THE EMERGING ISSUE

PER- & POLYFLUOROALKYL SUBSTANCES (PFASs)

Big Picture, Challenges and Solutions

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Global PFASs Lead
Arcadis

PFASs

ARCADIS Design & Consultancy for natural and built assets

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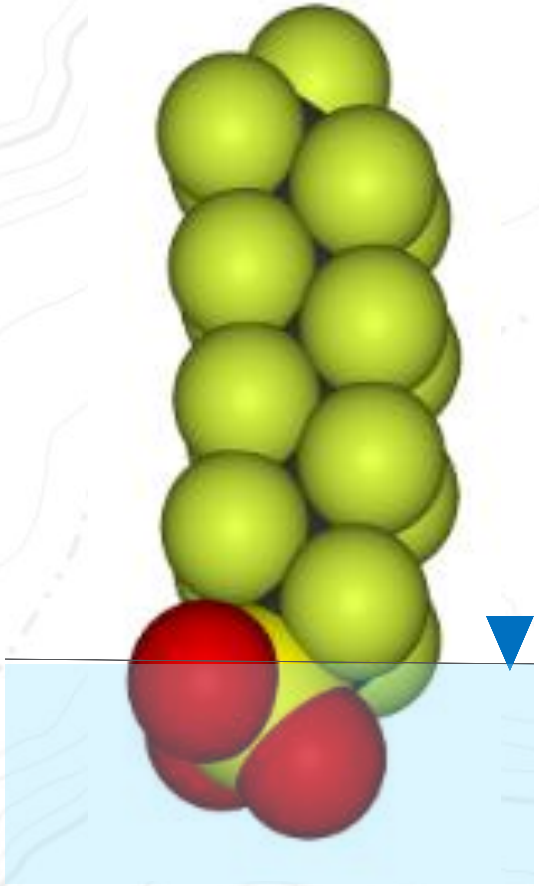
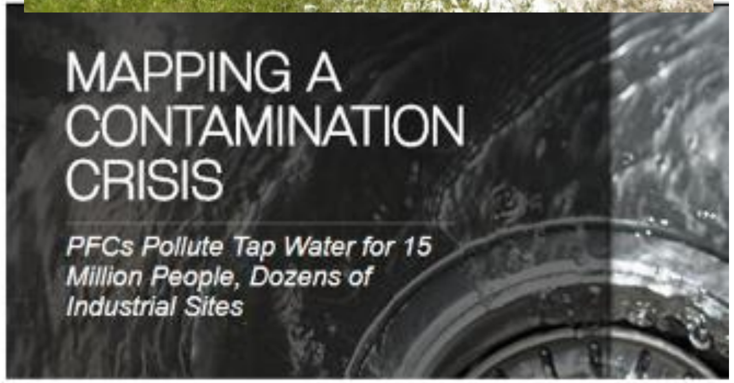




PFASs

PFASs Introduction

PFAS comprises many thousands of compounds –multiple sources

Advanced analytical methods are being adopted to measure PFAS

PFAS are impacting drinking water worldwide

None of the PFASs biodegrade, some biotransform to daughter compounds that are extremely persistent

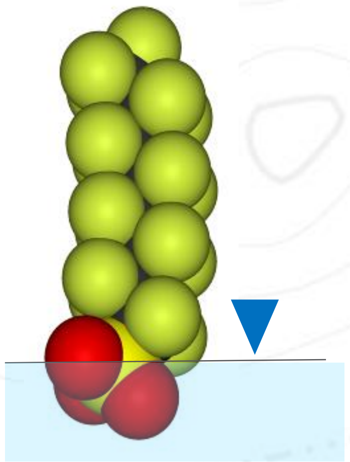
Some PFAS are classed as persistent organic pollutants

Dramatically increasing regulatory concern

PFASs

Unique Characteristics of PFASs

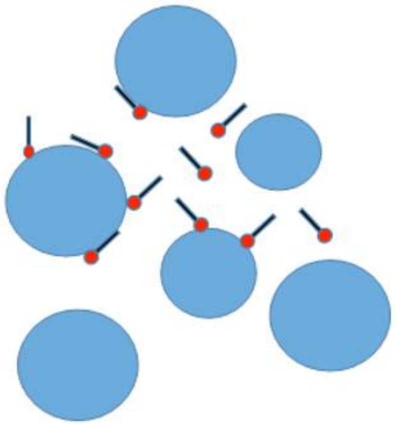
Longer chain PFASs stick their tails in the air -the longer perfluoroalkyl chains migrate to the gas:liquid interface, so stratify in solution



PFASs bioaccumulate via interaction with proteins (not fats) -PFASs bind to β–lipoproteins, as mistaken for fatty acids

PFASs tend to be soluble in water -PFASs can be very mobile in the environment as water soluble, unlike most other POPs.

Long chain PFASs are initially excreted in humans then reabsorbed -humans have one the highest levels of renal reabsorption so fail to excrete long chain PFASs, whereas monkeys, mice and rats can excrete at faster rates

