBSTANCES

Big Picture, Challenges and Solutions

Ian Ross Ph.D.

Contents

Anti-Adhésif garanti SANS PFOA
guaranteed WITHOUT PFOA
PFOS-Free Solutions
Meet EPA Requirements
GREEN TEK
Produit écologique

Questions

Does it work?

Can I use it?

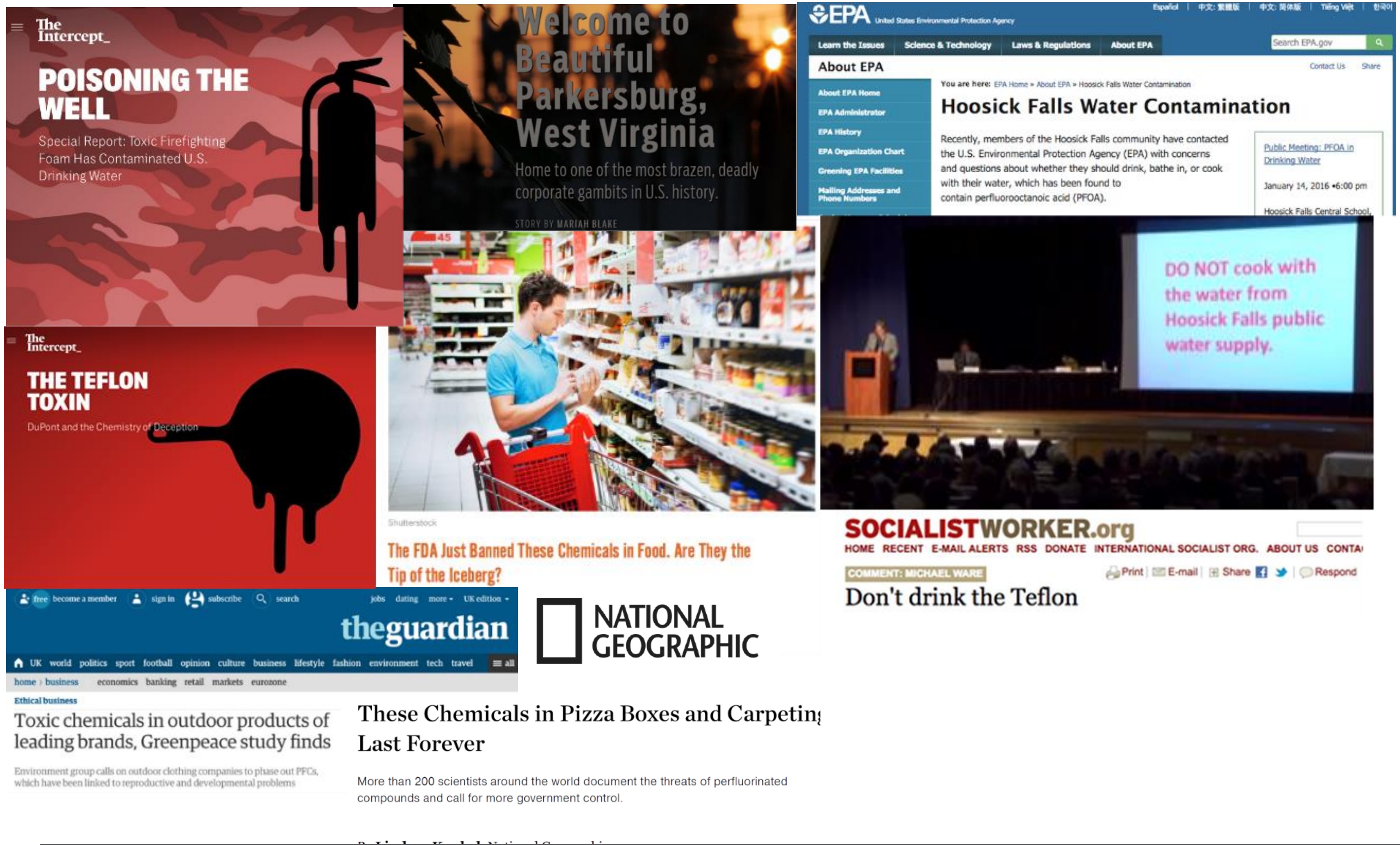
Are the local community exposed?

Litigation –class action?

How much is it going to cost to clean it up?

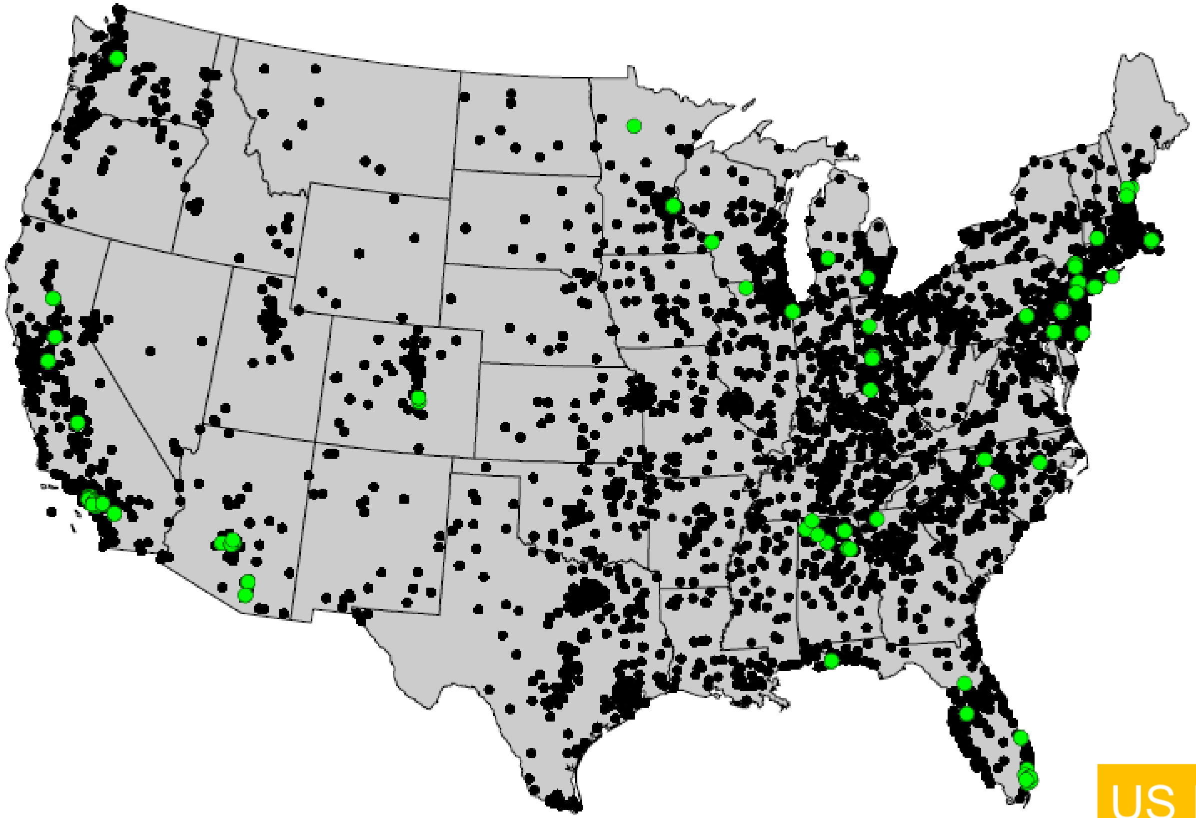
Understanding the Chemistry = Understanding the Liability

PFAS News 2015 / 2016



Detections of PFAS in drinking water has caused spiraling regulatory concern

PFASs in US Public Water Supplies



USEPA UMCR 3, May 2016

INDEPENDENT News Voices Culture Lifestyle Tech Sport Daily Edition

News › World › Americas

Six million Americans drinking water containing unsafe levels of unregulated chemicals, study finds

In one Delaware town, the levels of one such chemical in the water supply were 25 times higher than the EPA deems safe

Tim Walker US Correspondent | @timwalker | Tuesday 9 August 2016 22:57 BST |

ABC NEWS

Just In Australia World Business Sport Science Arts Analysis Fact

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Oakey residents begin class action against Defence Department over toxic firefighting foam

By Elly Bradfield, Kirrin McKechnie and Nick Wiggins

Updated 11 Jul 2017, 4:36am

US EPA has established the drinking water health advisory levels at 70 ng/L for PFOA/PFOS 19th May 2016

https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

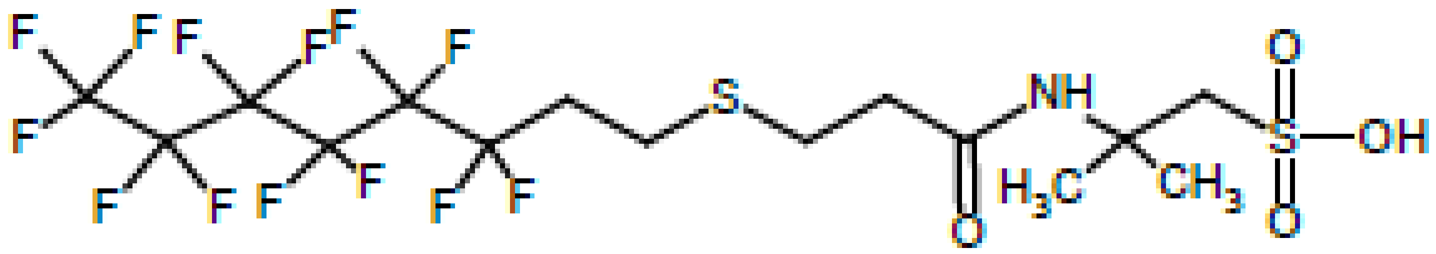
Detected in ~ 2% of large public water supplies

KEMI
Swedish Chemicals Agency

Chemical Analysis of Selected Fire-fighting Foams on the Swedish Market 2014

PM 6/15

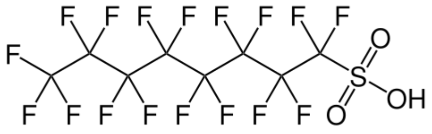
Tentatively identified PFAS as a main ingredient is 6:2 FTSAS (fluorotelomermercaptoalkylamido sulfonate).



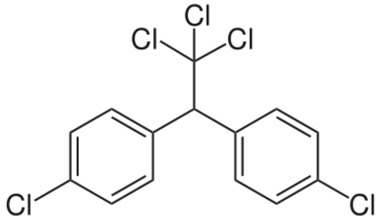
Persistent Organic Pollutants

Stockholm Convention Definition:

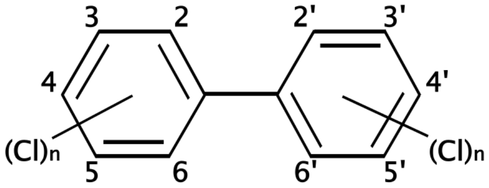
- Organic chemical substances
- Remain intact for exceptionally long periods of time (many years);
- Become widely distributed throughout the environment
- Accumulate in the fatty tissue of living organisms including humans, and are found at higher concentrations at higher levels in the food chain; and
- Are toxic to both humans and wildlife



PFOS



DDT



PCBs

Persistent Organic Pollutants

If chemical are “PBT”, they can be restricted under European REACH:

- **P**ersistent:
  - Half lives > 40 days in freshwater, >120 days in soil
- **B**ioaccumulative:
  - Bioconcentration factor/bioaccumulation factor in fish >2000
- **T**oxic
  - Human: Chronic toxicity, carcinogenic/mutagenic/reprotoxic
  - Ecological: No effect concentration (NOEC) <0.01 mg/L

Persistent Organic Pollutants

Alternative to PBT is vPvB under REACH

- **v**ery **P**ersistent:
  - Half lives > 60 days in freshwater, >180 days in soil
- **v**ery **B**ioaccumulative
  - Bioconcentration factor or bioaccumulation factor in fish >5000
- Requirement for toxicity no longer necessary to restrict the chemical
- Also **P**ersistent **M**obile and **T**oxic (PMT) suggested as more n realistic assessment to manage risk to receptors from man made chemicals

Microbial Metabolism

Eat (Electron Donor)

Hydrocarbons (BTEX)

Explosives

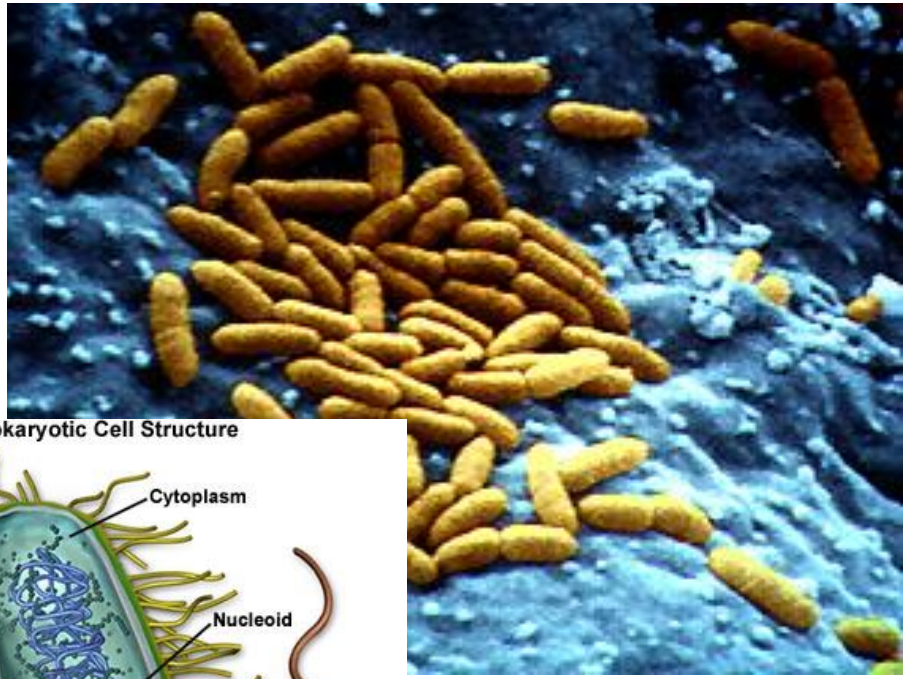
Amines

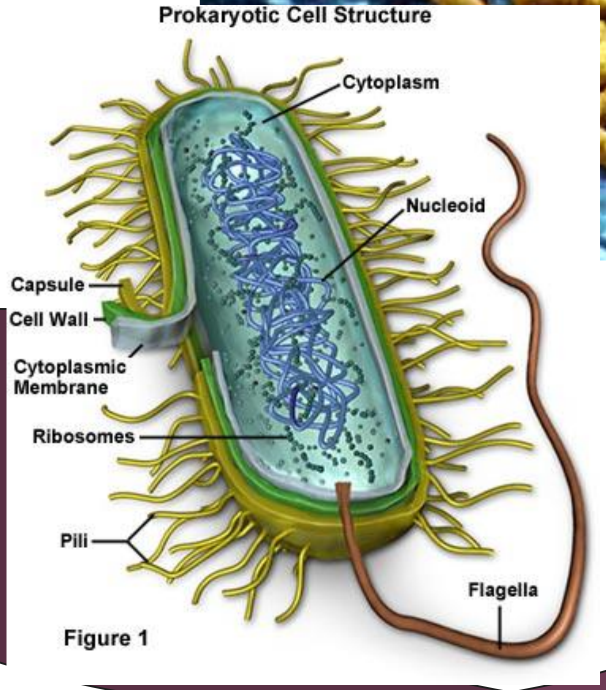
TCE*/DCE/VC

Pesticides

Solvents

PAHs





Breathe
(Electron Acceptor)

Mn^{4+}

Fe^{3+}

O_2

NO_3

SO_4

CO_2

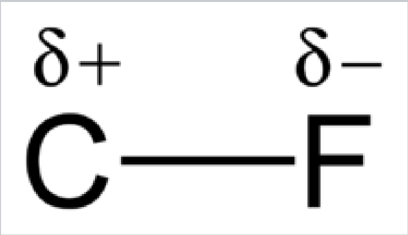
PCE/TCE/DCE/VC

* Cometabolic

Carbon–fluorine bond

From Wikipedia, the free encyclopedia

The **carbon–fluorine bond** is a polar covalent bond between carbon and fluorine that is a component of all organofluorine compounds. It is the third strongest single bond in organic chemistry—behind the Si-F single bond and the O-F single bond, and relatively short—due to its partial ionic character. The bond also strengthens and shortens as more fluorines are added to the same carbon on a chemical compound. As such, fluoroalkanes like tetrafluoromethane (carbon tetrafluoride) are some of the most unreactive organic compounds.



The partial charges in the polarized carbon–fluorine bond

Contents [hide]

Electronegativity and bond strength [edit]

The high electronegativity of fluorine (4.0 for F vs. 2.5 for carbon) gives the carbon–fluorine bond a significant polarity/dipole moment. The electron density is concentrated around the fluorine, leaving the carbon relatively electron poor. This introduces ionic character to the bond through partial charges ($C^{\delta+}$—$F^{\delta-}$). The partial charges on the fluorine and carbon are

Poor Reversibility of Exposure (Conceptual)

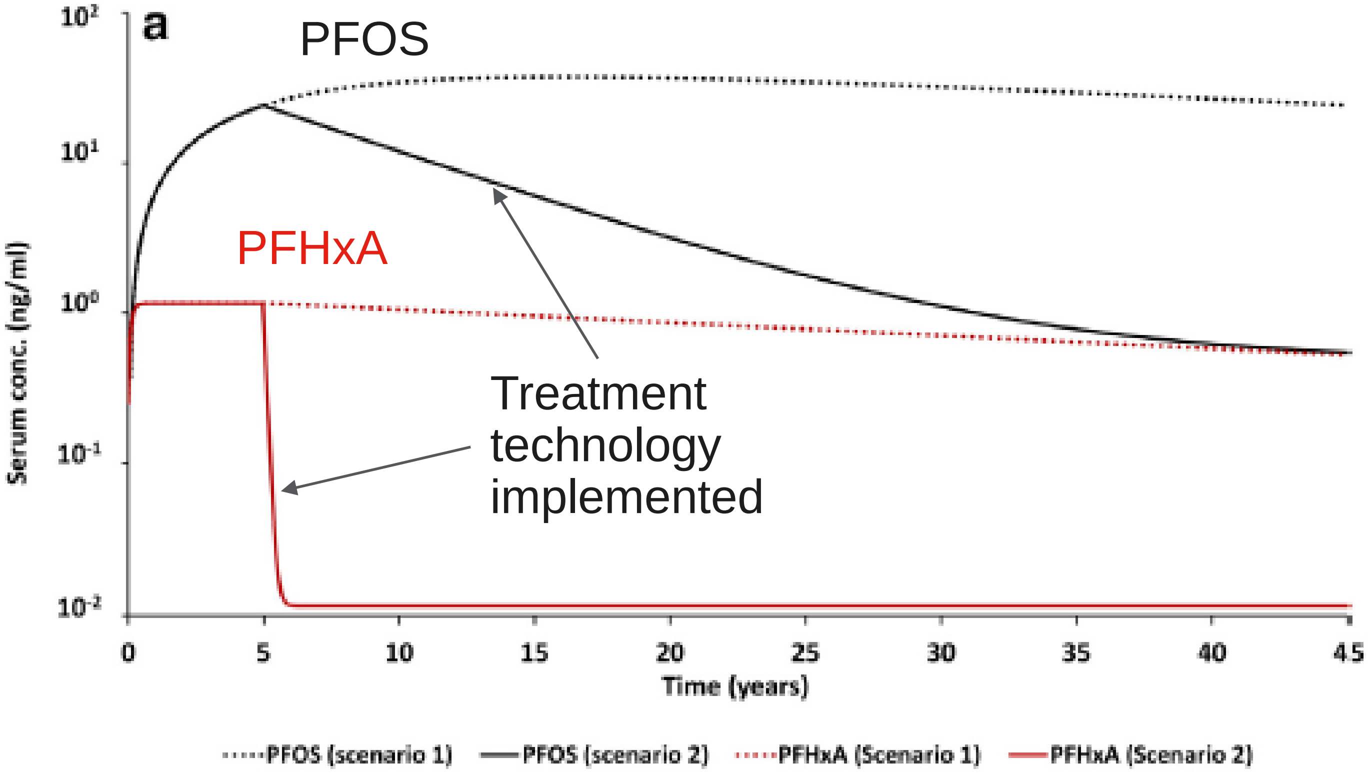
Poorly reversible exposure of a chemical can occur two ways:

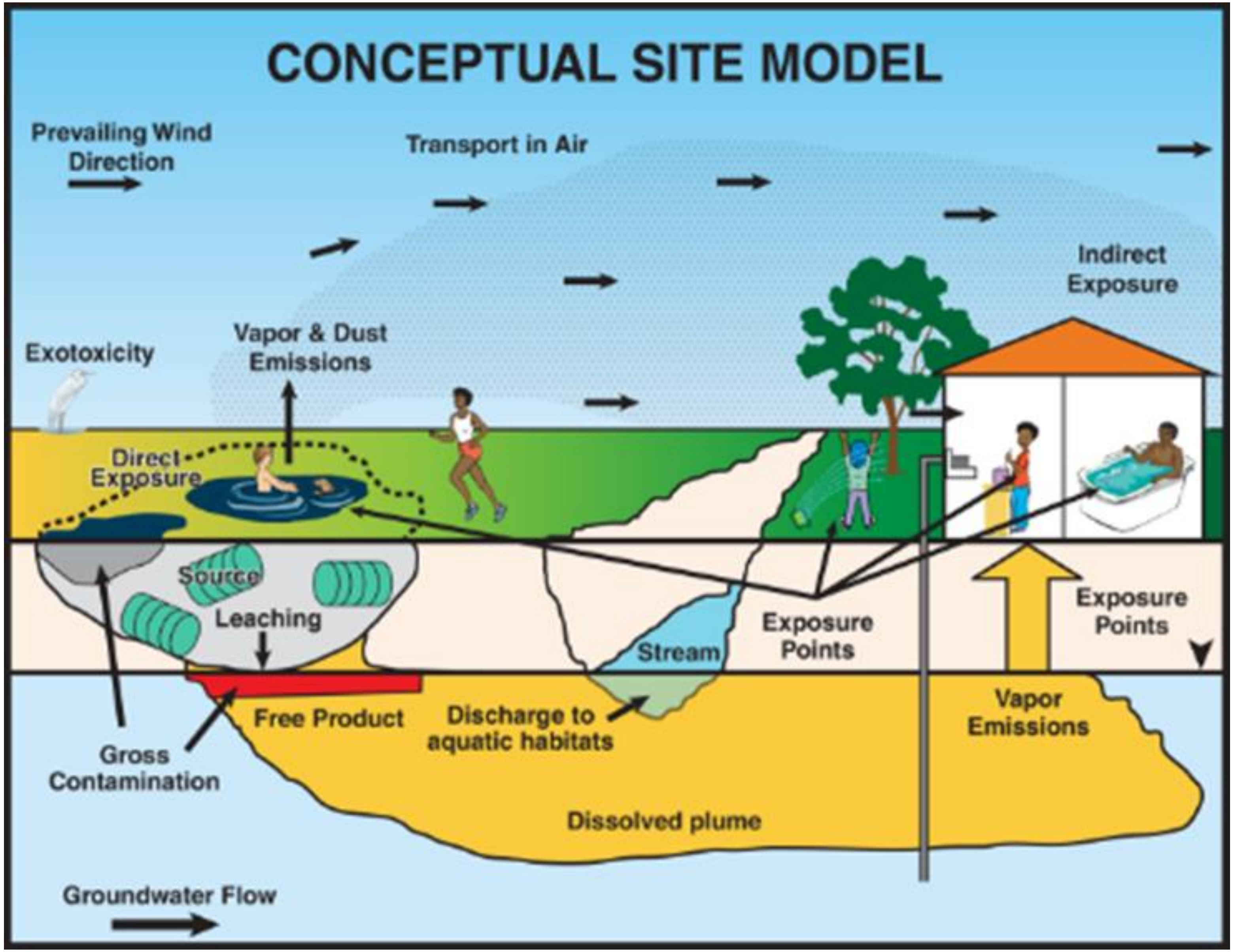
- The chemical has slow elimination kinetics in organisms (bioaccumulative)

or

- Due to environmental recalcitrance, exposure is steady (extreme persistence)

(Cousins *et al.* Environ. Int. 2016




CONCEPTUAL SITE MODEL
Prevailing Wind Direction
Transport in Air
Indirect Exposure
Exotoxicity
Vapor & Dust Emissions
Direct Exposure
Source
Leaching
Stream
Exposure Points
Exposure Points
Free Product
Discharge to aquatic habitats
Vapor Emissions
Gross Contamination
Dissolved plume
Groundwater Flow

Environmental Consequences
Long Term Ultra-Persistence vs Short Term Effects

A New Ranking From U.S. News & World Repo

U.S.News BEST STATES

RANKINGS STATES DATA EXPLORER VIDEOS NEWS

NEWS / BEST STATES / IOWA NEWS

Spilled Milk From Tanker in Iowa Causes Fish Kill Worries

The Iowa Department of Natural Resources says in a news release that the crash of a tanker hauling milk east of Fontanelle Sunday evening caused a spill.

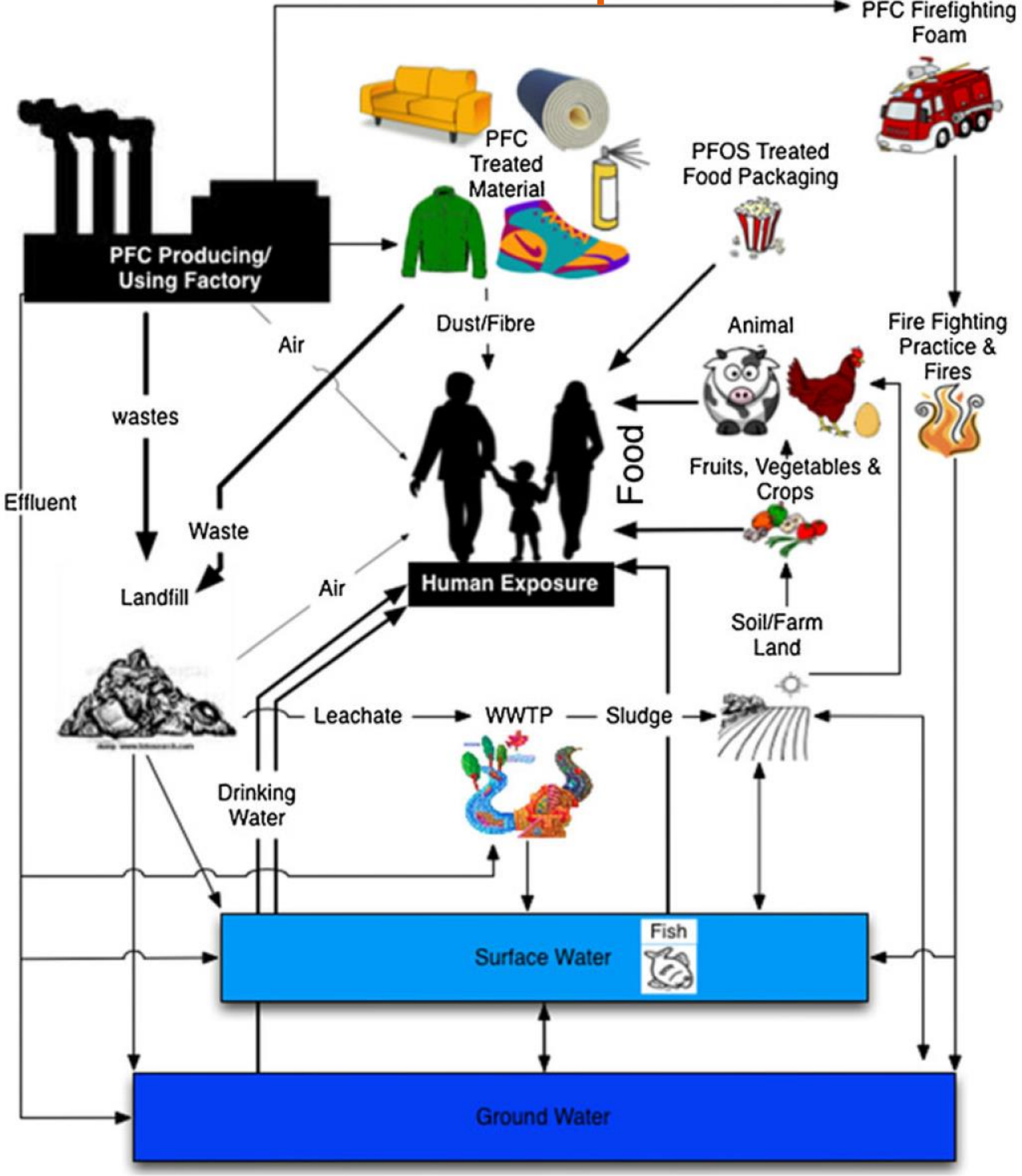
June 20, 2017, at 4:08 p.m.

- Milk may cause a short term fish kill by diminishing dissolved oxygen

- Ultra-persistent ingredients can cause long term pollution potentially affecting future generations

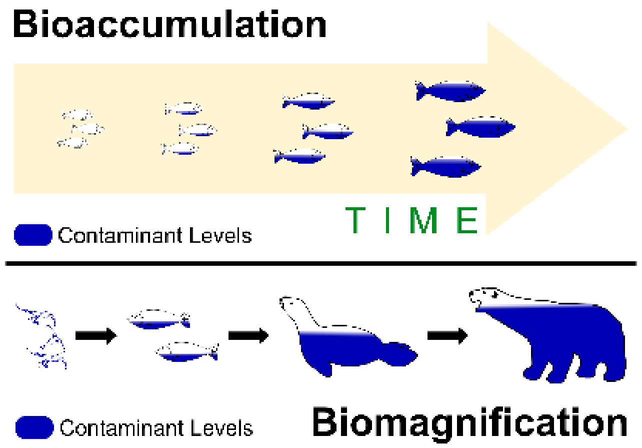
Potential PFAS Exposure Pathways

ARCADIS Design & Consultancy for natural and built assets



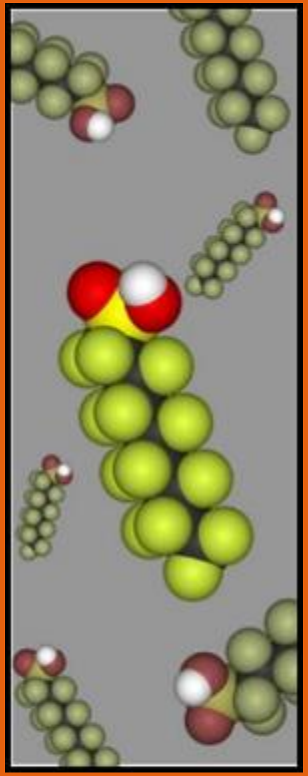
The PFAS web

Oliaei et al. Environ. Sci. Pollut Res (2013) 20: 1977-1992

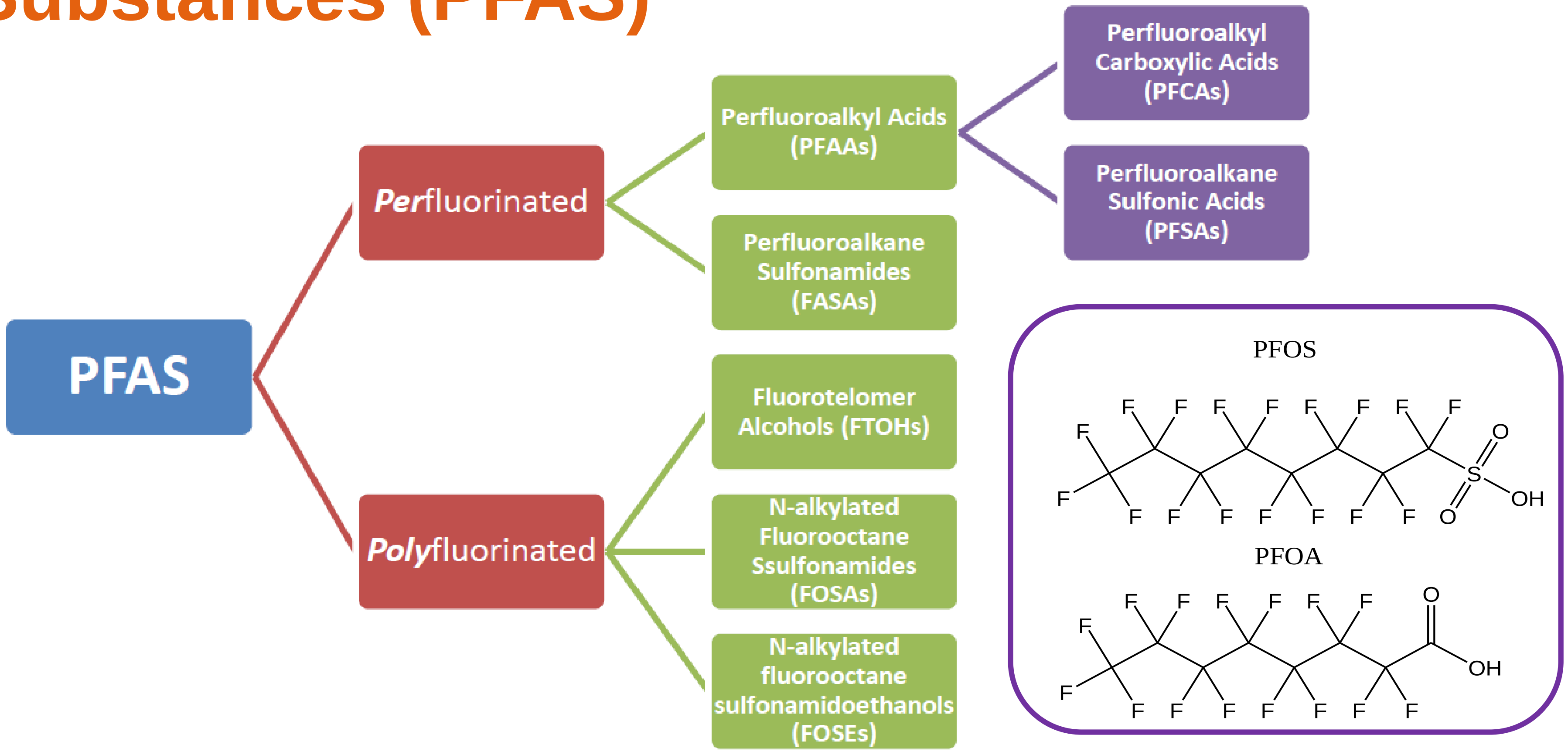


PFAS PROPERTIES

Parameter	PFOS (Giesy, 2010; OECD, 2002)	PFOA (EFSA, 2008)
CAS number	1763-23-1	335-67-1
Chemical formula		$C_7H_{15}COOH$
Molar weight	538,23 g/mol	414,07 g/mol
Boiling point	n.a.	189-192 °C



What are Poly and Perfluorinated Alkyl Substances (PFAS)



PFAS include PFOS, PFOA and approx. 3,000 fluorinated compounds

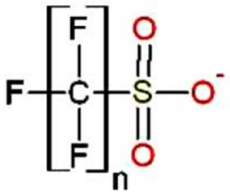
Perfluorinated compounds (PFCs)

ARCADIS Design & Consultancy for natural and built assets

- Perfluorinated Compounds (PFCs) generally are the **Perfluoroalkyl acids (PFAAs)**
- PFAAs include:
  - Perfluoralkyl carboxylates (PFCAs) e.g. PFOA
  - Perfluoralkyl sulfonates (PFSAs) e.g. PFOS
  - Perfluoralkyl phosphinic acids (PFPiS); perfluoroalkyl phosphonic acids (PFPAs)
- There are many PFAAs with differing chain lengths, PFOS and PFOA have 8 carbons (C8) - octanoates

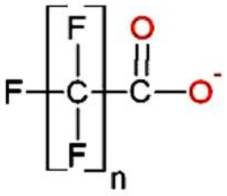
C1 **M**ethane
C2 **E**thane
C3 **P**ropane
C4 **B**utane
C5 **Pe**ntane
C6 **H**e**x**ane
C7 **H**e**p**tane
C8 **O**ctane
C9 **N**onane
C10 **D**ecane
C11 **U**nodecane
C12 **Do**decane
C13 **Tr**idecane
C14 **Te**tradecane

Perfluoroalkyl Sulfonates[L]



PFBS	n = 4
PFPeS *	n = 5
PFHxS	n = 6
PFHpS	n = 7
PFOS	n = 8
PFNS *	n = 9
PFDS	n = 10

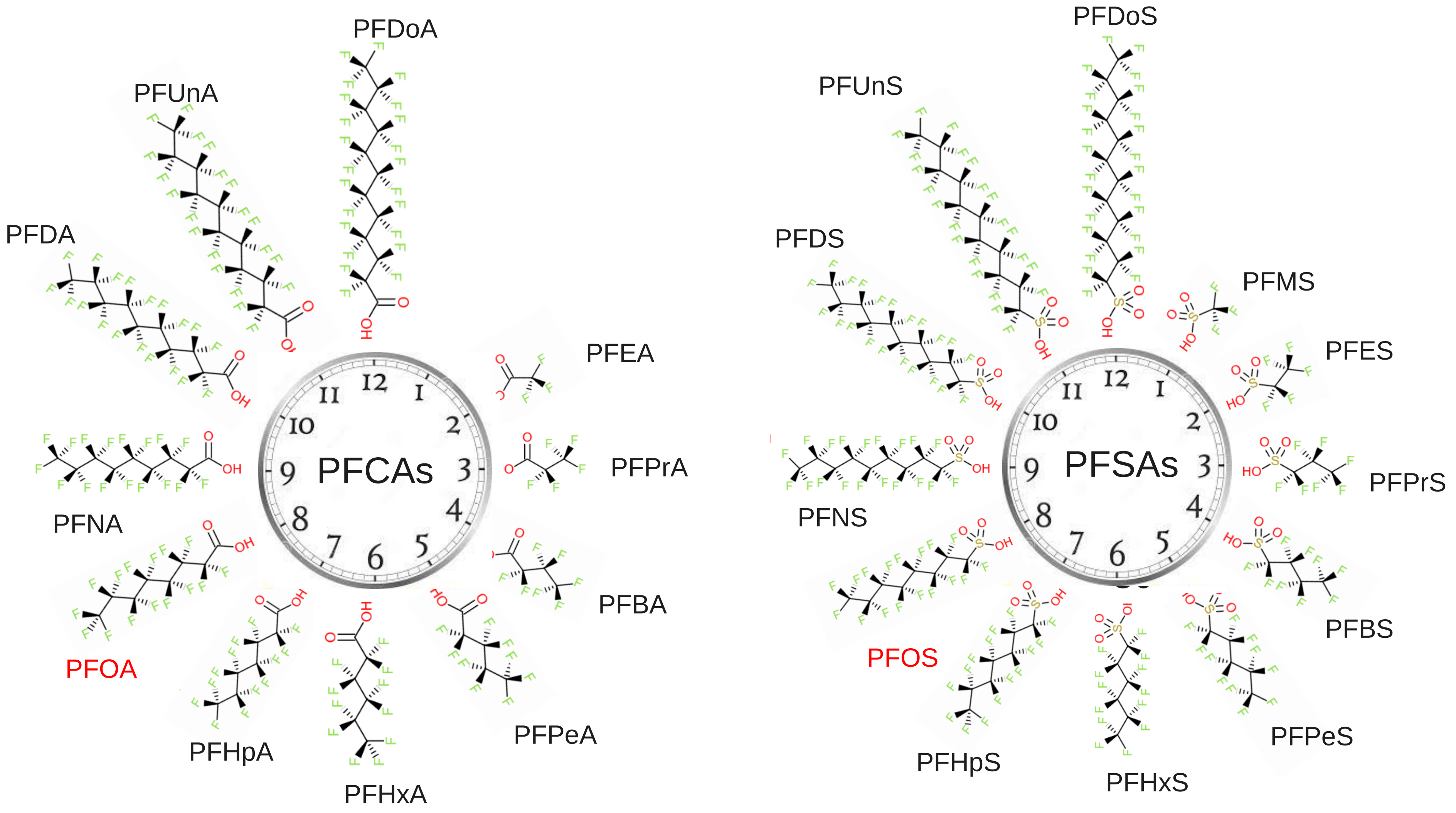
Perfluoroalkyl Carboxylates[L]