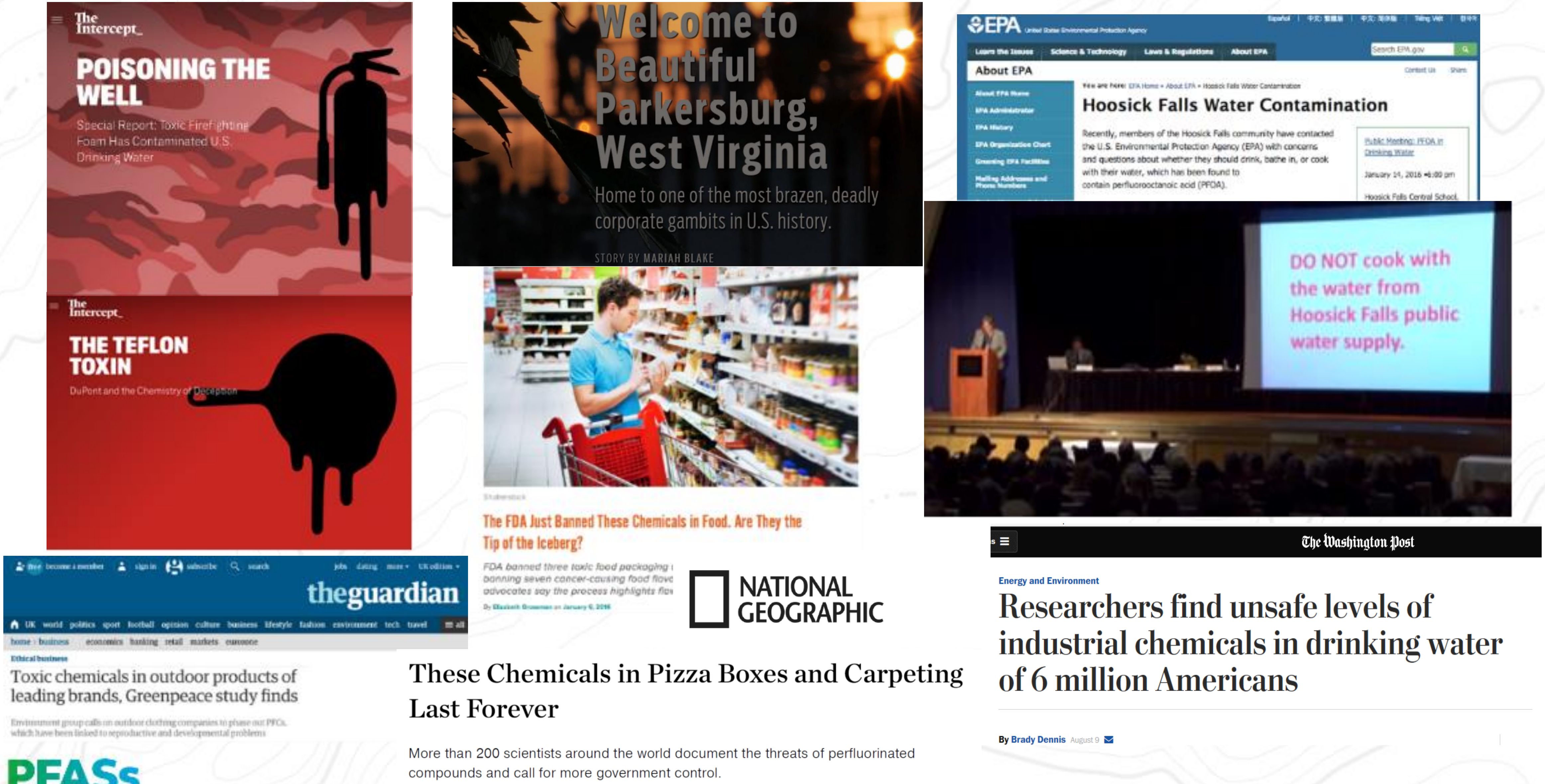


PFASs tend to stick together -long chain PFAAs have been identified as layers on surfaces agglomerating by via "molecular brush"

Increased concentrations of PFAAs observed at WWTP outflow vs inlet – PFAA precursosrs are transformed in municipal / biological / oxidative treatment processes