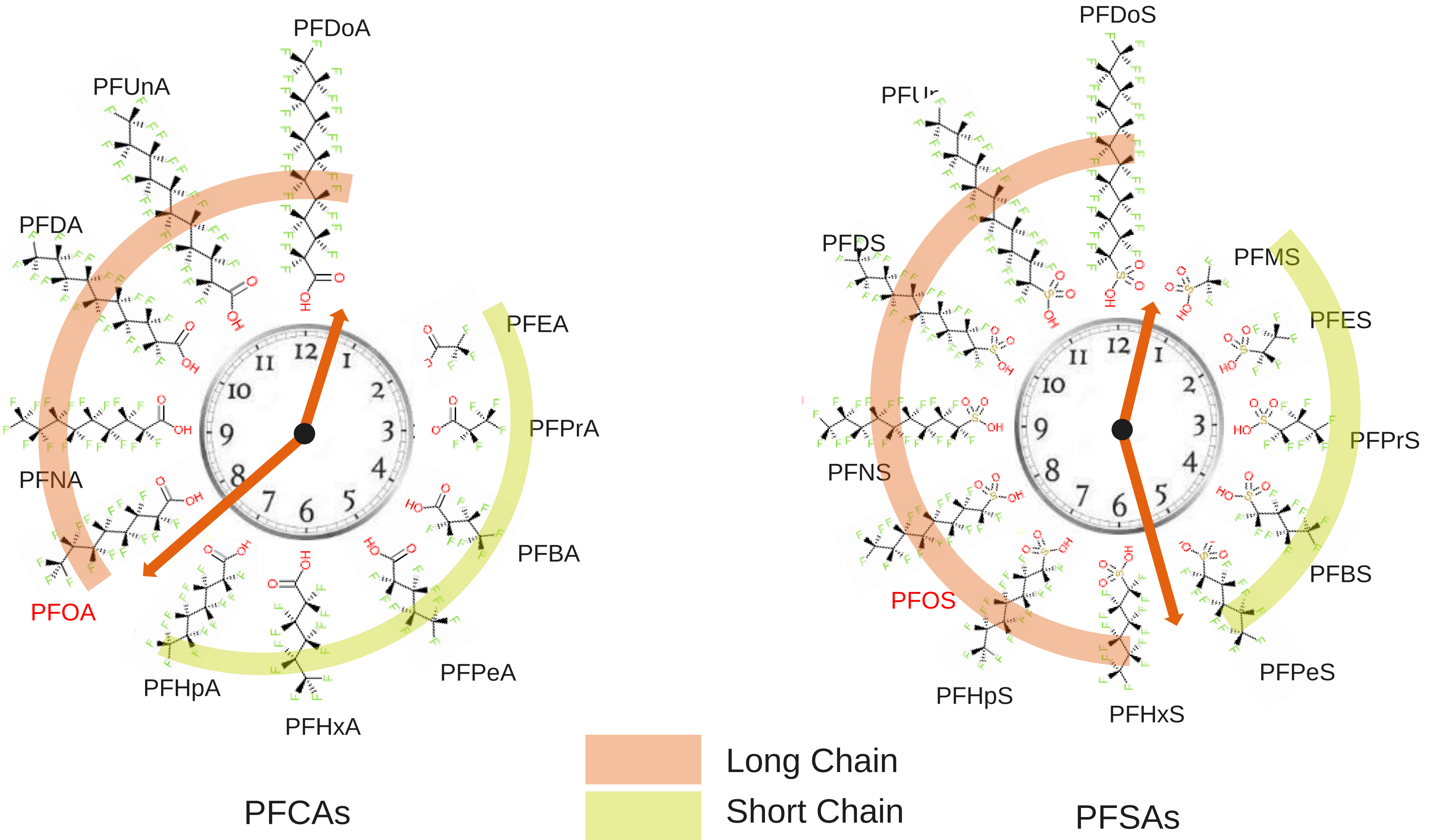
PFBA	n = 4
PFPeA	n = 5
PFHxA	n = 6
PFHpA	n = 7
PFOA	n = 8
PFNA	n = 9
PFDA	n = 10
PFUdA	n = 11
PFDoA	n = 12
PFTrA	n = 13
PFTeA	n = 14

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS
Will J. Backe,[†] Thomas C. Day,[†] and Jennifer A. Field[*,‡]

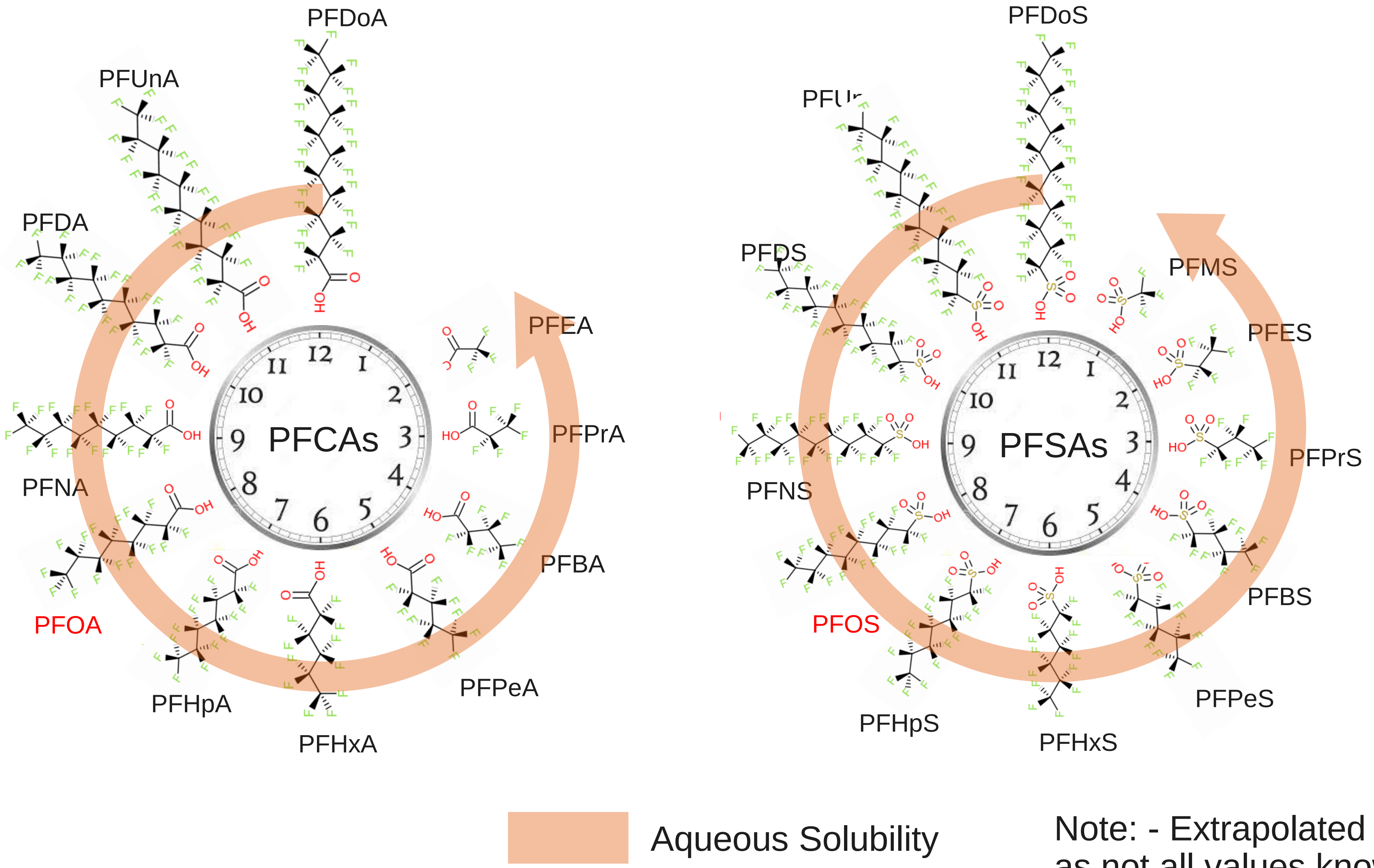
PFAAs totally resist biodegradation & biotransformation so are extremely persistent


PFCAs
PFDoA
PFUnA
PFDA
PFNA
PFOA
PFHpA
PFHxA
PFPeA
PFBA
PFPrA
PFEA
PFSAs
PFDoS
PFUnS
PFDS
PFNS
PFOS
PFHpS
PFHxS
PFPeS
PFBS
PFPrS
PFES
PFMS

Long Chain vs. Short Chain

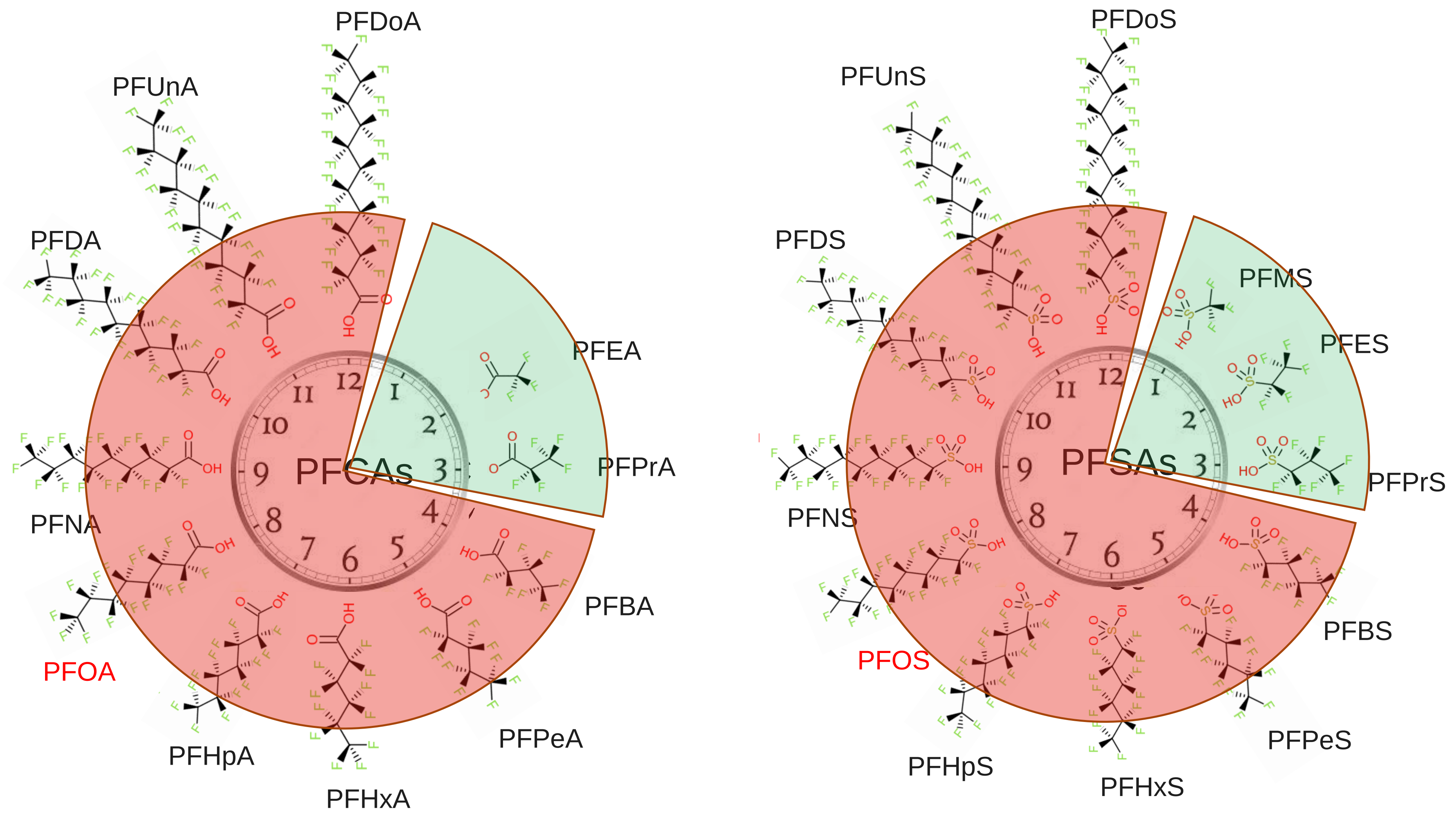


Physio-chemical Properties



Note: - Extrapolated trend data as not all values known for all PFAS

Detectable with Commercial Analytical Techniques



C4 and higher compounds detectable by commercial techniques

C3 and below currently undetectable

Perfluorinated Compounds in Consumer Products

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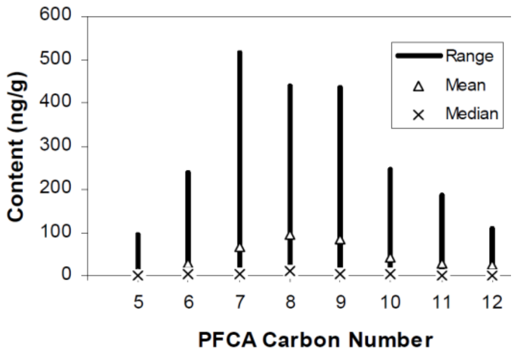
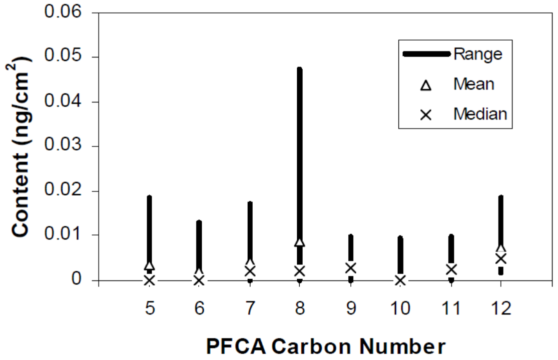
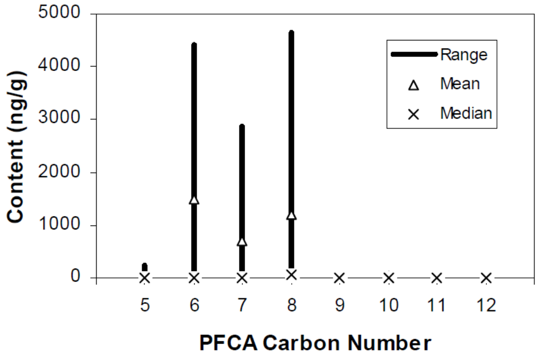
- Historical focus has mainly been on PFOA and PFOS, but PFAS-containing products contain a mixture of differing chain length PFAAs
- In this study C5 to C12 perfluorinated carboxylates (PFCA) are detected in PFOA (C8) containing consumer products
- Similar diversity of PFAA chain lengths may be expected in other PFAS-containing products and PFAS-contaminated areas



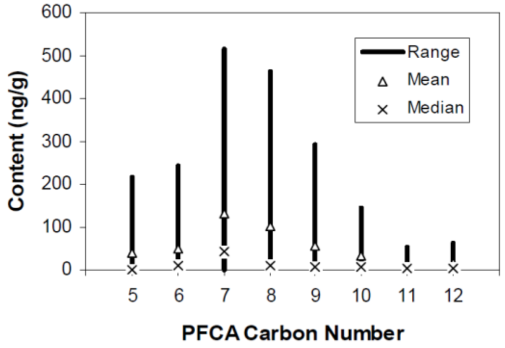
Treated Home Textiles



Non-stick cookware



Food contact paper



Pre-Treated Carpet

Data from Guo et al. 2009, U.S. EPA; Polyfluorinated substances and perfluorinated sulfonates were not measured

Lena Vierke, Claudia Staude, Éva Fetter, Stephan Brendel, Annegret Biegel-Engler
Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany

Concerns on short-chain PFASs – High mobility

- Short-chain PFASs can occur in raw water and can therefore be found in drinking water
- Short-chain PFASs cannot be eliminated from water with the commonly applied measures (e. g. Lundgren et al. 2014)

Emotion\fotolia.com

Potential exposure of humans via drinking water

See also presentation from Michael Neumann on persistent, mobile and toxic (PMT) substances under REACH

Examples:

- 18% of 85 Spanish tapwater samples (Gellrich et al., 2013)
- 23% of 26 German tapwater samples (Llorca et al., 2012)
- 86% of 7 tapwater samples from six EU Countries (Ullah et al., 2011)
- 49% of 26 waterworks along the river Rhine (Wilhelm et al., 2010)

Concerns on short-chain PFASs – Enrichment in plants

- Plant uptake shown by several studies e.g. for wheat, maize, grass and vegetables
- Enrichment in edible parts of plants
- Benchmarking with PFOA: PFHxA higher uptake and higher transfer to edible parts of plants

(Felitzeter et al. 2014; Krippner et al. 2015; Wen et al. 2014; Yoo et al. 2011)

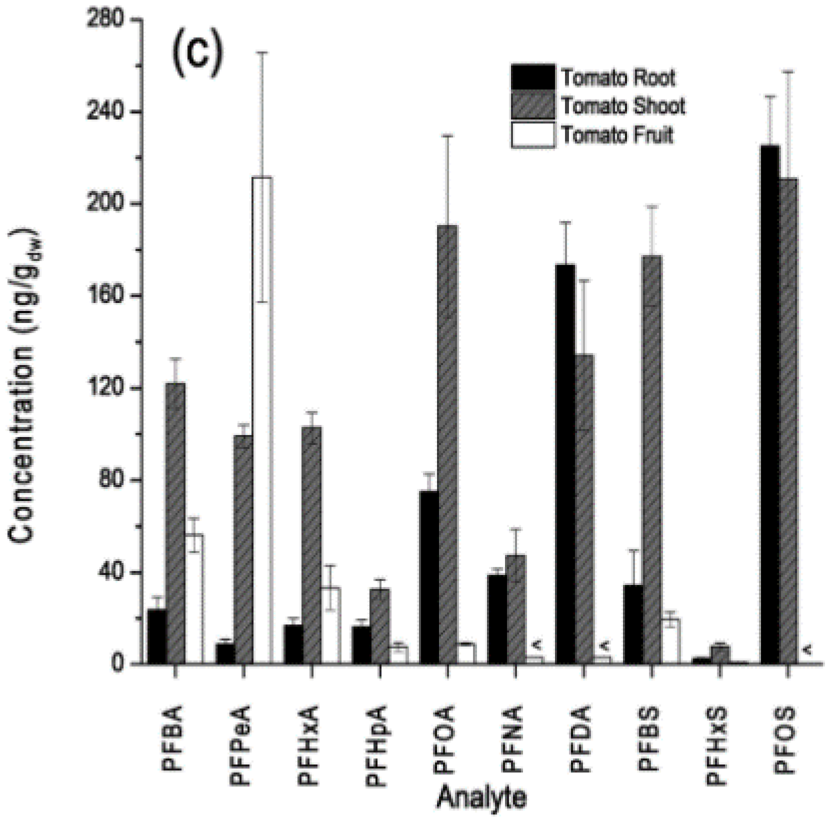
Potential exposure of humans via food

Source: Marc Rathman\ fotolia.de

Environmental Science & Technology
Article
pubs.acs.org/est

Perfluoroalkyl Acid Distribution in Various Plant Compartments of Edible Crops Grown in Biosolids-Amended soils

Andrea C. Blaine,[†] Courtney D. Rich,[†] Erin M. Sedlacko,[†] Lakhwinder S. Hundal,[‡] Kuldip Kumar,[‡] Christopher Lau,[§] Marc A. Mills,[#] Kimberly M. Harris,[∥] and Christopher P. Higgins[†,*]



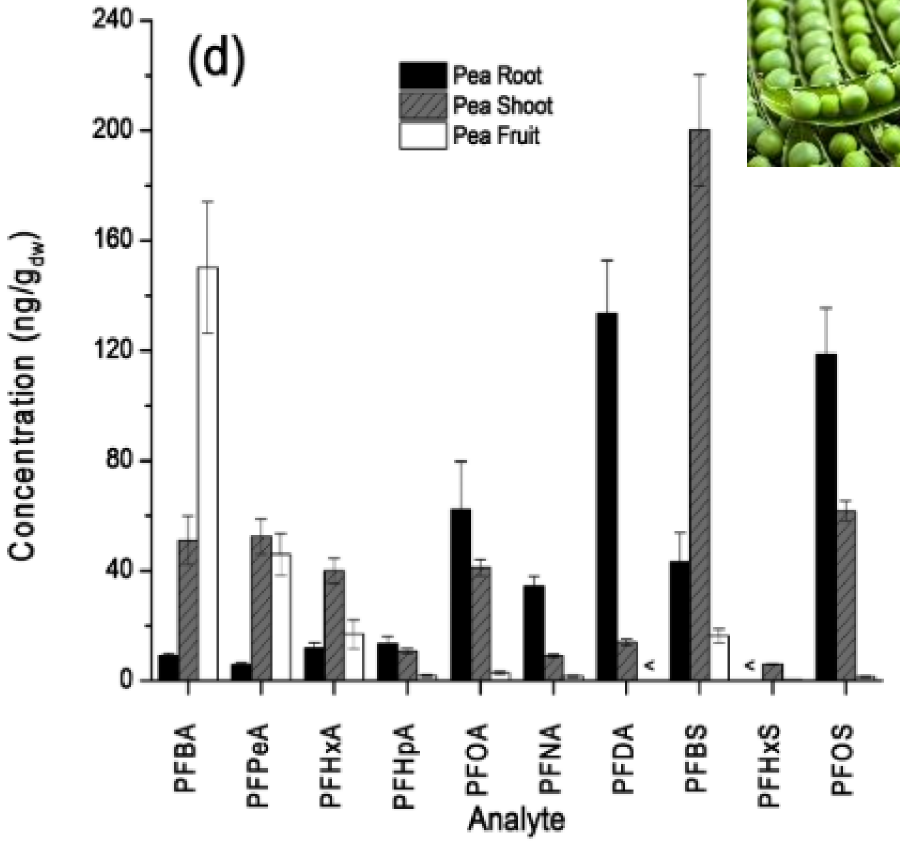


Figure 2. Concentrations of PFAAs in greenhouse radish (a), celery (b), tomato (c), and pea (d) grown in industrially impacted soil. Values for tomato fruit are from a previous study.[9] Bars represent means and standard errors of five determinations. Values less than the LOQ are denoted by <; LOQs for respective matrix and analyte are listed in SI Table S4 and Table S5.