PFASs

PFAS News

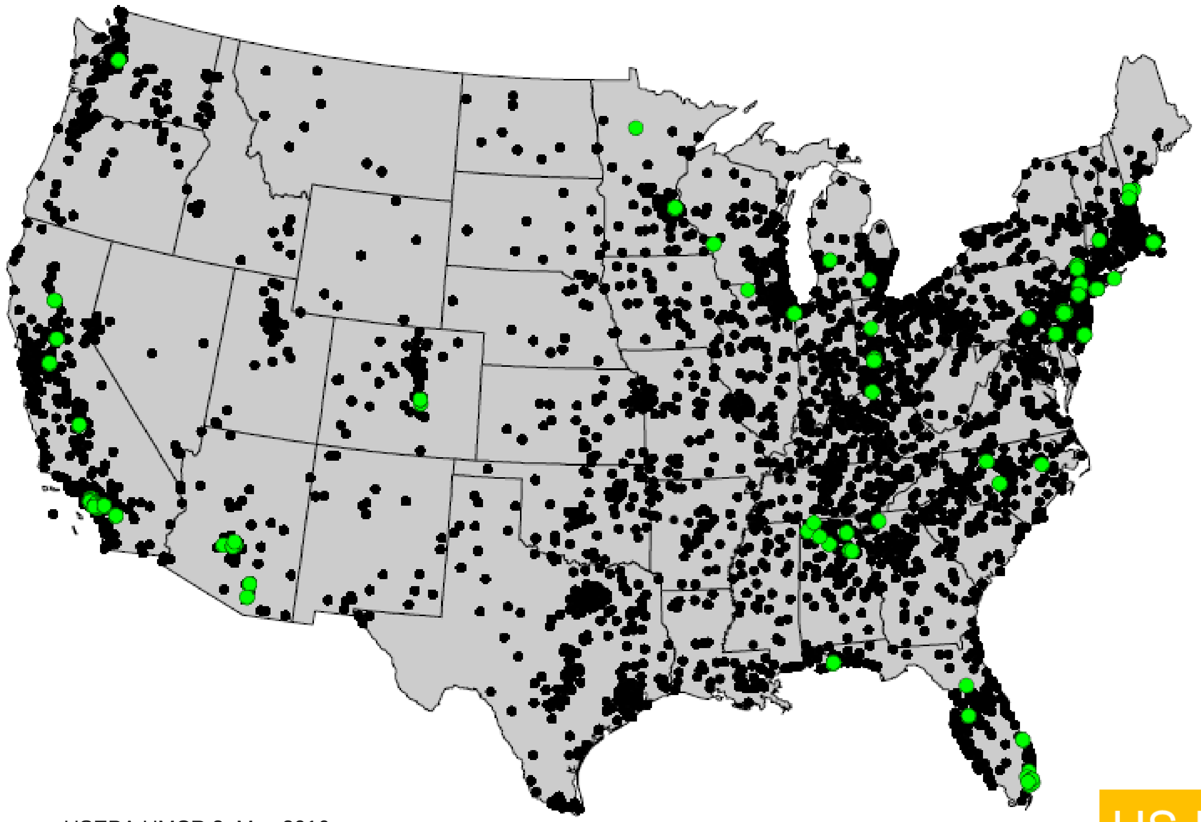


PFASs

Detections of PFAS in drinking water has caused spiraling regulatory concern

PUBLISHED MAY 1, 2015

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 |

The Intercept_

WITH NEW EPA ADVISORY, DOZENS OF COMMUNITIES SUDDENLY HAVE DANGEROUS DRINKING WATER

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-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

Detected in ~ 2% of large public water supplies

ChemicalWatch
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US ATSDR releases 'suppressed' PFAS tox profile

Study confirms EPA guidelines 'woefully underestimate risk', says NGO

21 June 2018 / PFCs, Toxicology, United States

The US Agency for Toxic Substances and Disease Registry has released a controversial draft toxicological profile on four per- and polyfluoroalkyl substances (PFASs). The move comes amid uproar over allegations that other federal agencies were suppressing its release.

Last month, internal EPA emails released under a public records request showed concern that the ATSDR was planning to publish a study with minimal risk levels (MRLs) for the PFASs far below those set by the EPA. One White House staffer feared this would result in a "public relations nightmare".

ATSDR
AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY

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http://www.nytimes.com/2016/01/10/magazine/the-lawyer-who-became-duponts-worst-nightmare.html?_r=0

TIME

IDEAS LAW

Erin Brockovich: It's Not Just Flint—America Has a Scary Water Problem

Erin Brockovich and Ken Cook Feb. 8, 2016

Erin Brockovich is a consumer advocate, and Ken Cook is president of the Environmental Working Group.

We must reform our broken chemical laws to prevent more tragedies

Most Americans take our drinking water for granted: turn the tap, fill a glass and drink. Only when a community's health and safety are imperiled do we pay heed to the threat of industrial chemicals in our water supplies. The grave

INVESTIGATION

Toxic Secrets: Where the sites with PFAS contamination are near you

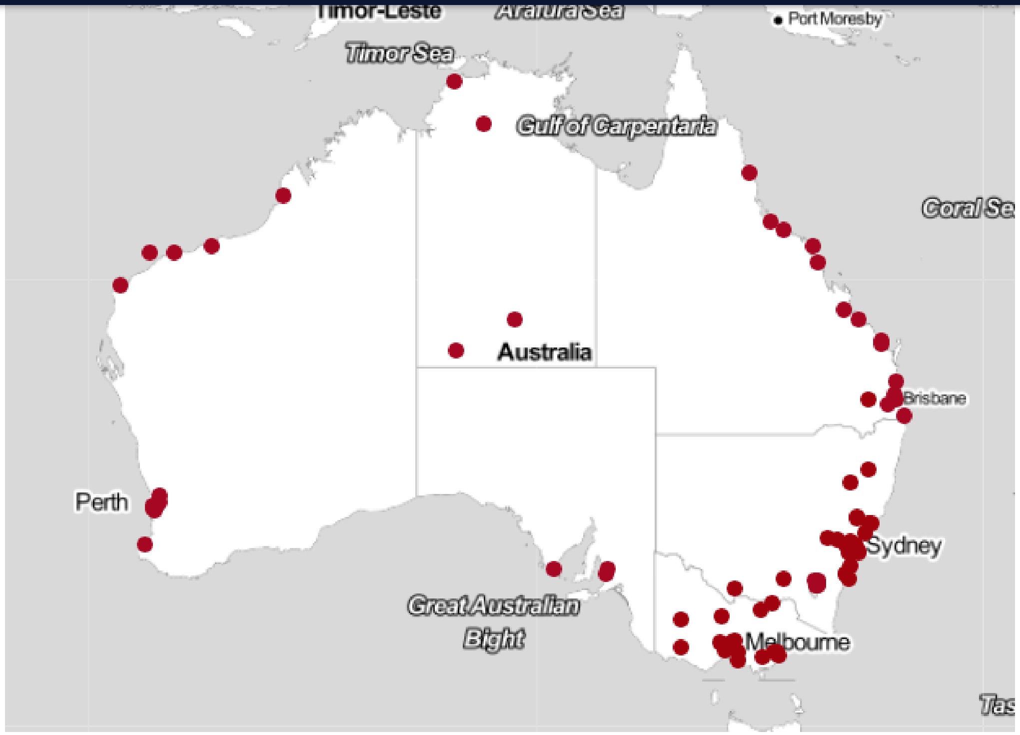
By Carrie Fellner & Patrick Begley

17 JUNE 2018

Sites under investigation

At least 90 sites across Australia are under investigation for elevated levels of per- and poly-fluoroalkyl [PFAS] chemicals.

The Sydney Morning Herald



Leaflet | Map tiles by Stamen Design, under CC BY 3.0. Data by OpenStreetMap, under CC BY SA.

https://www.smh.com.au/world/north-america/toxic-secrets-the-town-that-3m-built-where-kids-are-dying-of-cancer-20180613-p4zl83.html
https://www.smh.com.au/national/report-into-toxic-chemicals-finds-pfas-worse-than-thought-20180621-p4zmy8.html
https://www.smh.com.au/lifestyle/health-and-wellness/toxic-secrets-professor-bragged-about-burying-bad-science-on-3m-chemicals-20180615-p4zlsc.html
https://www.smh.com.au/national/nsw/toxic-secrets-where-the-sites-with-pfas-contamination-are-near-you-20180616-p4zlxc.html

PFASs

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Toxic firefighting chemicals 'the most seminal public health challenge'

US environmental official says Pfas chemicals found in firefighting foam is contaminating water supplies

Christopher Knaus

@knausc

Wed 18 Oct 2017 00.52 EDT

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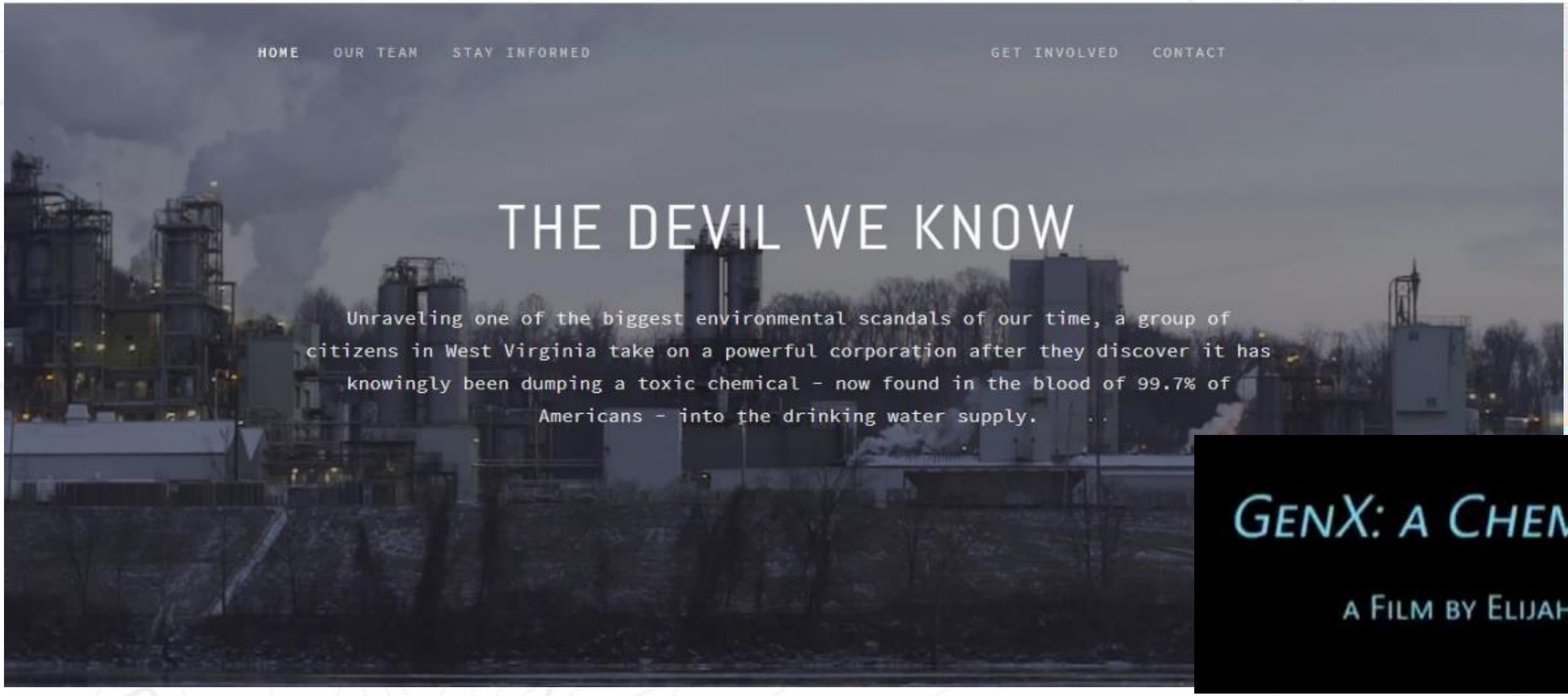
CDC Centers for Disease Control and Prevention
CDC 24/7: Saving Lives, Protecting People™

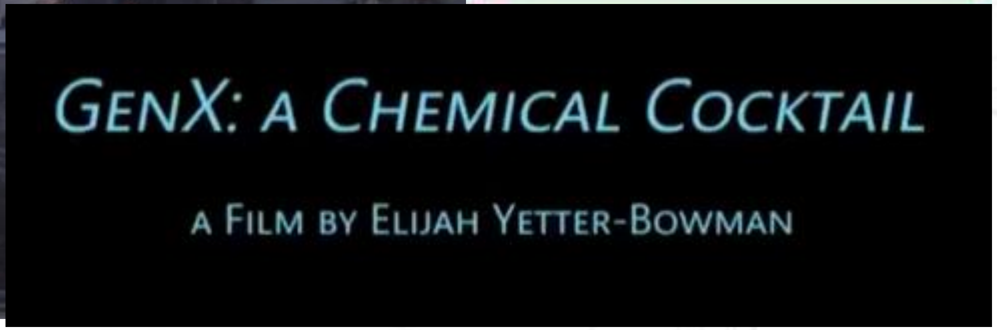
Patrick Breysse, Director of the CDC's National Centre for Environmental Health, described the chemicals as "one of the most seminal public health challenge for the next decades"

Breysse estimated 10 million Americans were currently drinking contaminated water.