Lena Vierke, Claudia Staude, Éva Fetter, Stephan Brendel, Annegret Biegel-Engler
Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany
ICCE 2017 Oslo

Regulation needs support from research: Short-chain PFASs under REACH

Umwelt Bundesamt

Concerns on short-chain PFASs – Exposure of organisms

- REACH criterion for bioaccumulation based on the bioconcentration factor is not fulfilled (Martin et al. 2003)
- Half-lives in organisms including humans range from a few hours to a few days (e. g. Chengelis et al., 2009; Gannon et al., 2011; Numata et al., 2014; Russell et al. 2013)
- Binding to proteins (Bischel et al. 2011)
- Occurrence in humans (e. g. Lee and Mabury 2011)
- Unclear whether short-chain PFASs bioaccumulate

Sufficient exposure durations for provoking adverse effects in organism


Tomasz Trojanowski/Fotolia.com

Lena Vierke, Claudia Staude, Éva Fetter, Stephan Brendel, Annegret Biegel-Engler
Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany

Concerns on short-chain PFASs

- Persistent in the environment
- High mobility: Potential exposure of humans via drinking water
- Enrichment in plants: Potential exposure of humans via food

→ Permanent and non-reversible exposure of organisms

- Exposure of organisms: Sufficient for provoking adverse effects in organism

What will happen in the long-term? Predictions needed!
- Background concentrations
- Effects on human health

Knowledge on uses and emissions needed

Lena Vierke, Claudia Staude, Éva Fetter, Stephan Brendel, Annegret Biegel-Engler
Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany

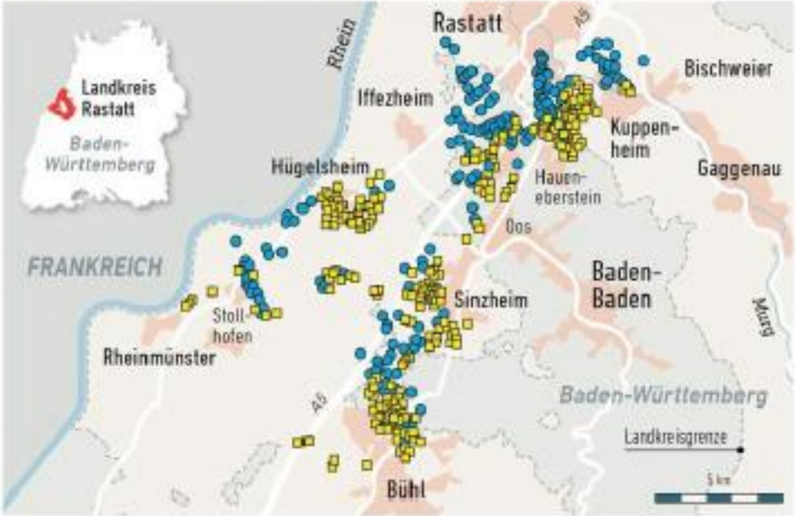
Concerns on short-chain PFASs – Rastatt case in Germany

- PFASs-polluted fertilizer
- 400 ha contaminated agricultural area
- Occurrence of short- and long-chain PFASs in soil and groundwater
- Enrichment of short-chain PFASs in plants
- Contaminated drinking water
- 2 closed water works
- Agricultural production stop in highly contaminated areas
- Remediation seems not possible (technologies, costs, responsibilities)

Monitoring stations showing PFASs contamination

Groundwater

Soil



Quelle: Landkreis Rastatt/F.A.Z.-Karte sie.

Source: Marc Rathman\ fotolia.de

Lena Vierke, Claudia Staude, Éva Fetter, Stephan Brendel, Annegret Biegel-Engler
Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany

Regulation needs support from research: Short-chain PFASs under REACH

Umwelt Bundesamt

Concerns on short-chain PFASs – Overview

Short-chain PFASs
Persistent
• Based on read-across from long-chain PFASs • Long-range transport and findings in remote areas
Mobility and exposure of organisms
• Potential to contaminate drinking water resources • Difficult to be removed from water • Binding to proteins • Non-negligible half-lives in organisms • Enrichment in plants
Toxic
• No indications for ecotoxicity • Toxicity to humans to be assessed
• Potential endocrine disruptors

Representatives of European Authorities agreed: properties are of concern
(UBA-Workshop in October 2016)

BUT non-classical combination of concerns so far not covered by REACH

→ **regulatory activities under development**
→ **more scientific knowledge would be helpful to eliminate data gaps**

http://reach-info.de/dokumente/short-chain_workshop_summary.pdf

http://reach-info.de/dokumente/short-chain_workshop_summary.pdf

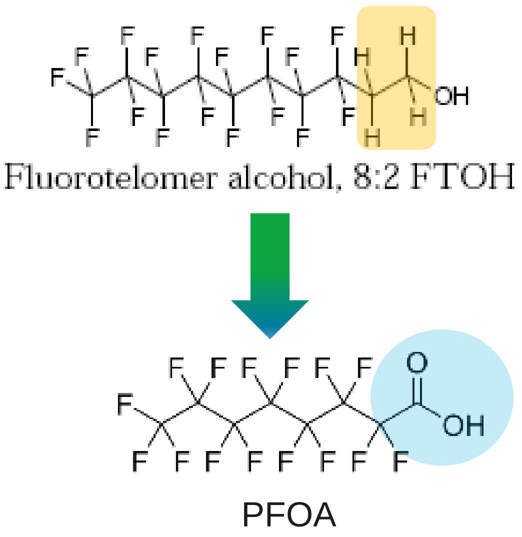
Bayerisches Landesamt für Umwelt

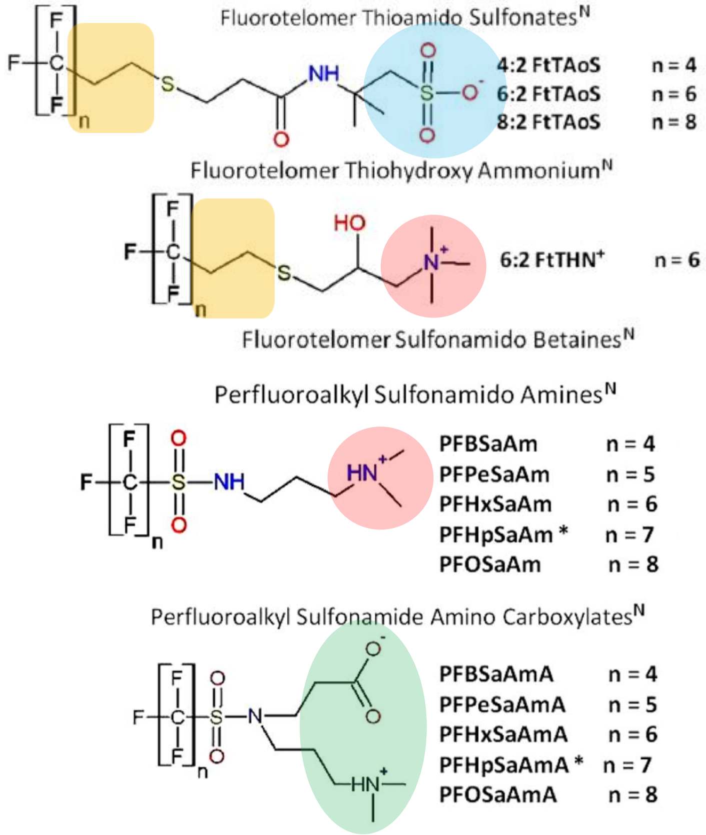
Leitlinien zur vorläufigen Bewertung von PFC-Verunreinigungen in Wasser und Boden

Stand: April 2017

Stoff	Vorläufiger Schwellenwert (SW) in µg/l	Summenbedingung
Perfluornonansäure **PFNA**	0,06	$\sum (C_n / SW_n) \leq 1$
Perfluoroktansulfonsäure **PFOS**	0,1	
Perfluoroktansäure **PFOA**	0,1	
Perfluorhexansulfonsäure **PFHxS**	0,1	
Perfluorhexansäure **PFHxA**	6,0	
Perfluorbutansulfonsäure **PFBS**	6,0	
Perfluorbutansäure **PFBA**	10,0	
Perfluordekansäure **PFDA**	0,1	
H4-Polyfluoroktansulfonsäure **H4PFOS**	0,1	
Perfluoroktansulfonamid **PFOSA**	0,1	
Perfluorheptansulfonsäure **PFHpS**	0,3	
Perfluorheptansäure **PFHpA**	0,3	
Perfluorpentansäure **PFPeA**	3,0	

Polyfluorinated Compounds -Precursors





Thousands of polyfluorinated precursors to PFAAs have been commercially synthesized for bulk products

The common feature of the precursors is that they will **biotransform** to make PFAA's as persistent "dead end" daughter products

PFAS do not biodegrade i.e. mineralise

Some precursors are fluorotelomers

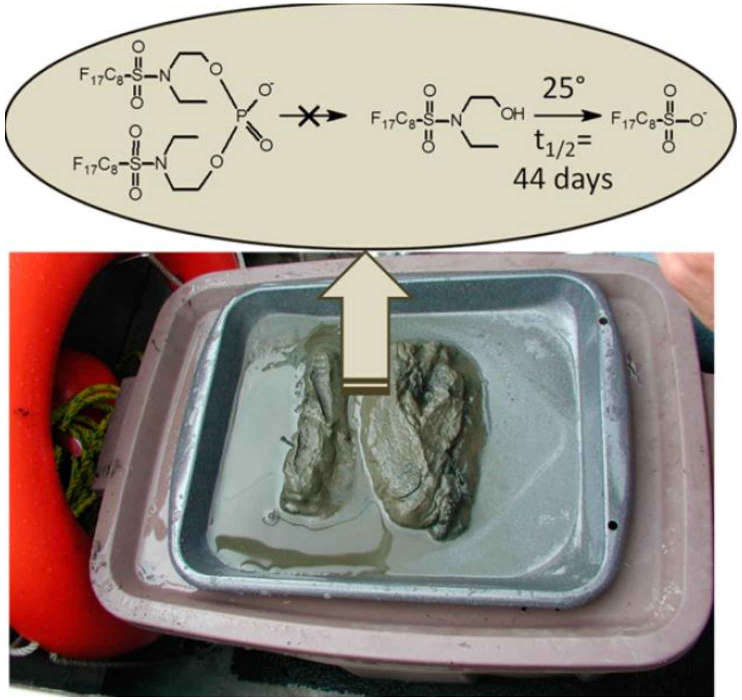
Some are cationic (positively charged) or zwitterionic (mixed charges) –this influences their fate and transpor in the environment

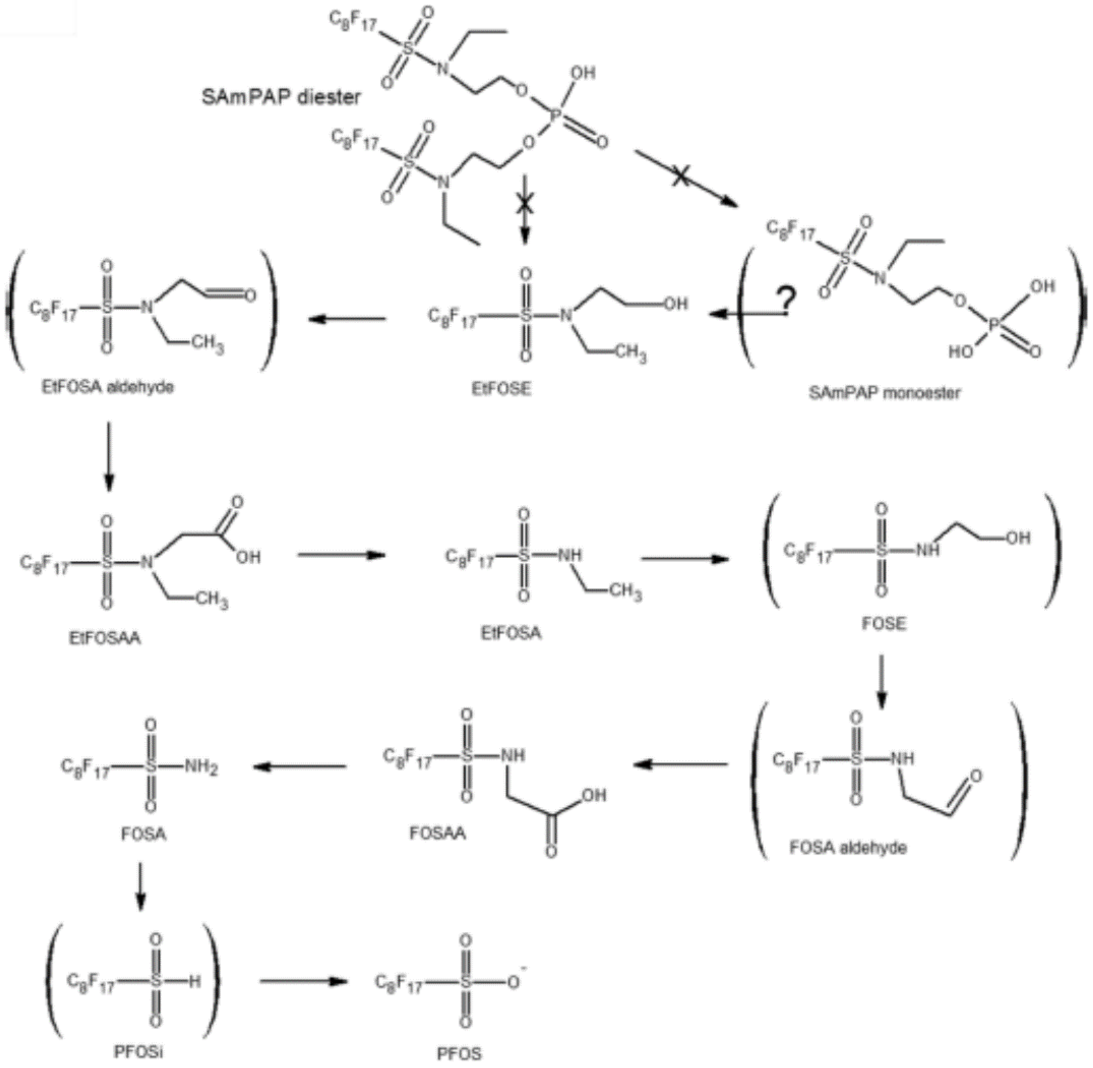
Cationic / zwitterionic PFAS tend to be less mobile than anionic PFAAs and so can potentially be retained longer in "source zones"

Environmental fate and transport will be complex as PFAS comprise multiple chain lengths and charges

Biodegradation of *N*-Ethyl Perfluorooctane Sulfonamido Ethanol (EtFOSE) and EtFOSE-Based Phosphate Diester (SAmPAP Diester) in Marine Sediments

Jonathan P. Benskin,*,†,‡ Michael G. Ikonomou,‡ Frank A. P. C. Gobas,§ Timothy H. Begley,∥ Million B. Woudneh,† and John R. Cosgrove†





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Precursors Biotransform to PFAAs *In Vivo*

Environ. Sci. Techno

Elucidating the Pathways of Poly- and Perfluorinated Acid Formation in Rainbow Trout

CRAIG M. BUTT,[†] DEREK C.G. MUIR,[‡] AND SCOTT A. MABURY*,[†]

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CRITICAL REVIEW www.rsc.org/jem | Journal of Environmental Monitoring

PFOS or PreFOS? Are perfluorooctane sulfonate precursors (PreFOS) important determinants of human and environmental perfluorooctane sulfonate (PFOS) exposure?†

Jonathan W. Martin,*[ab] Brian J. Asher,[b] Sanjay Beesoon,[a] Jonathan P. Benskin[a] and Matthew S. Ross[b]

Received 17th June 2010, Accepted 2nd September 2010
DOI: 10.1039/c0em00295j

Environ. Sci. Technol. **200**

Production of Perfluorinated Carboxylic Acids (PFCAs) from the Biotransformation of Polyfluoroalkyl Phosphate Surfactants (PAPS): Exploring Routes of Human Contamination

JESSICA C. D'EON AND SCOTT A. MABURY*

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Metabolic products and pathways of fluorotelomer alcohols in isolated rat hepatocytes

Jonathan W. Martin[a,*], Scott A. Mabury[b], Peter J. O'Brien[a]

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Estimating the contribution of precursor compounds in consumer exposure to PFOS and PFOA

Robin Vestergren[a], Ian T. Cousins[a,*], David Trudel[b], Matthias Wormuth[b], Martin Scheringer[b]

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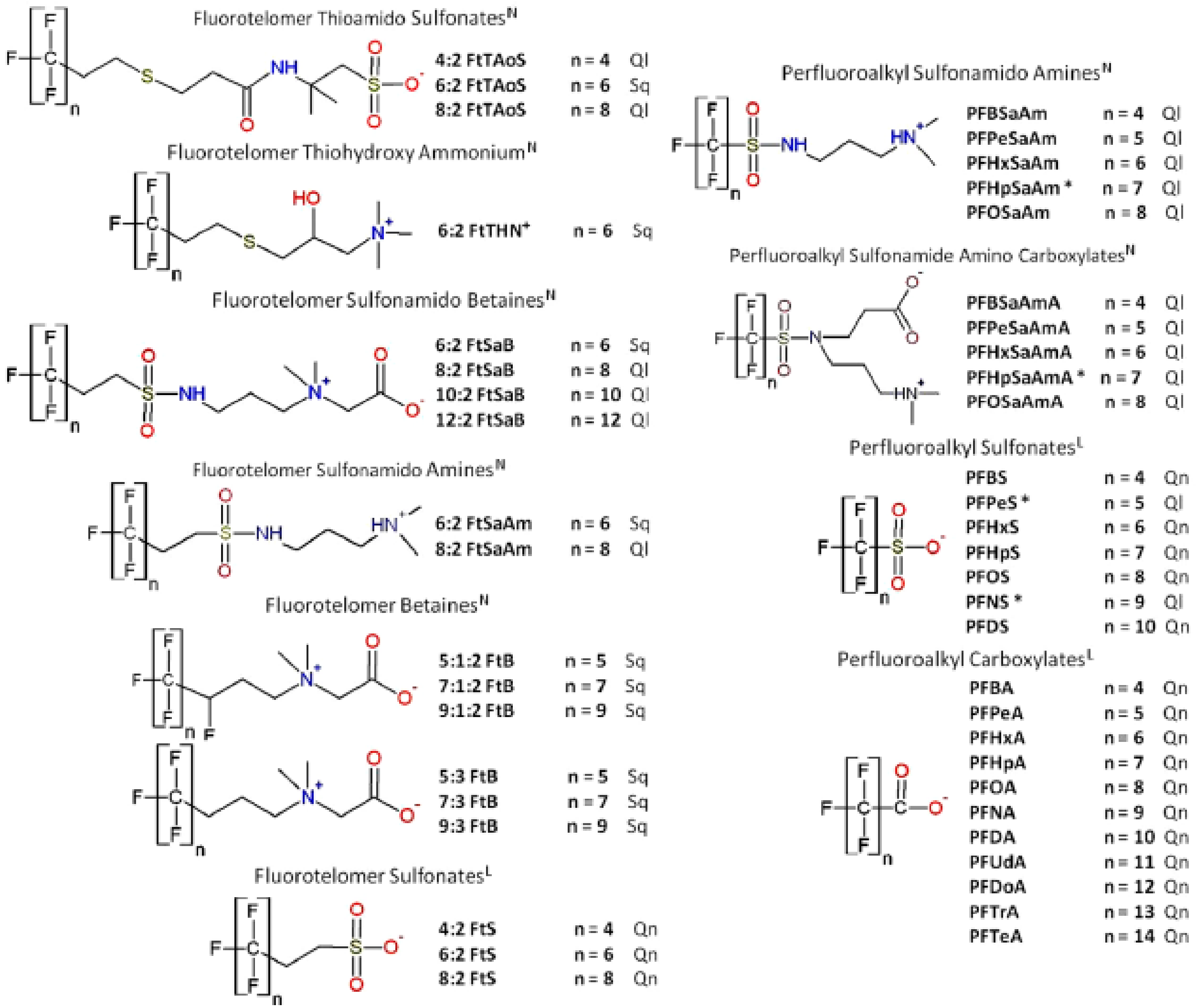
. Several authors have emphasized that there may be additional sources of human exposure to these chemicals from precursor compounds including fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (PFOSAs) and amidoalcohols (PFOSEs) that are metabolized to form PFOA and PFOS, respectively (Hagen et al., 1981; Seacat et al., 2003; Tomy et al., 2004; Xu et al., 2004; Martin et al., 2005; Fasano et al., 2006; Xu et al., 2006; Nabb et al., 2007).