He said soon "we think that hundreds of millions of Americans will be drinking water with levels of these chemicals above levels of concern"

Coming Soon…





https://www.thedevilweknow.com/

https://www.genxthefilm.org/

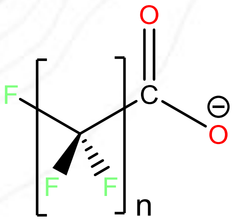
PFASs

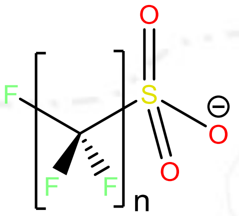
Perfluoroalkyl Acids (PFAAs)

- **Perfluoroalkyl acids (PFAAs)** previously termed Perfluorinated Compounds (PFCs) generally are the and include:
  - Perfluoralkyl carboxylates (PFCAs) e.g. PFOA
  - Perfluoroalkyl sulfonates (PFSAs) e.g. PFOS
  - Perfluoroalkyl phosphinic acids (PFPiS); perfluoroalkyl phosphonic acids (PFPAs)
  - Perfluoroalkyl ethers e.g. GenX
- There are many PFAAs with differing chain lengths (generally C1-C18)

Perfluoroalkyl acid naming references the number of fluorinated (n) carbons

C1	Methane
C2	Ethane
C3	Propane
C4	Butane
C5	Pentane
C6	Hexane
C7	Heptane
C8	Octane
C9	Nonane
C10	Decane
C11	Undecane
C12	Dodecane





Perfluoroalkyl Carboxylates (PFCA)*

n=1	Perfluroethanoic acid (PFEtA)
n=2	Perfluoropropanoic acid (PFPrA)
n=3	Perfluorobutanoic acid (PFBA)
n=4	Perfluoropentanoic acid (PFPeA)
n=5	Perfluorohexanoic acid (PFHxA)
n=6	Perfluoroheptanoic acid (PFHpA)
n=7	Perfluorooctanoic acid (PFOA)
n=8	Perfluorononanoic acid (PFNA)
n=10	Perfluorodecanoic acid (PFDA)
n=11	Perfluoroundecanoic acid (PFUdA)
n=12	Perfluorododecanoic acid (PFDoA)

Perfluoroalkyl Sulfonates (PFSA)

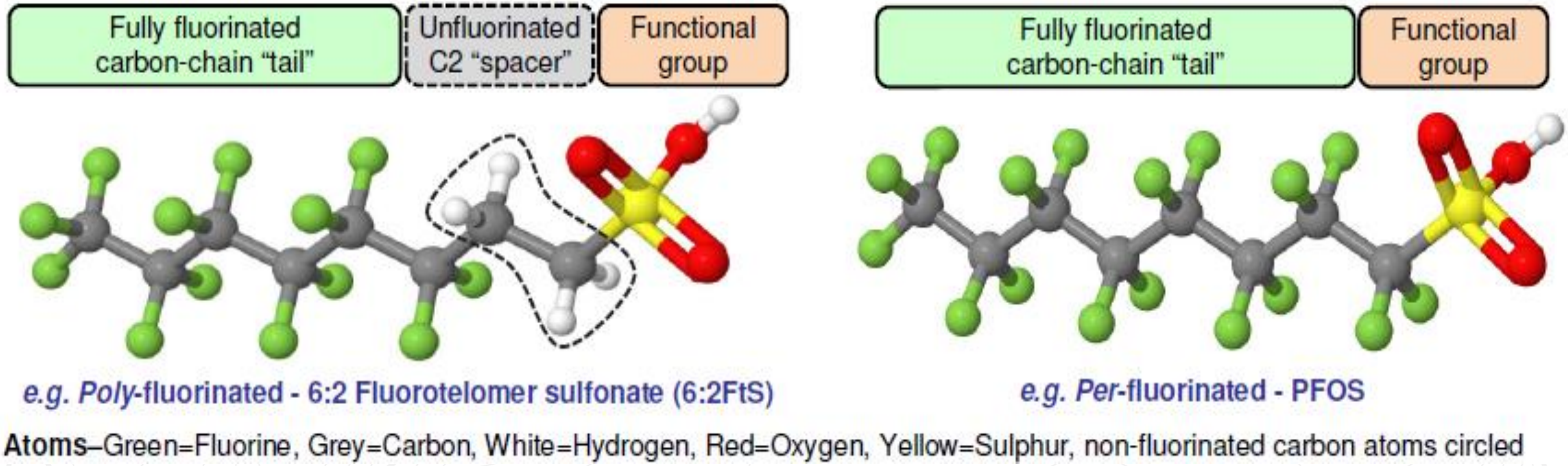
n=1	Perfluoromethanesulfonic acid (PFMeS)
n=2	Perfluoroethanesulfonic acid (PFEtS)
n=3	Perfluoropropanesulfonic acid (PFPrS)
n=4	Perfluorobutanesulfonic acid (PFBS)
n=5	Perfluoropentanesulfonic acid (PFPeS)
n=6	Perfluorohexanesulfonic acid (PFHxS)
n=7	Perfluoroheptanesulfonic acid (PFHpS)
n=8	Perfluorooctanesulfonic acid (PFOS)
n=9	Perfluorononanesulfonic acid (PFNS)
n=10	Perfluorodecanesulfonic acid (PFDS)
n=11	Perfluoroundecansulfonic acid (PFUdS)
n=12	Perfluorododecansulfonic acid (PFDoS)

* The final carbon atom in PFCA's unlike in PFSA's is part of the head group and not fluorinated.

PFAAs totally resist biodegradation – are ultra-persistent

PFASs

Polyfluorinated Compounds – PFAA Precursors



PFASs

https://www.ehp.qld.gov.au/assets/documents/regulation/firefighting-foam-policy-notes.pdf

https://www.ehp.qld.gov.au/assets/documents/regulation/firefighting-foam-policy.pdf

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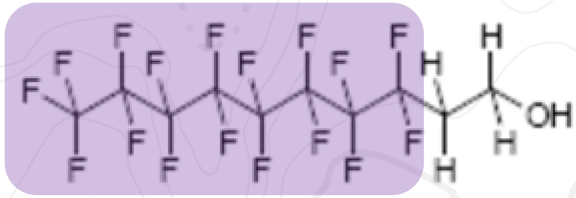
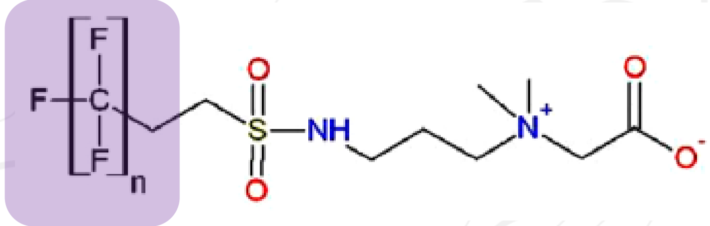
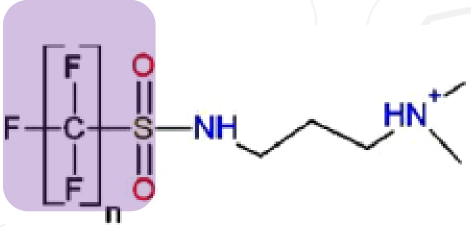
Perfluoroalkyl group –the forever functional group



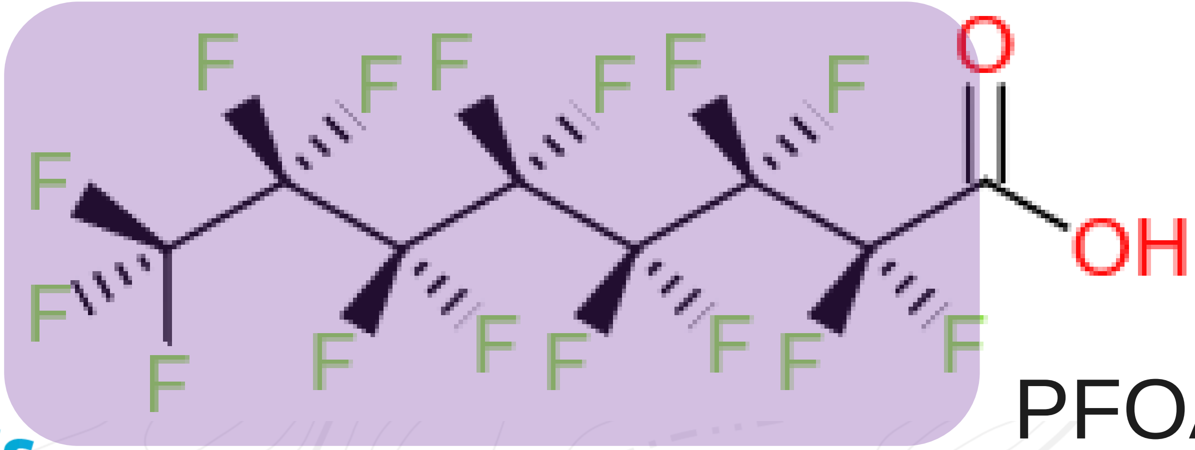
Fluorotelomer alcohol, 8:2 FTOH



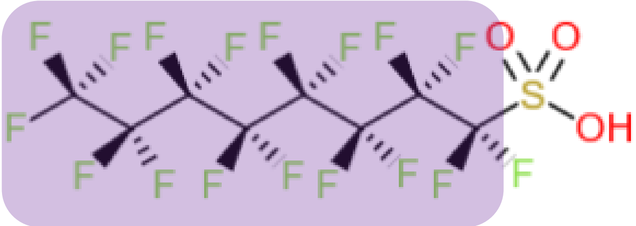
Fluorotelomer Sulfonamido Betaines



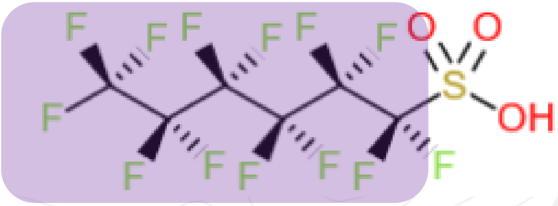
Perfluoroalkyl Sulfonamido Amines



PFOA



PFOS



PFHxS

PFASs

Poly- and Perfluoroalkyl Substances (PFASs)

More Commonly Regulated

Polyfluorinated compounds (~5,000 compounds)

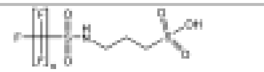
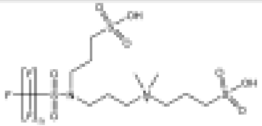
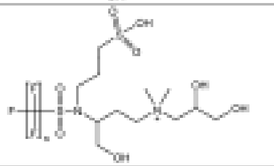
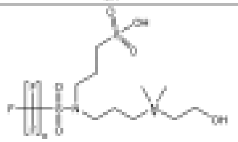
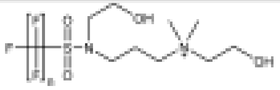
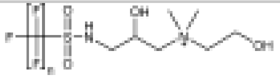
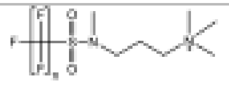
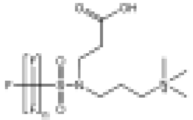
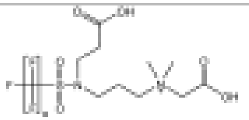
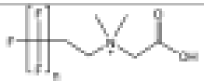
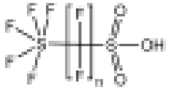
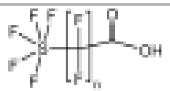
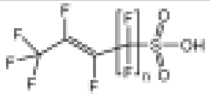
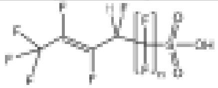
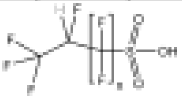
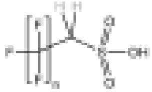
Perfluorinated Compounds (PFCs) aka Perfluoroalkyl Acids (PFAAs)
~25 common individual compounds but ~100's compounds
PFOS ,PFOA, PFHxS, PFBA, GenX

Microbial / Higher Organism Biotransformation

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[*,#]