Diversity of PFAS Characterised in AFFF



Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS

Will J. Backe,[†] Thomas C. Day,[†] and Jennifer A. Field*[,‡]

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[‡]1007 Agricultural and Life Science Building, Department of Molecular and Environmental Toxicology, Oregon State University,

AFFF Composition

Precursors →

Older ECF foams contain precursors to PFAA's of varying chain lengths and PFOS

	1989 mg/L	1993a mg/L	1993b mg/L	1998 mg/L	2001 mg/L
PFBSaAm[a]	9	120 ± 2.0	180	140	110
PFPeSaAm[a]	8	140 ± 1.8	180	140	110
PFHxSaAm[a]	189	660 ± 8.1	850	743	690
PFHpSaAm	ND	12 ± 0.40	15	30	24
PFOSaAm	9.9	62 ± 1.1	75	67	37
PFBSaAmA[a]	ND	140 ± 3.1	120	110	150
PFPeSaAmA[a]	4	200 ± 6.3	170	140	130
PFHxSaAmA[a]	ND	930 ± 13	850	850	960
PFHpSaAmA	ND	17 ± 0.16	17	34	44
PFOSaAmA[a]	ND	72 ± 0.81	58	53	65
PFBS	380	220 ± 2.0	160	210	250
PFPeS	210	120 ± 1.5	80	90	120
PFHxS	1700	910 ± 14	760	850	900
PFHpS	410	120 ± 2.0	120	93	140
PFOS	15000	8000	9300	6700	7900
PFNS	160	53 ± 0.97	56	9	27
PFDS	102	51 ± 0.34	52	11	27
PFBA	37	24 ± 0.48	35	31	38
PFPeA	47	36 ± 0.14	52	43	48
PFHxA	170	99 ± 1.1	110	99	170
PFHpA	54	25 ± 0.28	22	26	37
PFOA	150	83 ± 1.3	93	86	170
PFNA	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND
PFUdA	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND
PFTrA	ND	ND	ND	ND	ND
PFTeA	ND	ND	ND	ND	ND
PFS/PFA[b]	39	35	34	28	20
% Precursors	1.2	19.5	18.8	21.9	19.1
% PFOS	80.5	66.1	69.6	63.5	65.0
% Shorter Chain PFAAs	18.3	14.4	11.5	14.7	15.9

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS

Will J. Backe, Thomas C. Day, and Jennifer A. Field

AFFF Composition

100% Precursors

More recent foams contain fluorotelomers which are precursors to PFAA's of varying chain lengths but no PFOS or PFOA

	2005 mg/L	2010 mg/L	2002 mg/L	2003 mg/L	2009 mg/L	NR[a] mg/L
4:2 FtTAoS[c]	26	ND	25	ND	ND	ND
6:2 FtTAoS	6,100	11,000	4,900	ND	ND	ND
8:2 FtTAoS[c]	1,100	24	170	ND	ND	ND
4:2 FtS	ND	ND	ND	ND	ND	ND
6:2 FtS	ND	ND	ND	42	ND	53
8:2 FtS	ND	ND	ND	19	ND	56
6:2 FtTHN[+]	ND	ND	2,200	ND	ND	ND
6:2 FtSaB	ND	ND	ND	4,600	ND	4,800
8:2 FtSaB[d]	ND	ND	ND	540	ND	1,800
10:2 FtSaB[d]	ND	ND	ND	450	ND	830
12:2 FtSaB[d]	ND	ND	ND	210	ND	430
6:2 FtSaAm	ND	ND	ND	2,100	ND	3,400
8:2 FtSaAm[e]	ND	ND	ND	450	ND	720
5:1:2 FtB	ND	ND	ND	ND	2,000	ND
7:1:2 FtB	ND	ND	ND	ND	4,700	ND
9:1:2 FtB	ND	ND	ND	ND	1,900	ND
5:3 FtB	ND	ND	ND	ND	530	ND
7:3 FtB	ND	ND	ND	ND	610	ND
9:3 FtB	ND	ND	ND	ND	430	ND

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS

Will J. Backe,[†] Thomas C. Day,[†] and Jennifer A. Field[*,‡]

ANALYTICAL TOOLS

Analysis by LCMSMS via EPA Method 537 or similar

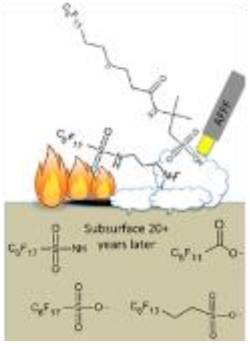
- **US EPA Method 537: Analysis for selected PFAS in drinking water**
  - 12 PFAAs and 2 Precursors:
    - PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUA, PFDoA, PFTrA, PFTeA
    - PFBS, PFHxS, PFOS
    - N-EtFOSAA, N-MeFOSAA
- **Method 537 has been adapted with more analytes to other media**
  - Up to 39 individual analytes (laboratory dependent)
  - Groundwater with PFAS LODs ranging as low as 0.09 ng/L
  - Availability of standards and other factors limit the number of PFAS that can be measured with a single method
  - Thousands of precursors and their transient metabolites makes synthesis of a comprehensive set of standards unrealistic

Conventional analysis will not reflect total PFAS mass

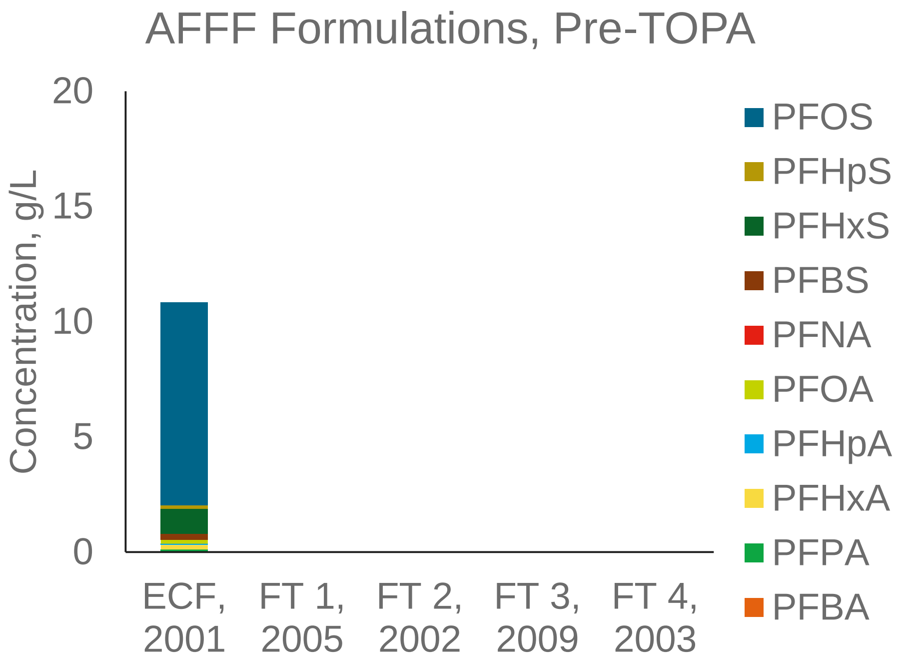
Advanced Analytical Techniques
Expanding analytical tool box to assess total PFAS

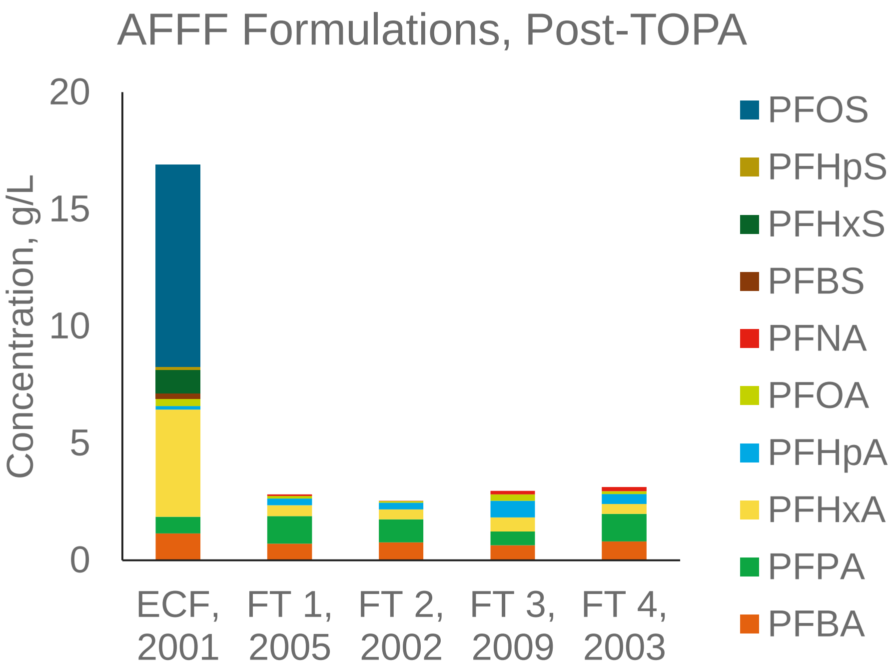
ARCADIS Design & Consultancy for natural and built assets

- **Total oxidizable precursor (TOP) Assay**
  - Initial LC-MS/MS analysis with re-analysis following oxidative digest
  - Detection limits to ~ 2 ng/L (ppt)
  - Commercially available in UK, Australia, under development in US
- **Particle-induced gamma emission (PIGE) Spectroscopy**
  - Isolates organofluorine compounds on solid phase extraction, measures total fluorine
  - Detection limits to ~ 15 ug/L (ppb) F
  - Commercially available in US
- **Adsorbable organofluorine (AOF)**
  - Isolates organofluorine compounds with activated carbon and measures F by combustion ion chromatography
  - Detection limits to ~ 1 ug/L (ppb) F
  - Commercially available in Germany, Australia
- **Time of Flight MS (LCQTOF) MS**
  - Identifies multiple precursors via mass ions capture and accurate mass estimation (to 0.0001 of a Dalton) to give empirical formulae (e.g. $C_{10}F_{21}O_3N_2H_4$)



TOP Assay Applied to AFFF Formulations: Many formulations appear PFAS-free until precursors are revealed by TOP Assay





FT = Fluorotelomer-based AFFF

ECF = Electrochemical Fluorination- based AFFF

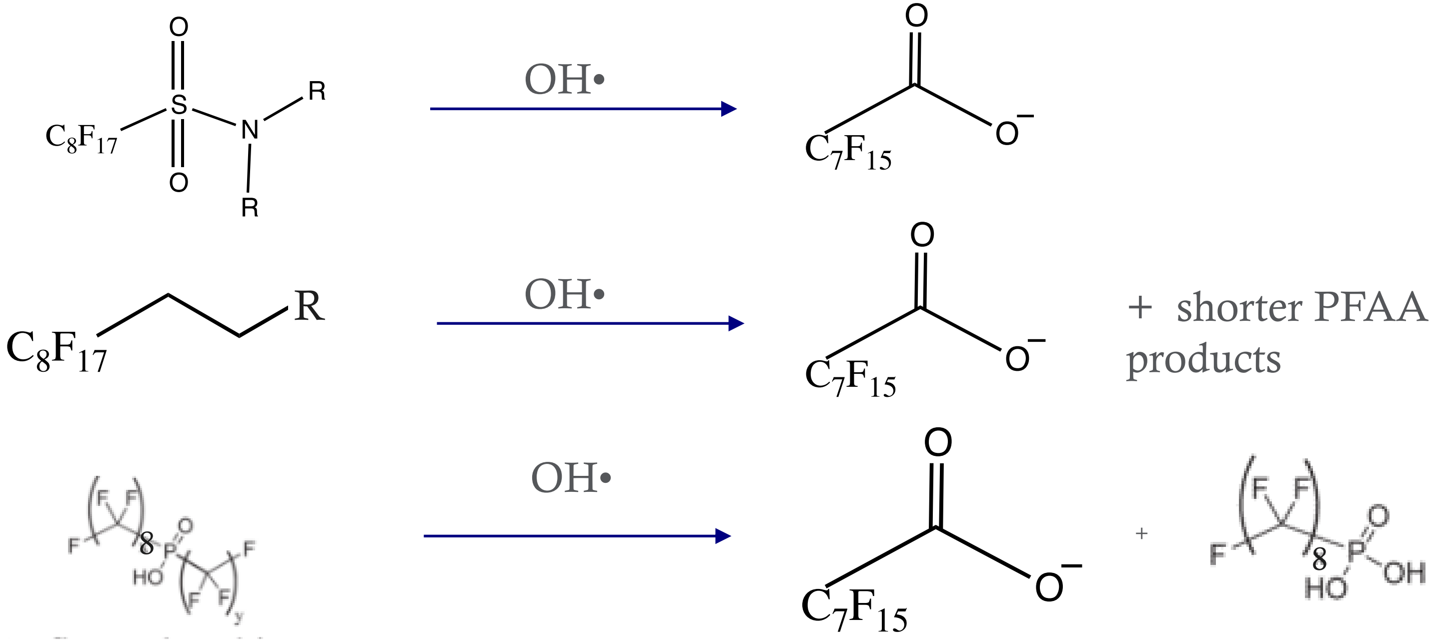
Total Oxidizeable Precursor Assay (TOP)

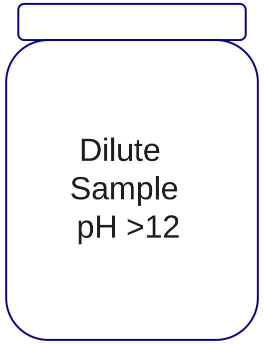
Oxidation of Precursors to PFAAs with OH•

PFSA Precursors

PFCA Precursors

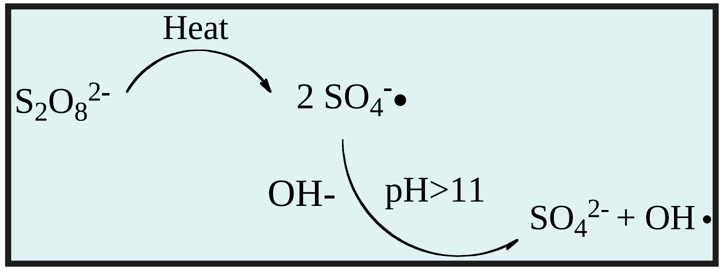
PFPA Precursors





85 °C 8

NaOH + $K_2S_2O_8$



Approach described in Houtz and Sedlak, *ES&T*, 2012

Digest AFFF precursors and measure the hidden mass: TOP Assay

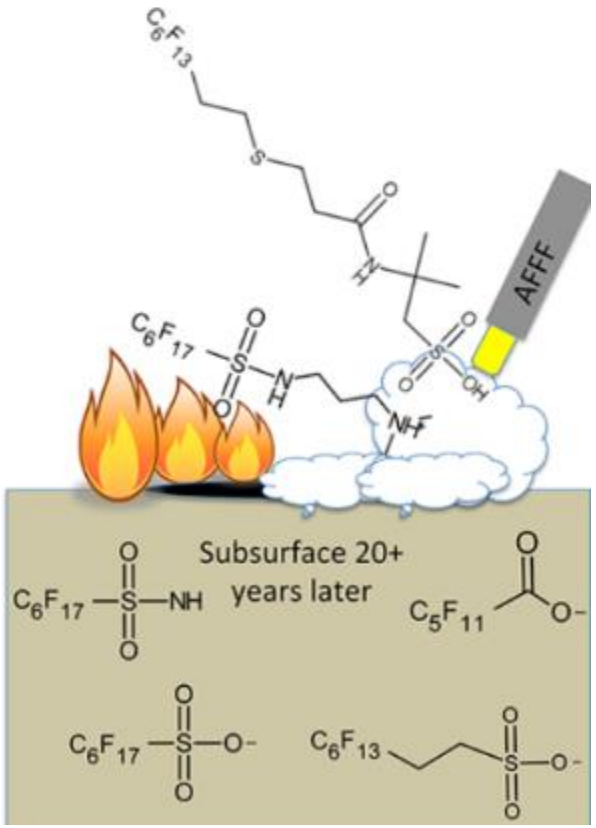
Microbes slowly make simpler PFAA's (e.g. PFOS / PFOA) from PFAS (PFAA precursors) over 20+ years

Need to determine precursor concentrations as they will form PFAAs

Too many PFAS compounds and precursors –so very expensive analysis

Oxidative digest convert PFAA precursors to PFAA's

Indirectly measure precursors as a result of the increased PFAAs formed



Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

Erika F. Houtz,† Christopher P. Higgins,‡ Jennifer A. Field,§ and David L. Sedlak†,*

Analytical tools fail to measure the hidden PFAS precursor mass, the TOP assay solves this

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

Prepared for the Concawe Soil and Groundwater Taskforce (STF/33):

J.W.N. Smith (Chair)
B. Beuthe
M. Dunk
S. Demeure
J.M.M. Carmona
A. Medve

M.J. Spence (Science Executive)

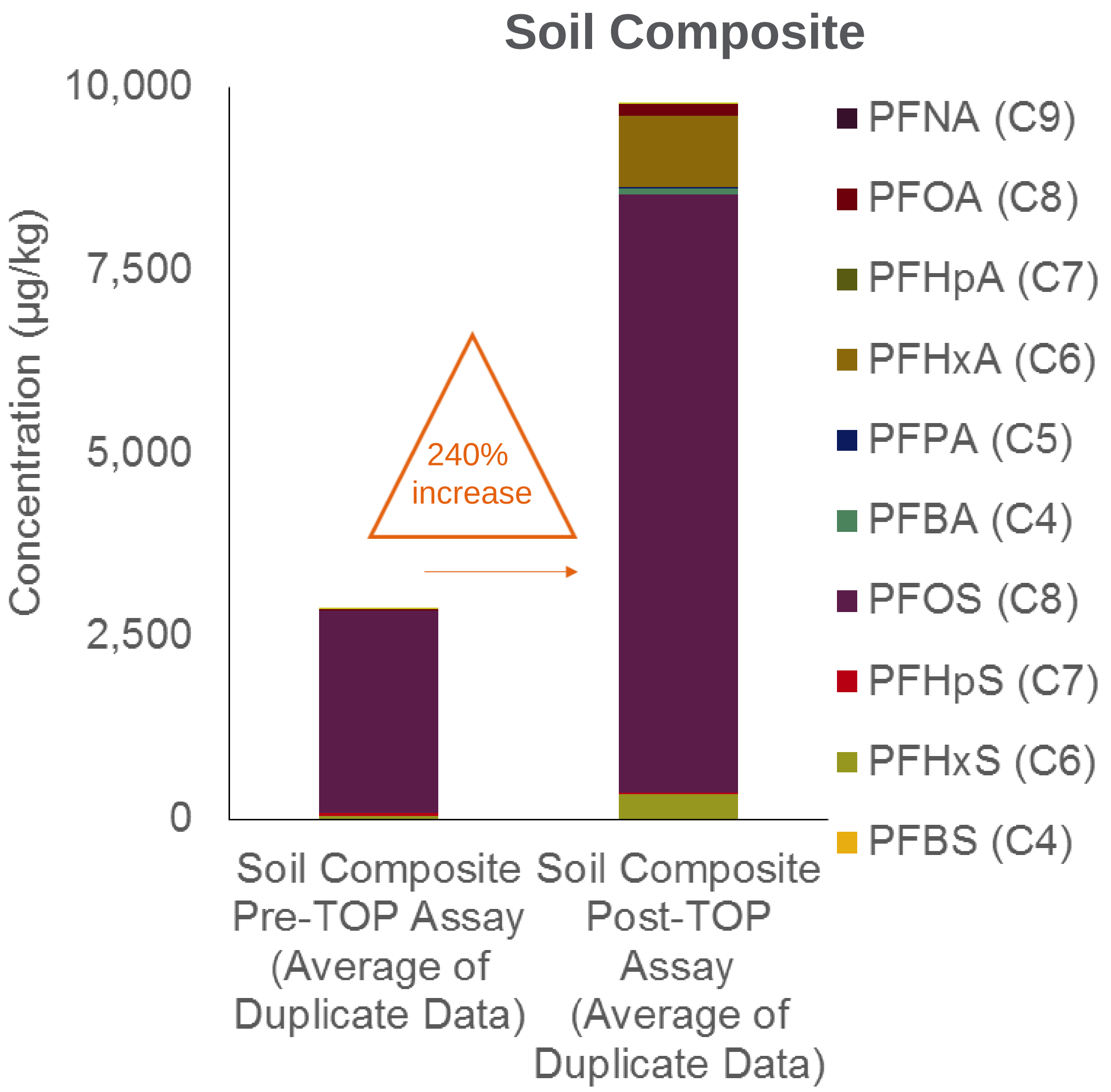
Prepared by ARCADIS:

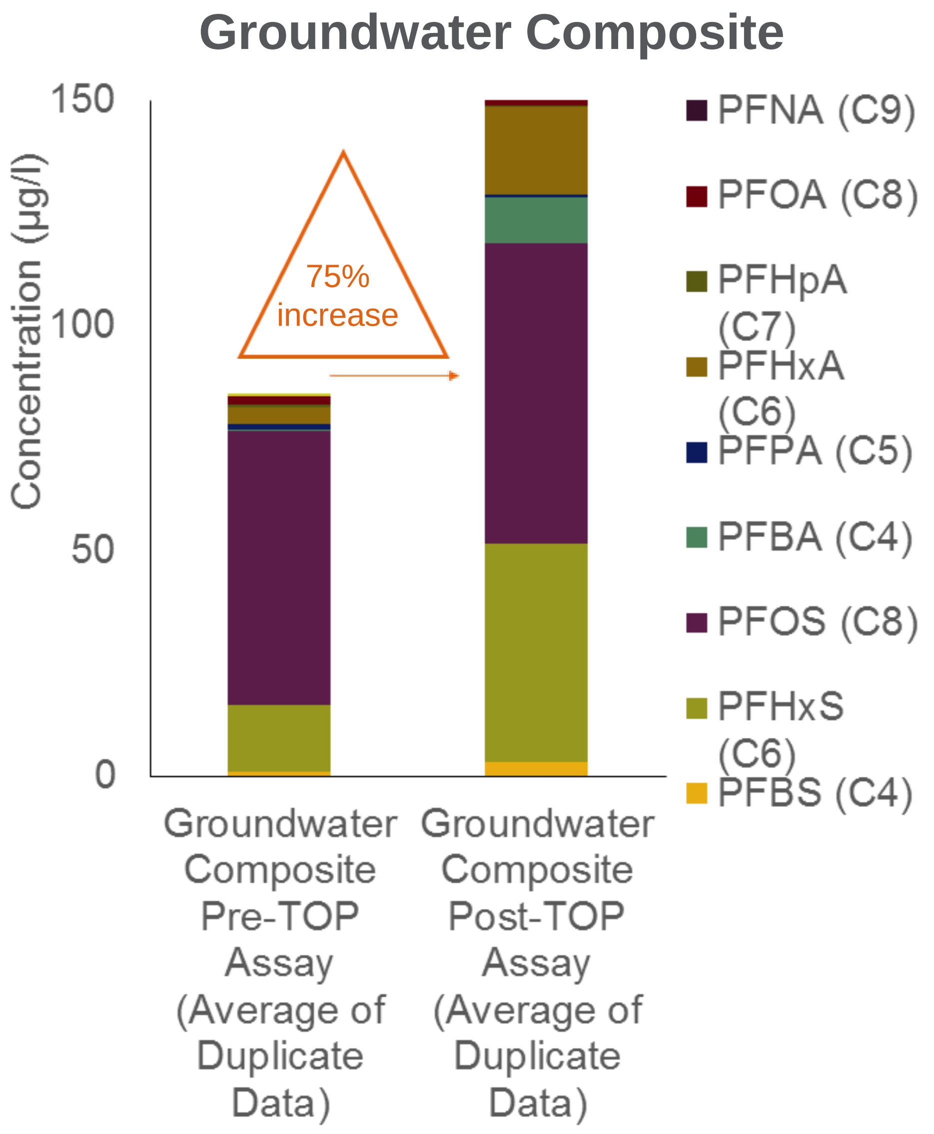
T. Pancras
G. Schrauwen
T. Held
K. Baker
I. Ross
H. Slenders

Analysis

While a range of standard methods are available for the analysis of PFSAs and PFCAs, the quantitative analysis of other PFAS substances is often difficult due to a lack of appropriate reference materials. To address this difficulty, analytical techniques have been developed whereby PFAS are quantitatively oxidized to fluoride (adsorbable organic fluorinated compounds (AOF) method), or a mixture of PFSAs and PFCAs (total oxidisable precursor (TOP) method). The TOP method is most sensitive, with a detection limit around 0,002 µg/l range, vs 1 µg/l for AOF.

Total Oxidizable Precursor (TOP) Assay
Fire Training Area





EPA Method 537 Underestimates the PFAS Mass

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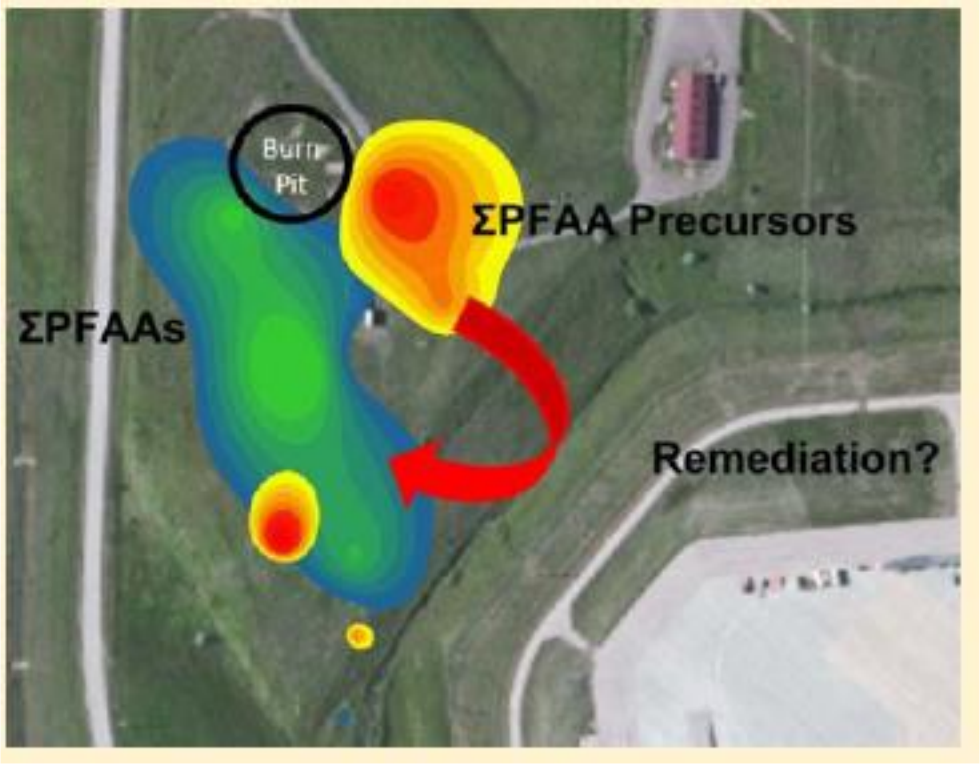
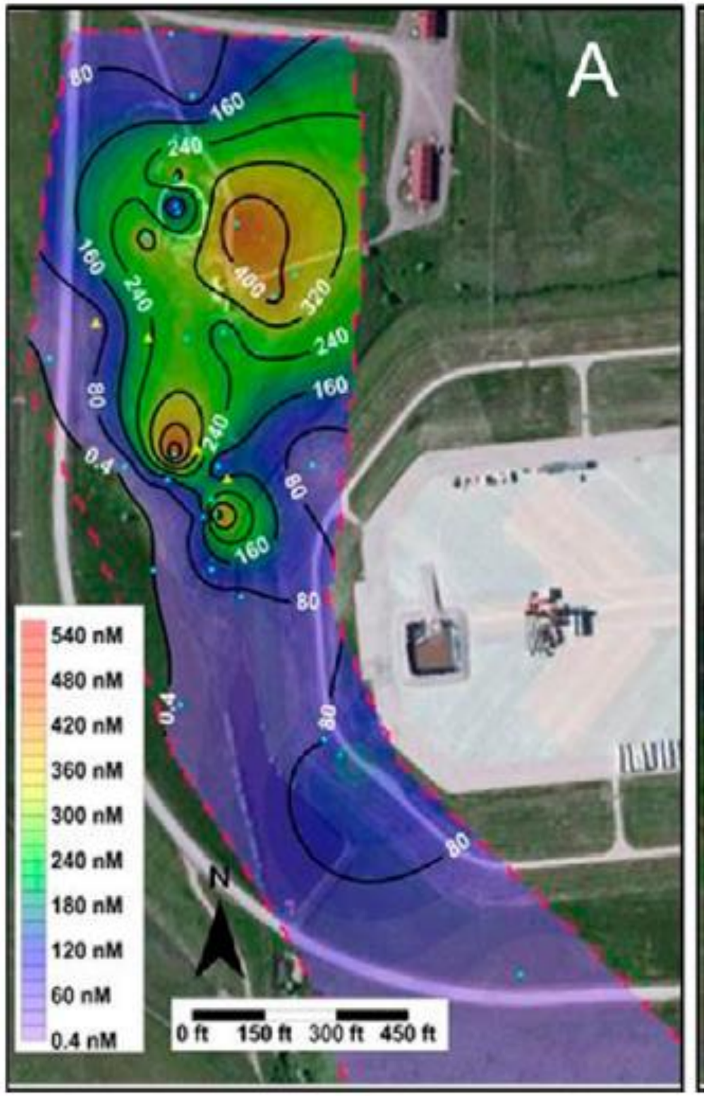
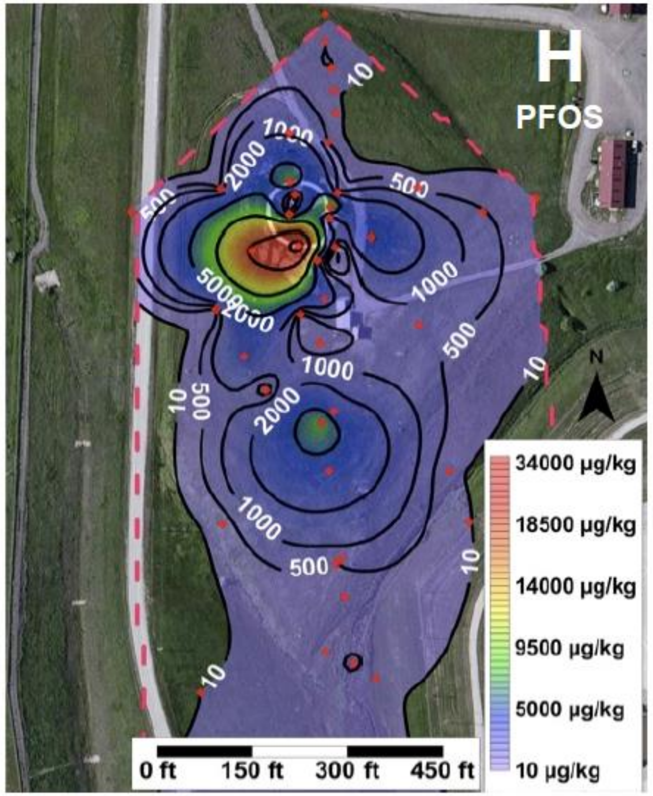
Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area

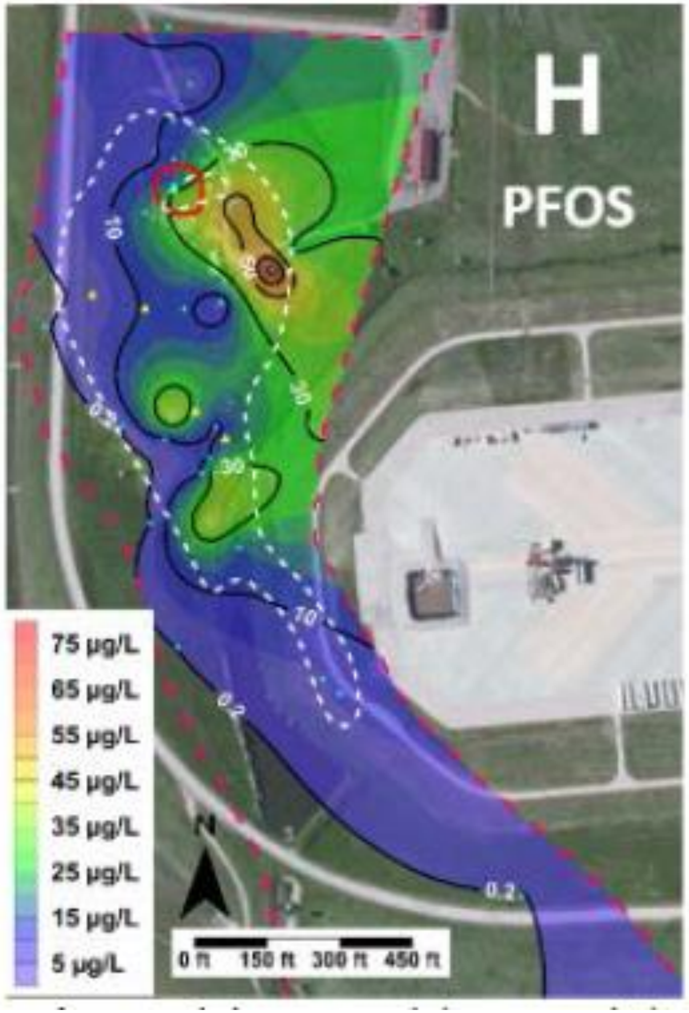
Meghan E. McGuire,[†] Charles Schaefer,[‡] Trenton Richards,[~] Will J. Backe,[§,¥] Jennifer A. Field,[⊥] Erika Houtz,[∥,¤] David L. Sedlak,[∥] Jennifer L. Guelfo,[†] Assaf Wunsch,[†] and Christopher P. Higgins*

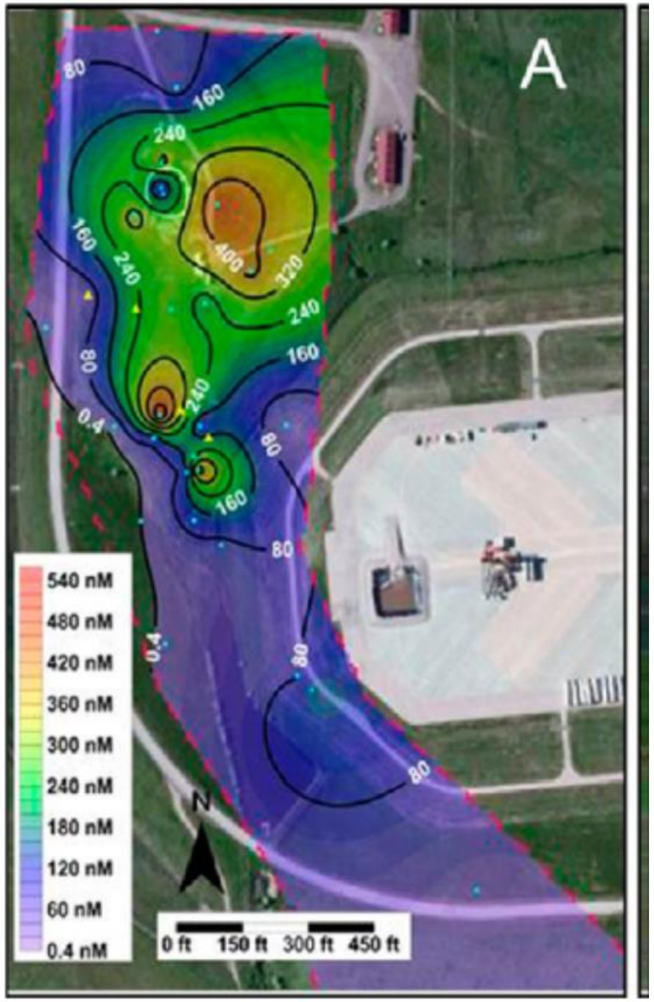




PFOS similar distribution to total PFAA-precursors







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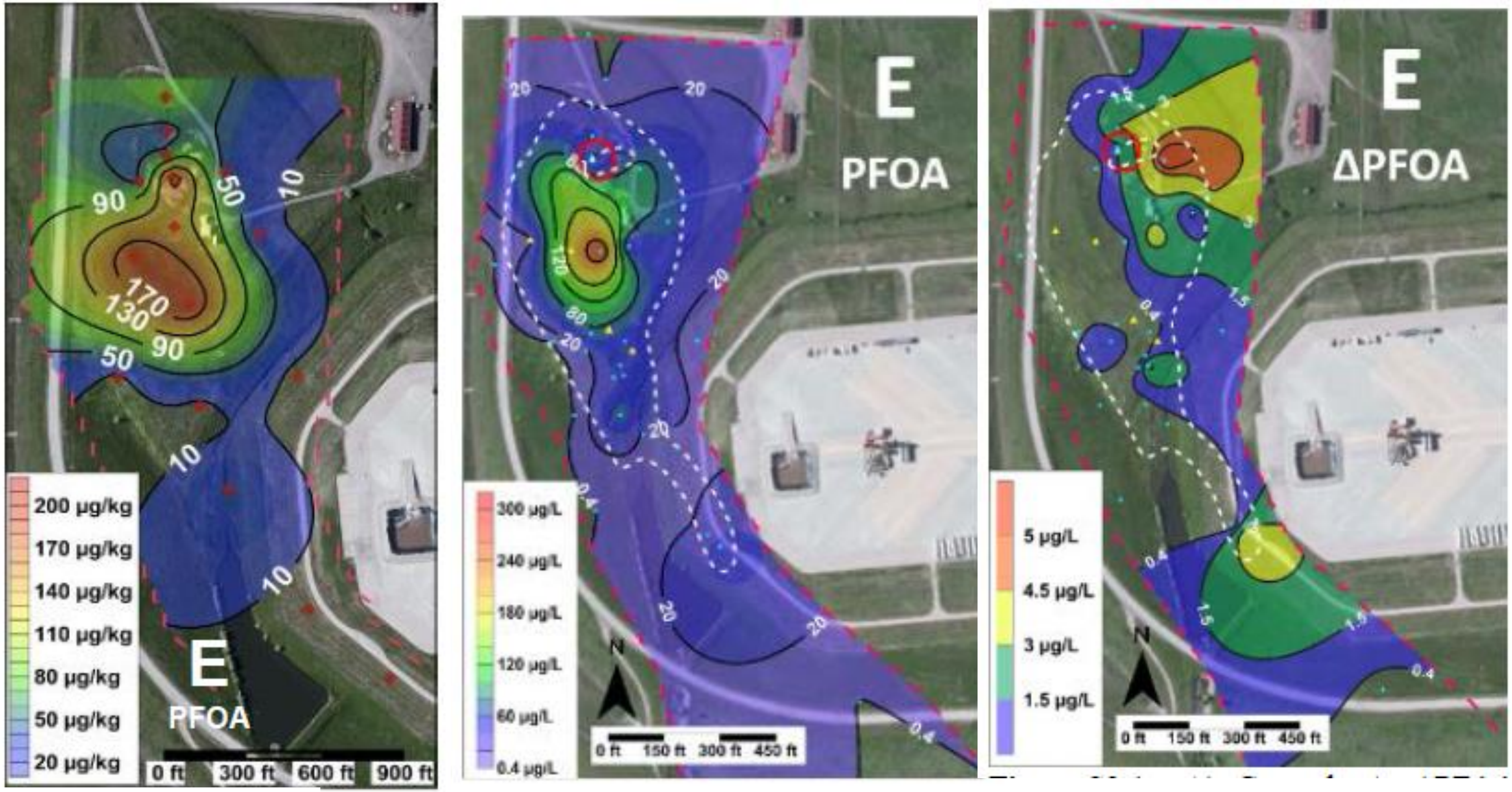
PFOA and PFOA-precursor distribution



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Evidence of Remediation-Induced Alteration of Subsurface Poly- and Perfluoroalkyl Substance Distribution at a Former Firefighter Training Area

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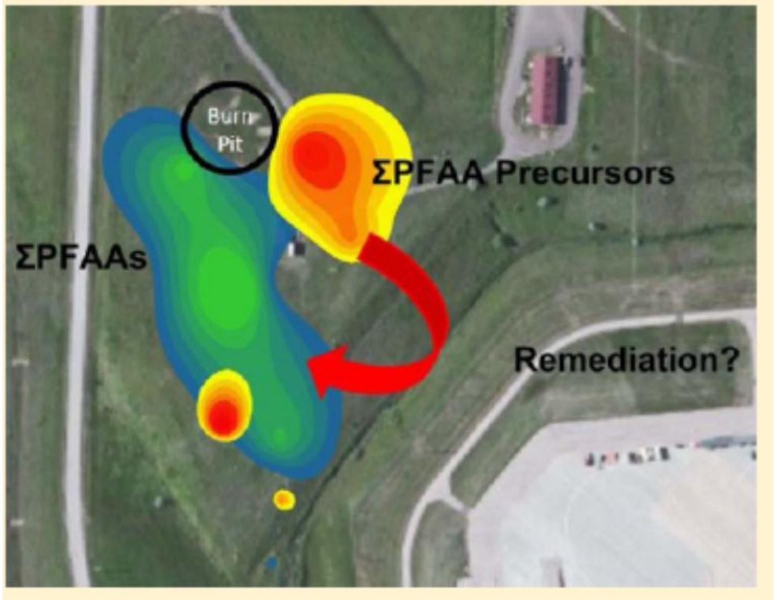
Possible explanations for the eastern source area:

- There is a secondary source to the east but surficial soils have been replaced
- Prior aerobic bioremediation in western source / plume targeting hydrocarbons, in the existing source enabled biotransformation of PFAA precursors



Conclusions

- Simply looking for PFCAs and not employing the TOP assay would obscure the actual potential for PFCA contamination

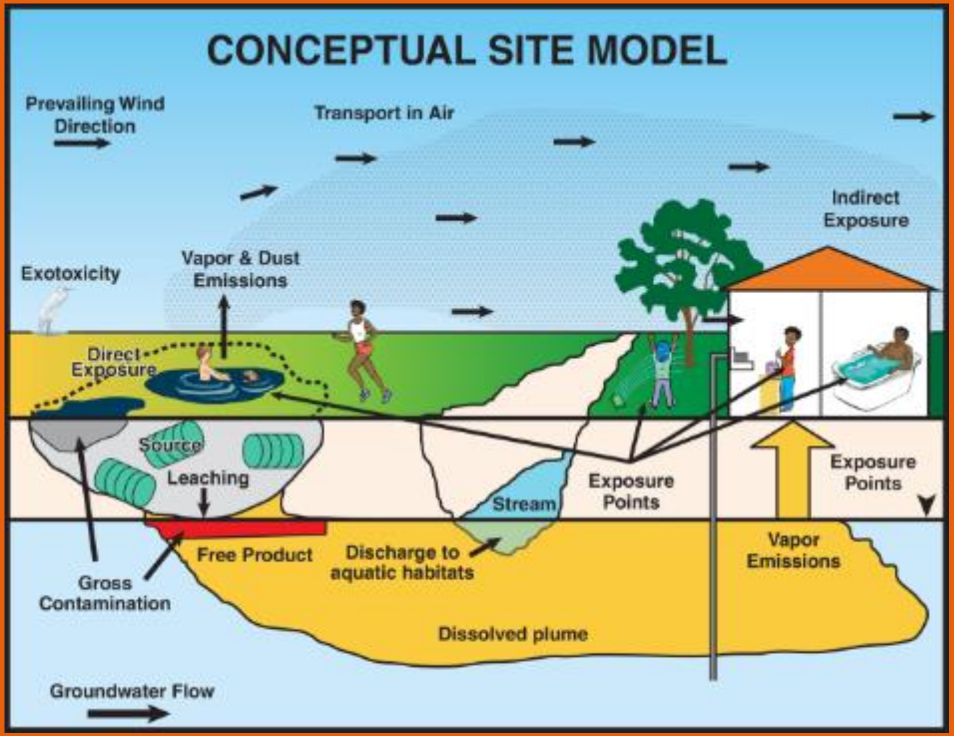
Aerobic Biotransformation Funnel –Precursors converted to PFAAs

All Polyfluorinated/ PFAA Precursor Compounds in Commerce

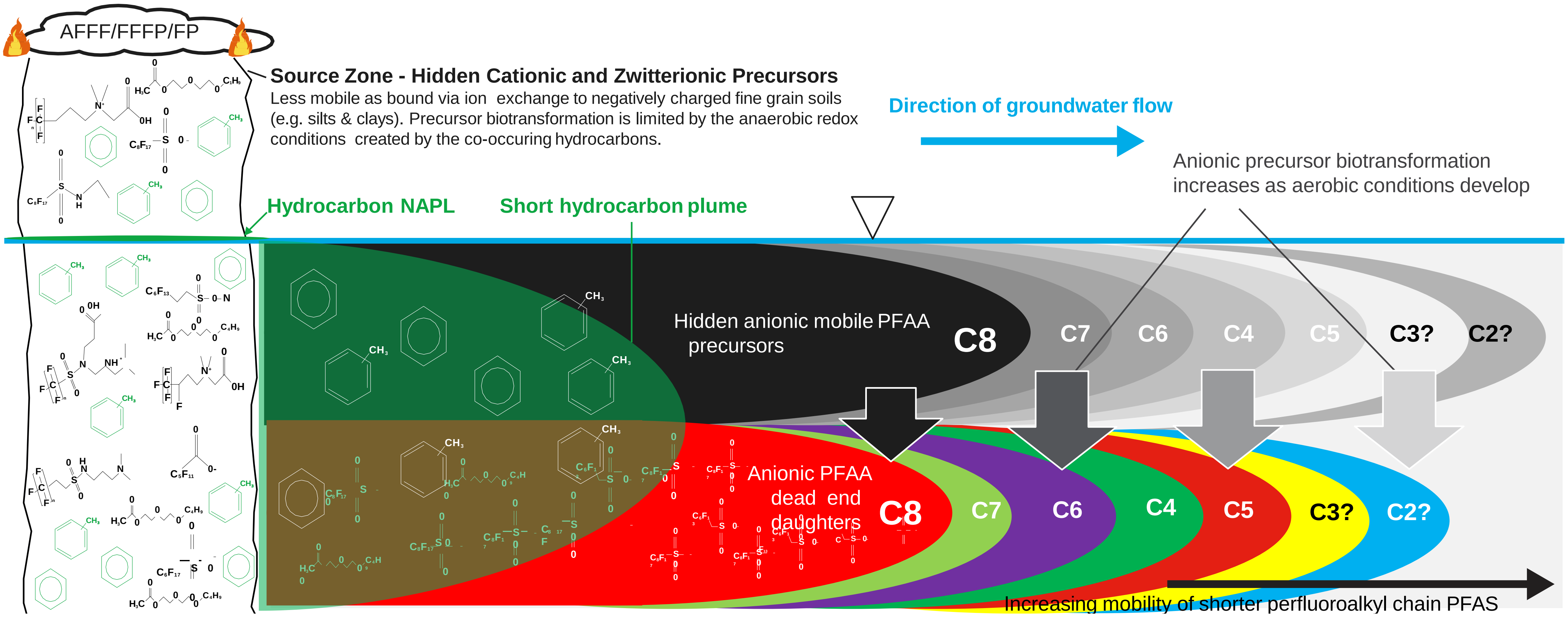
Hundreds of Common Intermediate Transformation Products

Approximately 25 PFSAs, PFCAs, PFPAs – collectively termed PFAAs

Conceptual Site Model



PFAS Source Zones, a CSM



AFFF Composition

Older ECF foams contain relatively mobile anionic PFOS in addition cationic / zwitterionic precursors to PFAAs which to which will be less mobile and potentially remain in the source area longer.

Biotransformation induces charge switching, such that less mobile precursors create more mobile PFAAs

	1989 mg/L	1993a mg/L	1993b mg/L	1998 mg/L	2001 mg/L
PFBSaAm[a]	9	120 ± 2.0	180	140	110
PFPeSaAm[a]	8	140 ± 1.8	180	140	110
PFHxSaAm[a]	189	660 ± 8.1	850	743	690
PFHpSaAm	ND	12 ± 0.40	15	30	24
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PFPeA	47	36 ± 0.14	52	43	48
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PFHpA	54	25 ± 0.28	22	26	37
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PFNA	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND
PFUdA	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND
PFTrA	ND	ND	ND	ND	ND
PFTeA	ND	ND	ND	ND	ND
PFS/PFA[b]	39	35	34	28	20
% Cationic	1.2	8.2	9.7	10.6	8.0
% Anionic	98.8	80.5	81.2	78.1	80.9
% Zwitterionic	0.0	11.2	9.1	11.2	11.1

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aque
Film Forming Foam Formulations and Groundwater from U.S.
Military Bases by Nonaqueous Large-Volume Injection HPLC-MS

Will J. Backe,[†] Thomas C. Day,[†] and Jennifer A. Field[*,‡]

AFFF Composition

More recent fluorotelomer foams contain only precursors which can be mixtures of anionic, cationic and zwitterionic species so will potentially have highly variable fate and transport characteristics depending on the formulation.

Biotransformation of less mobile precursors induces charge switching to more mobile PFAA's.

	2005	2010	2002	2003	2009	NR[a]
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
4:2 FtTAoS[c]	26	ND	25	ND	ND	ND
6:2 FtTAoS	6,100	11,000	4,900	ND	ND	ND
8:2 FtTAoS[c]	1,100	24	170	ND	ND	ND
4:2 FtS	ND	ND	ND	ND	ND	ND
6:2 FtS	ND	ND	ND	42	ND	53
8:2 FtS	ND	ND	ND	19	ND	56
6:2 FtTHN[+]	ND	ND	2,200	ND	ND	ND
6:2 FtSaB	ND	ND	ND	4,600	ND	4,800
8:2 FtSaB[d]	ND	ND	ND	540	ND	1,800
10:2 FtSaB[d]	ND	ND	ND	450	ND	830
12:2 FtSaB[d]	ND	ND	ND	210	ND	430
6:2 FtSaAm	ND	ND	ND	2,100	ND	3,400
8:2 FtSaAm[e]	ND	ND	ND	450	ND	720
5:1:2 FtB	ND	ND	ND	ND	2,000	ND
7:1:2 FtB	ND	ND	ND	ND	4,700	ND
9:1:2 FtB	ND	ND	ND	ND	1,900	ND
5:3 FtB	ND	ND	ND	ND	530	ND
7:3 FtB	ND	ND	ND	ND	610	ND
9:3 FtB	ND	ND	ND	ND	430	ND
% Cationic	0.0	0.0	30.2	30.3	0.0	34.1
% Anionic	100.0	100.0	69.8	0.7	0.0	0.9
% Zwitterionic	0.0	0.0	0.0	69.0	100.0	65.0

Zwitterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foam Formulations and Groundwater from U.S. Military Bases by Nonaqueous Large-Volume Injection HPLC-MS/MS

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Article
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Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts

Andrea K. Weber,[†] Larry B. Barber,[‡] Denis R. LeBlanc,[§] Elsie M. Sunderland,[†,#] and Chad D. Vecitis*[,†]

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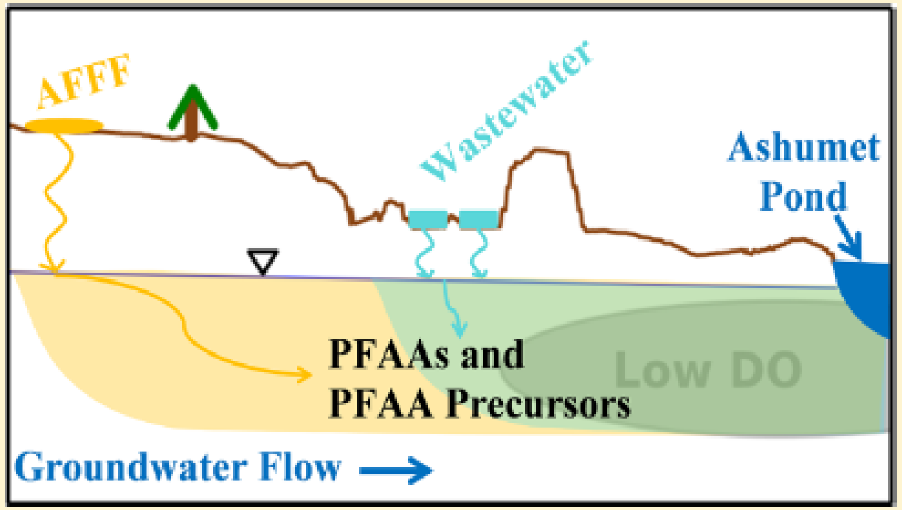
ABSTRACT: Growing evidence that certain poly- and perfluoroalkyl substances (PFASs) are associated with negative human health effects prompted the U.S. Environmental Protection Agency to issue lifetime drinking water health advisories for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in 2016. Given that groundwater is a major source of drinking water, the main objective of this work was to investigate geochemical and hydrological processes governing the subsurface transport of PFASs at a former fire training area (FTA) on Cape Cod, Massachusetts, where PFAS-containing aqueous film-forming foams were used historically. A total of 148 groundwater samples and 4 sediment cores were collected along a 1200-m-long downgradient transect originating near the FTA and analyzed for PFAS content. The results indicate that unsaturated zones at the FTA and at hydraulically downgradient former domestic wastewater effluent infiltration beds both act as continuous PFAS sources to the groundwater despite 18 and 20 years of inactivity, respectively. Historically different PFAS sources are evident from contrasting PFAS composition near the water table below the FTA and wastewater-infiltration beds. Results from total oxidizable precursor assays conducted using groundwater samples collected throughout the plume suggest that some perfluoroalkyl acid precursors at this site are transporting with perfluoroalkyl acids.



Sorption of Poly- and Perfluoroalkyl Substances (PFASs) relevant to Aqueous Film Forming Foam (AFFF)-impacted Groundwater by Biochars and Activated Carbon

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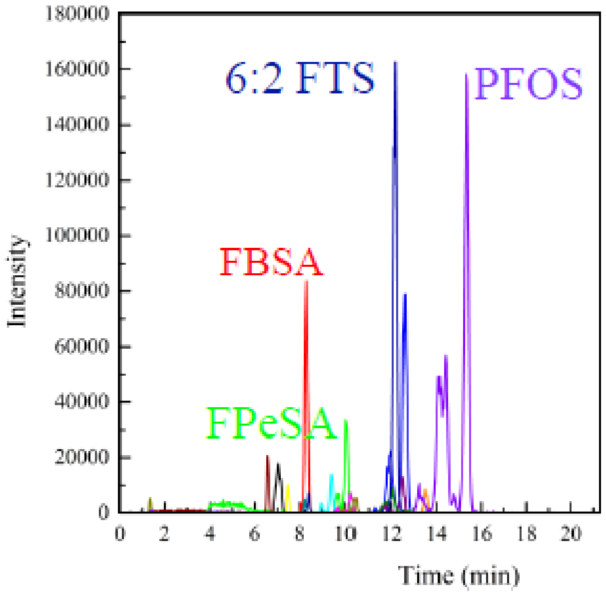
Results: PFASs present in water supply



PFOS: 33 μg/L
PFOA: 11 μg/L

- PFASs only observed in ESI-LC-QToF-MS analysis
- 30 PFASs observed using HRMS library and/or authentic standards
  - 5 perfluorocarboxylates (C4-C8)
  - 6 perfluorosulfonates (C3-C8)
  - 2 fluorotelomer sulfonates (4:2 & 6:2)
  - 4 perfluoroalkyl sulfonamides (C3-C6)
  - 11 recently discovered polyfluorinated PFASs
  - 2 PFOS-like derivatives

Other PFASs are likely present in AFFF-impacted drinking water supplies

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Estimating human exposure to PFOS isomers and PFCA homologues: The relative importance of direct and indirect (precursor) exposure

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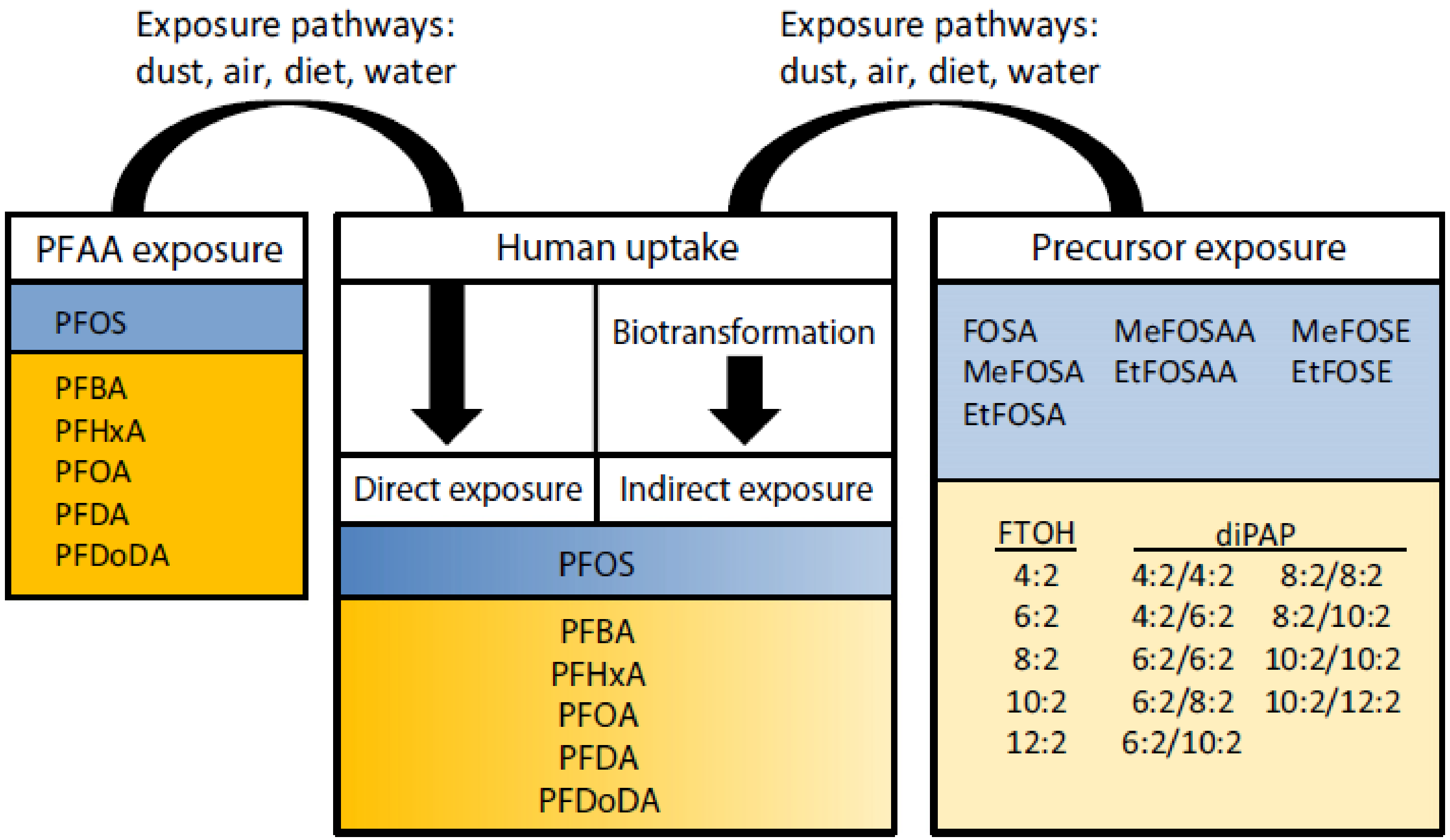

Fig. 1. Schematic of direct and indirect (precursor) exposure pathways for PFOS and PFCAs.