Class Number	Structure	n[a,b]	Acronym[c]	Confidence Level[d,e]	AFFF/CP Found In
1		3-6	N-SP-FASA	2b	B, C
2		3-8	N-SPAmP-FASA	2b	A, B, C, F
3		3-9	N-SHOPAmP-FASA	3[f]	C, D, E, F, G
4		4-6	N-SPHOEAmP-FASA	3	B, C
5		3-8	N-SPAmP-FASAPS	2b	A, B, C
6		3-6	N-diHOPAmHOB-FASA	3	B, C, O
7		2-6	N-diHOPAmHOB-FASAPS	3	A, B, C
8		2-8	N-HOEAmP-FASAPS	2b	A, B, C
9		2-8	N-HOEAmP-FASE	2b	A, B, C, D, E
10		4-6	N-HOEAmHOP-FASA	3	B, C
11		2-8	N-HOEAmP-FASA	2b	A, B, C, D, E
12		4-8	N-TAmP-N-MeFASA	3	B
13		3-8	N-TAmP-FASA	3	A, B, C, D, E, F, G
14		3-6	N-TAmP-FASAP	3	D, E, F, G
15		4-6	N-CMAmP-FASAP	2b	D, E, F, G
16		3-6	N-CMAmP-FASA	2b	D, E, F, G
17		6, 8, 10	CMAmE-FA	2b	L
18		4, 6, 8	CMAmB-FA	3	L
19	$C_{n+4}H_{10}O_3SN_2F_{2n+1}$	6, 8, 10	Not applicable	4	I, J
20	$C_{n+10}H_{20}O_5SN_2F_{2n+1}$ or $C_{n+10}H_{18}O_5SN_2F_{2n+1}$	Unknown	Not applicable	5	I, J
21		3-9	n-FSS-PFAS	2b	A, B, C, D, E, G, M, N
22		6-8	n+/-FSS-PFAA[f]	3	M, N
23	 Multiple isomers possible	1-10	UPFAS[g,h]	3	A, B, C, D, E, M, N, P
24	 Multiple isomers possible	1-6	H-UPFAS[g,h]	3	A, B, C, D, E, F, G, M
25	 Multiple isomers possible	0[i]-8	H-PFAS[g,h]	3	A, B, C, D, E, F, G, M, N, P
26	 Multiple isomers possible	5, 7	x:1 PFAS[f,h]	3	A, B, C, D, E, F, G, M, N, P

PFASs

Digest AFFF precursors and measure the hidden mass: TOP Assay

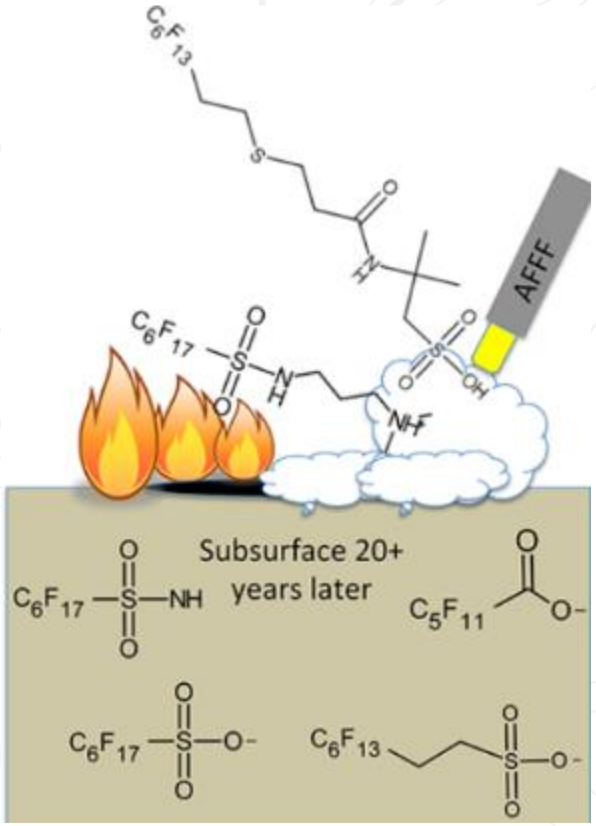
Microbes slowly make simpler PFAA's (e.g. PFOS / PFOA) from PFAS (PFAA precursors) over 20+ years