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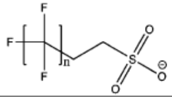
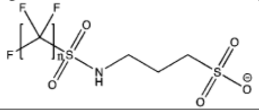
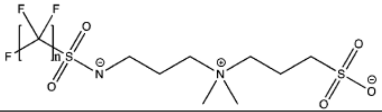
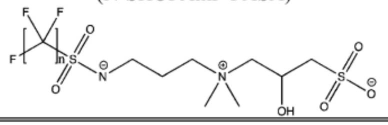
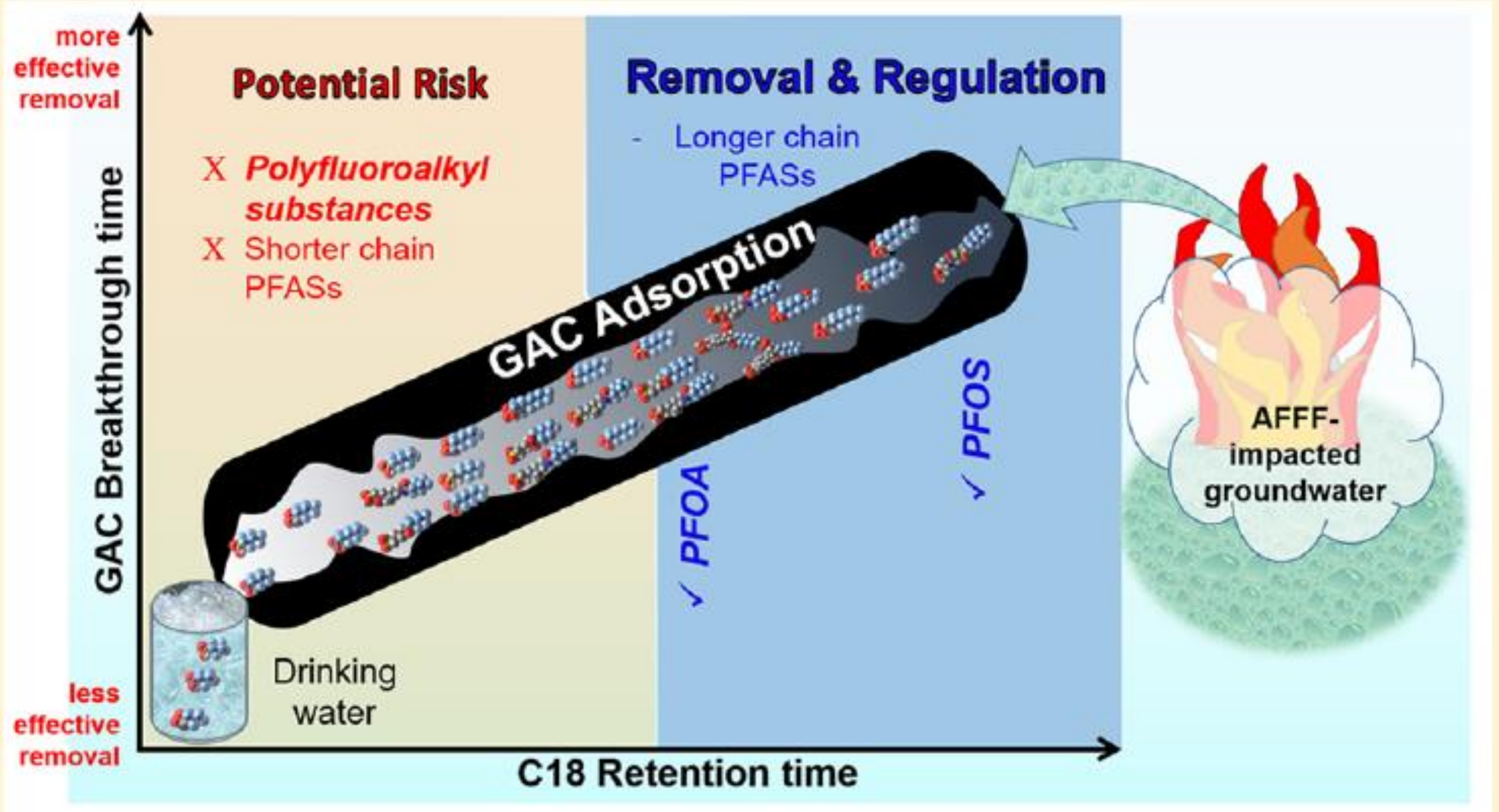
Xin Xiao,[†,‡,§] Bridget A. Ulrich,[‡] Baoliang Chen,[†,§] and Christopher P. Higgins*,[‡]

Fluorotelomer sulfonate (FtS) 
N-sulfopropyl perfluoroalkanesulfonamide (N-SP-FASA) 
N-sulfopropyl dimethylammoniopropyl perfluoroalkane sulfonamide (N-SPAmP-FASA) 
N-sulfohydroxypropyl dimethylammonio propyl perfluoroalkane sulfonamide (N-SHOPAmP-FASA) 



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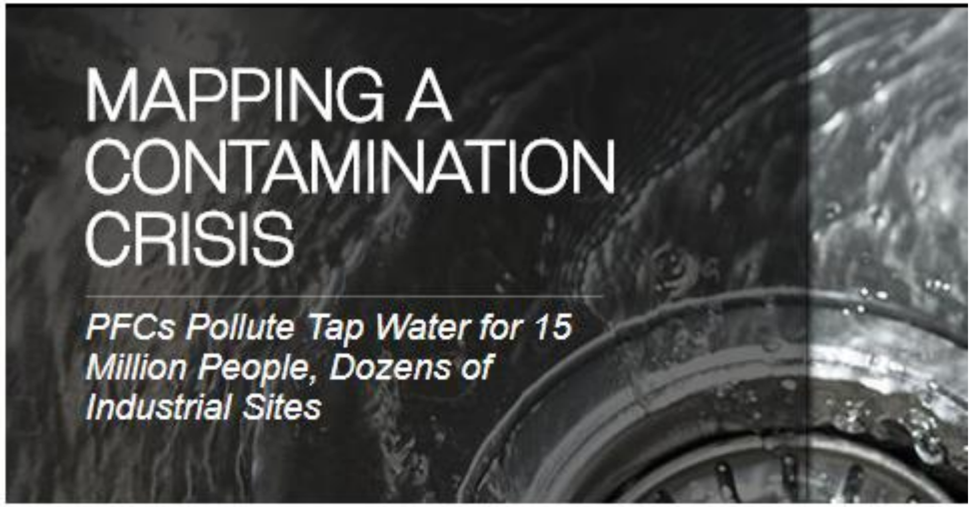

THURSDAY, JUNE 8, 2017

Bill Walker, Managing Editor, and Soren Rundquist, Director of Spatial Analysis

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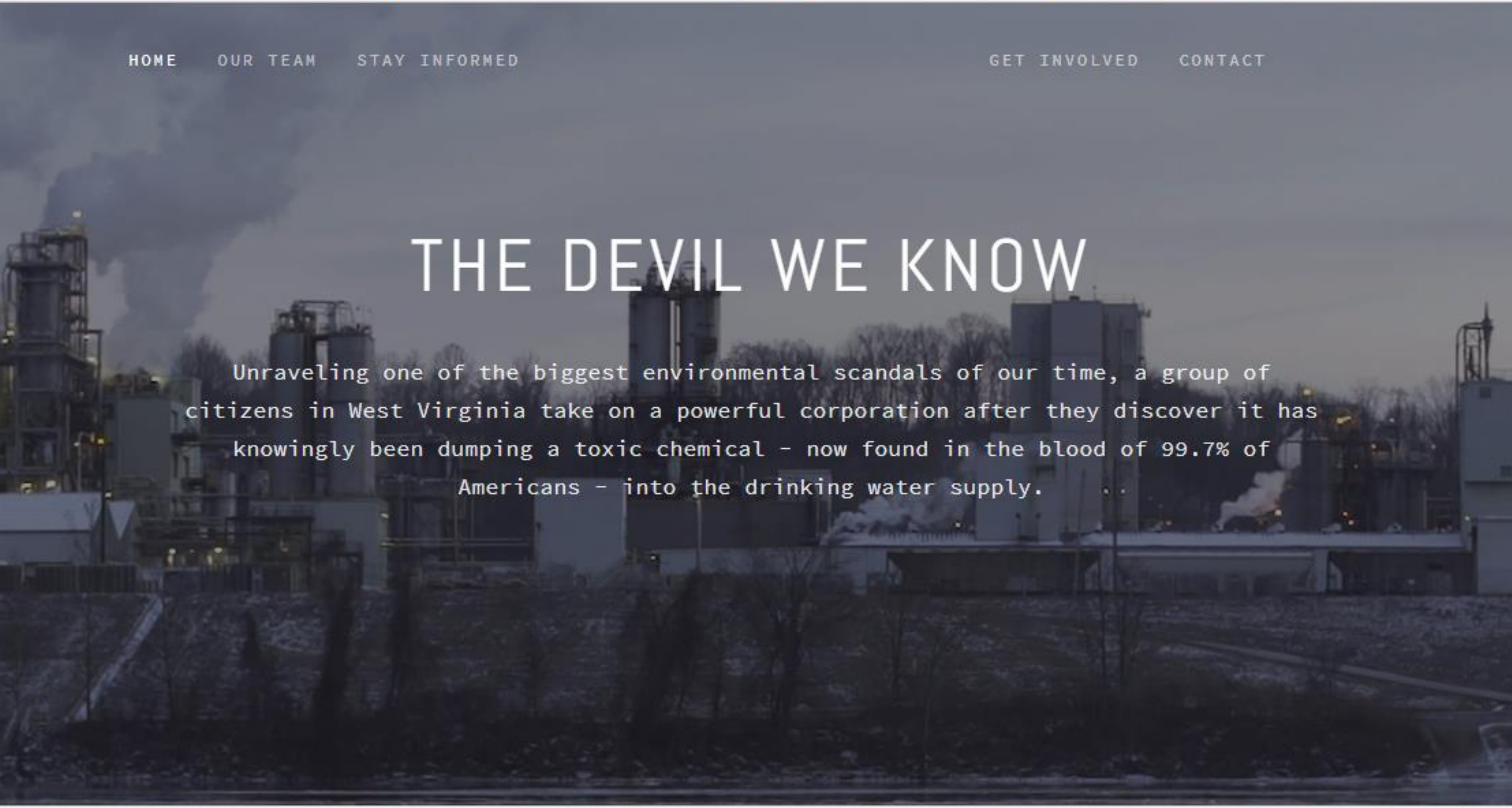
MAPPING A CONTAMINATION CRISIS

PFCs Pollute Tap Water for 15 Million People, Dozens of Industrial Sites

The known extent of the contamination of U.S. communities with PFCs – highly fluorinated toxic chemicals, also known as PFASs,[*] that have been linked to cancer, thyroid disease, weakened immunity and other health problems – continues to expand with no end in sight. New research from EWG and Northeastern University in Boston details PFC pollution in tap water supplies for 15 million Americans in 27 states and from more than four dozen industrial and military sources from Maine to California.

EWG and the **Social Science Environmental Health Research Institute** at Northeastern collaborated to produce an **interactive map** that combines federal drinking water data and information on all publicly documented cases of PFAS pollution from manufacturing plants, military air bases, civilian airports and fire training sites.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Unraveling one of the biggest environmental scandals of our time, a group of citizens in West Virginia take on a powerful corporation after they discover it has knowingly been dumping a toxic chemical - now found in the blood of 99.7% of Americans - into the drinking water supply.

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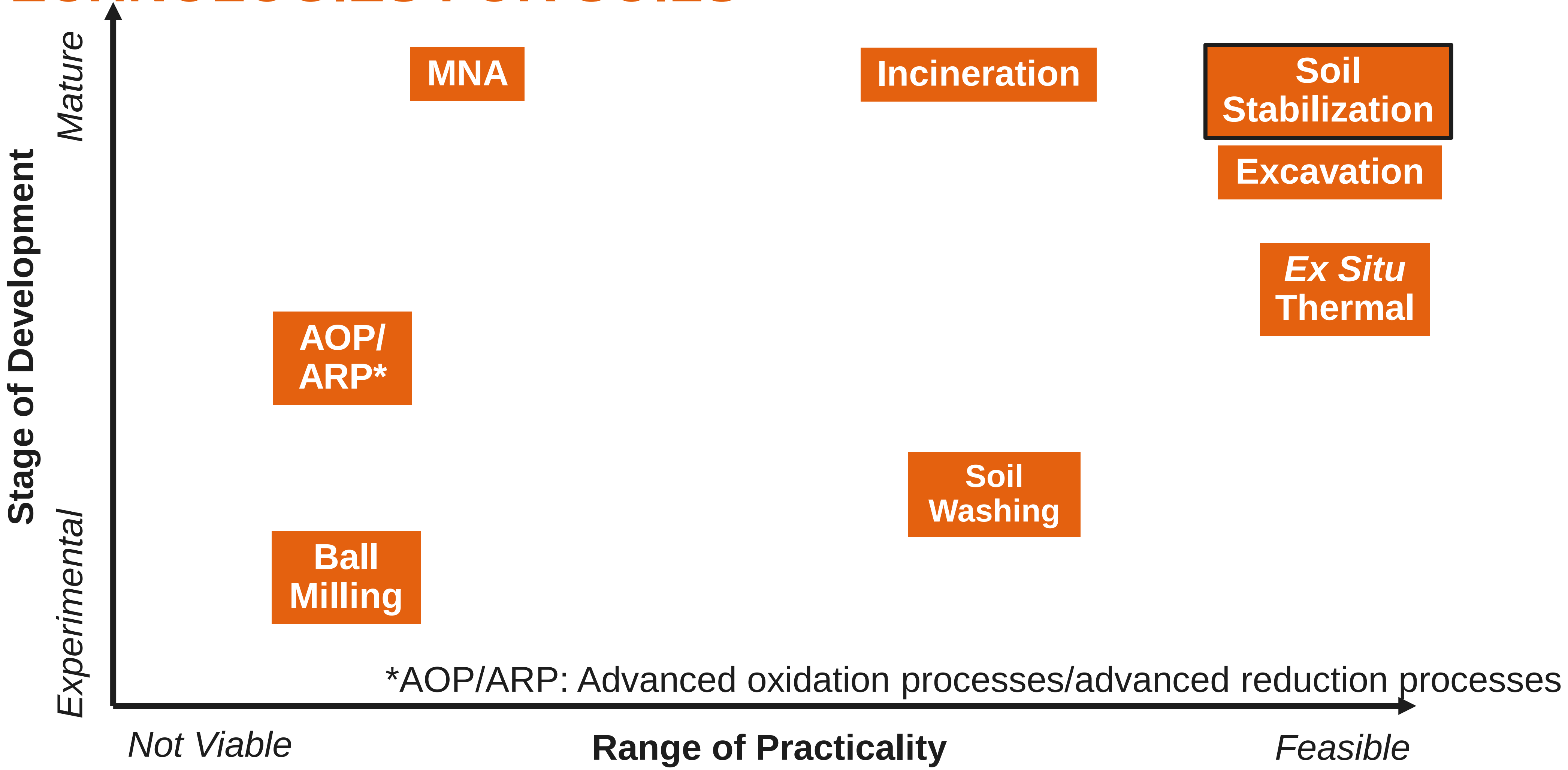
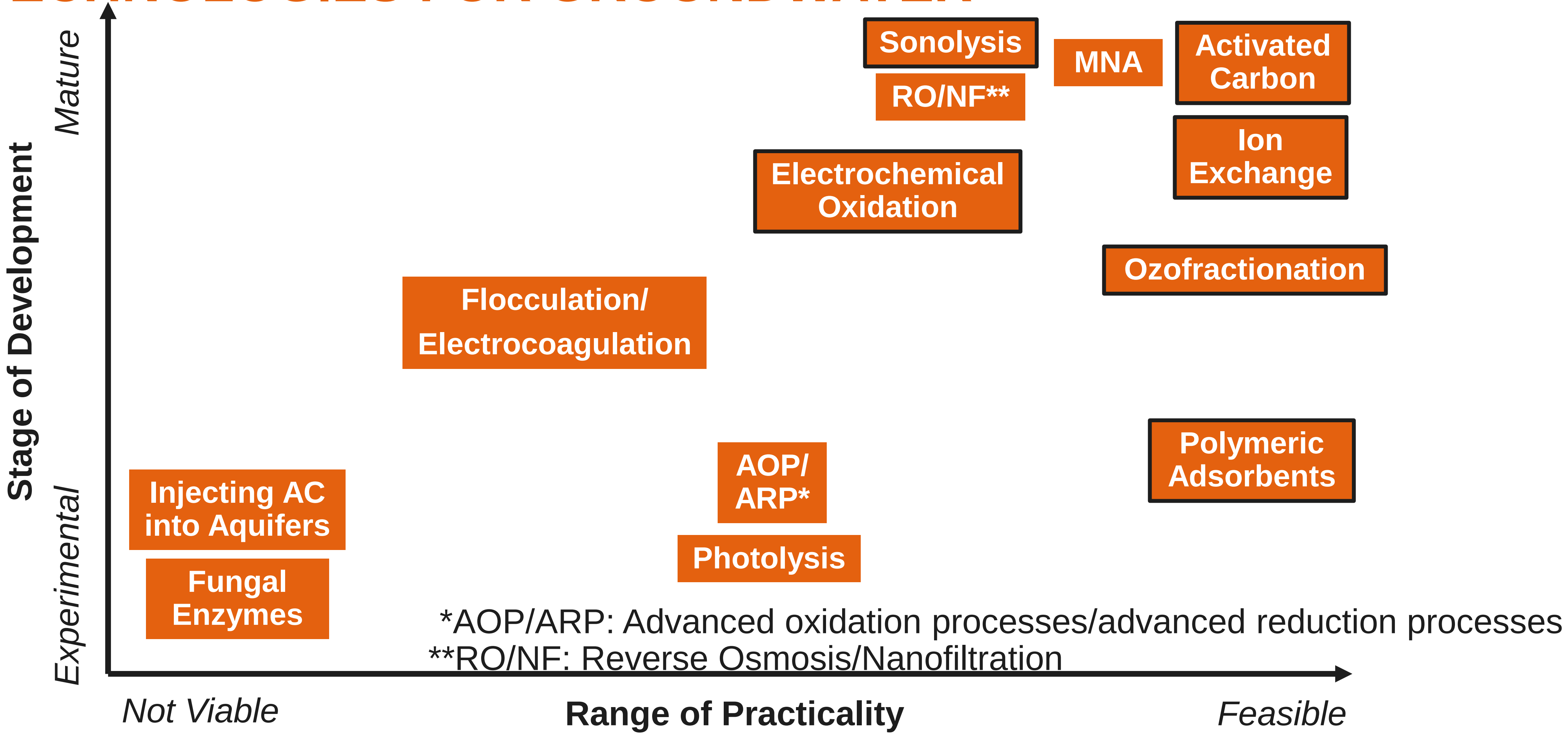
DEVELOPMENT AND PRACTICALITY: PFAS TREATMENT TECHNOLOGIES FOR SOILS



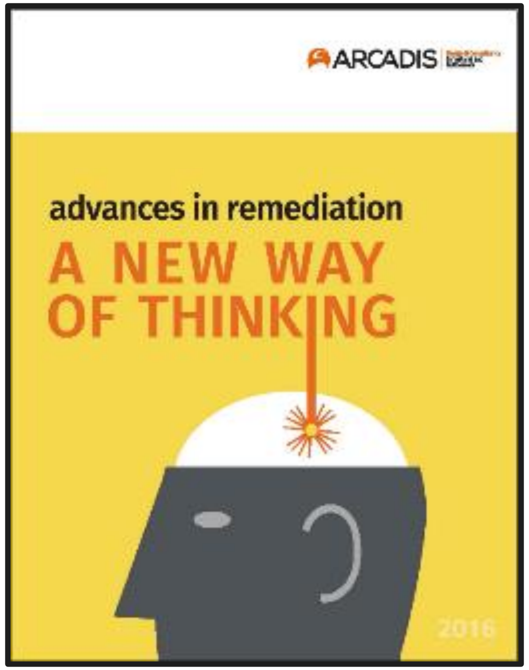
DEVELOPMENT AND PRACTICALITY: PFAS TREATMENT TECHNOLOGIES FOR GROUNDWATER

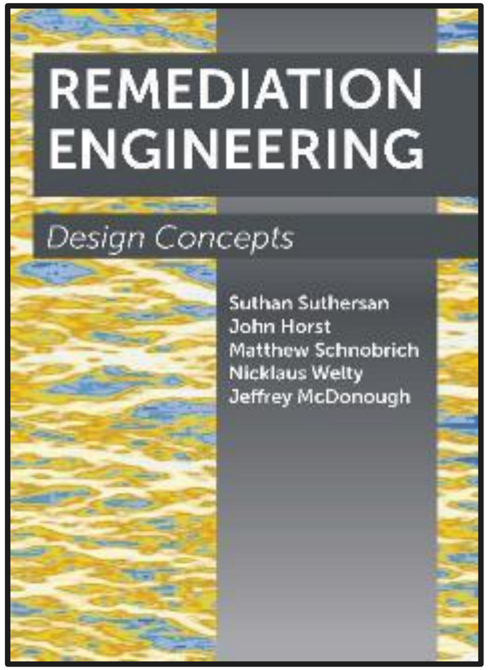


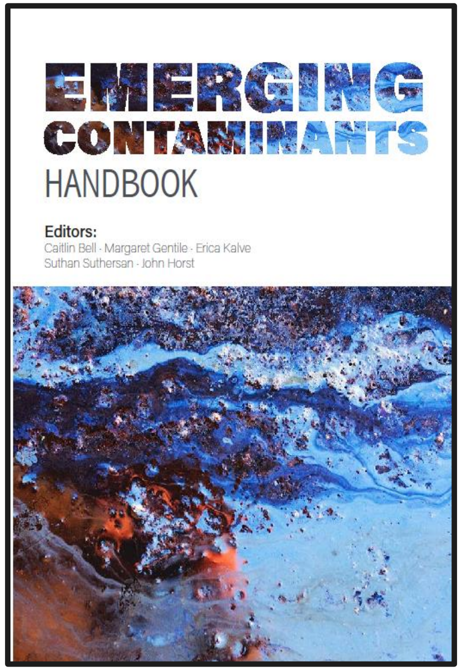
Summary

- PFAS do not biodegrade (mineralise) but biotransform to PFAAs as dead-end daughter products
- Regulations surrounding PFAS are evolving with lowering drinking water standards and a focus on increased interest in additional PFAAs
- PFAA precursor mass and multiple PFAAs likely accompany PFOS & PFOA in sources and plumes –depending on exact nature of source material
- Analysis of just PFAA's may significantly underrepresent the actual PFAS mass
- Technologies are evolving for ingenious remediation approaches

Recent Publications







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