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



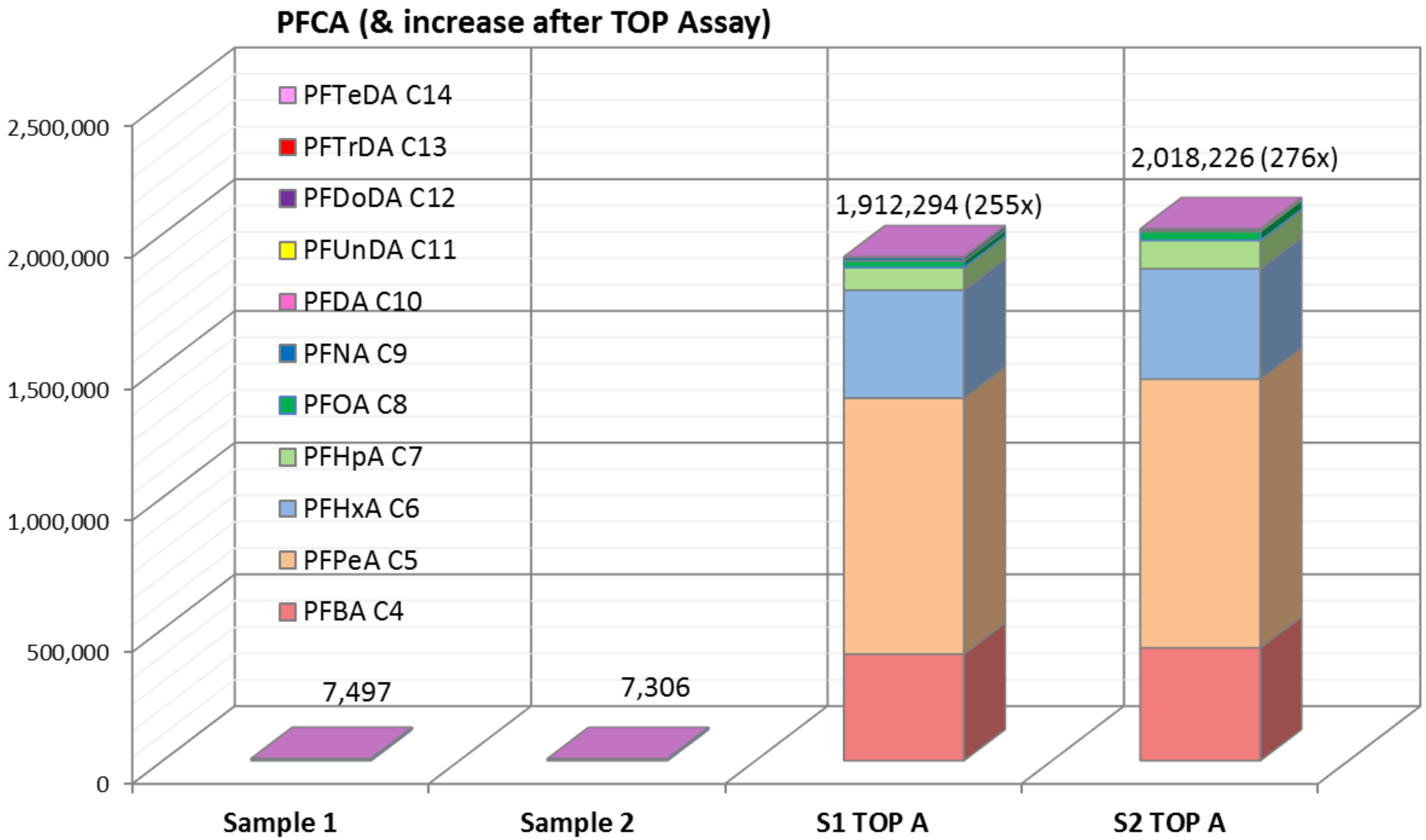
Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil

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

PFASs

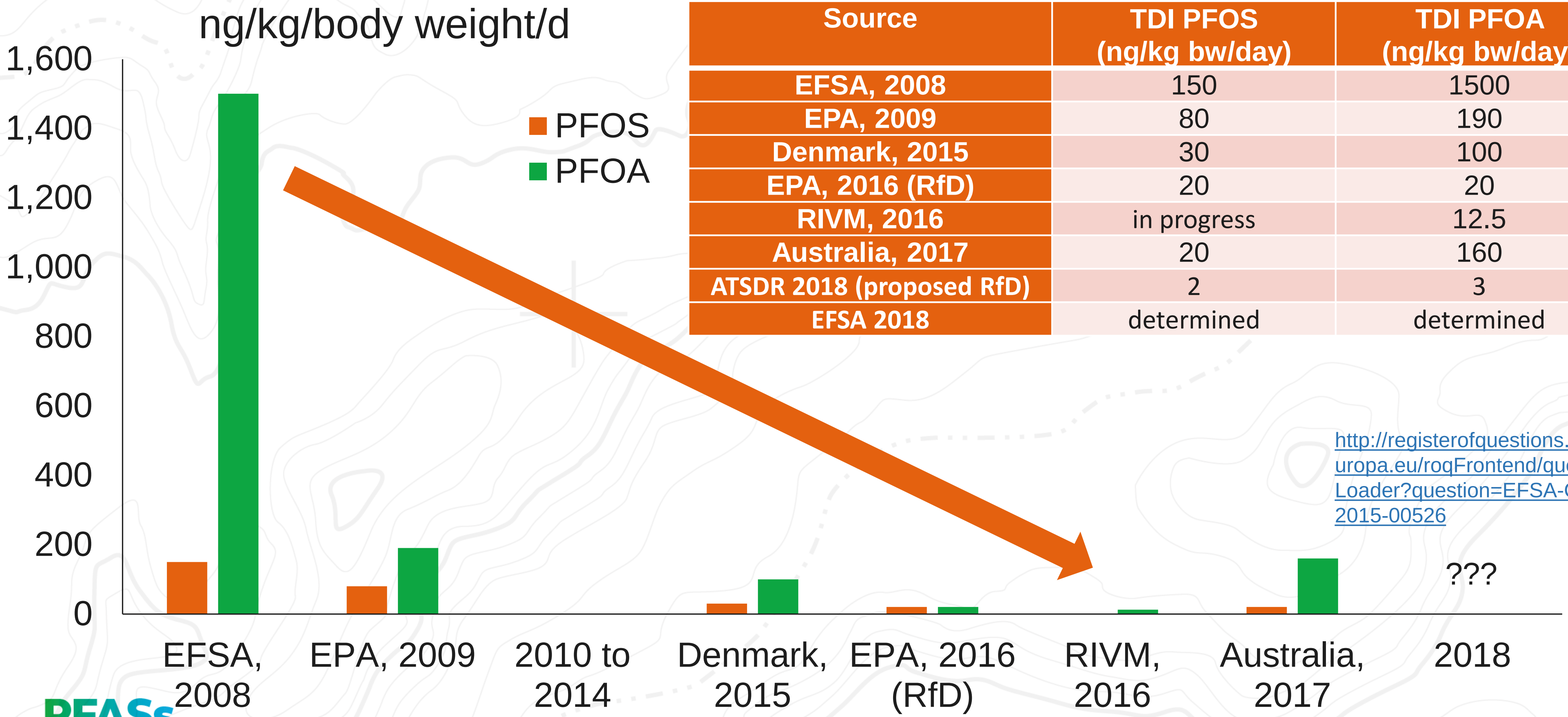
TOP Assay Applied to Surface Water from Recent C6 Fluorotelomer Foam Loss



Data Courtesy of Nigel Holmes Queensland DEHP

Aerobic Biotransformation Funnel: Conversion of Polyfluorinated Precursors to PFAAs

Tolerable Daily Intake (TDI)

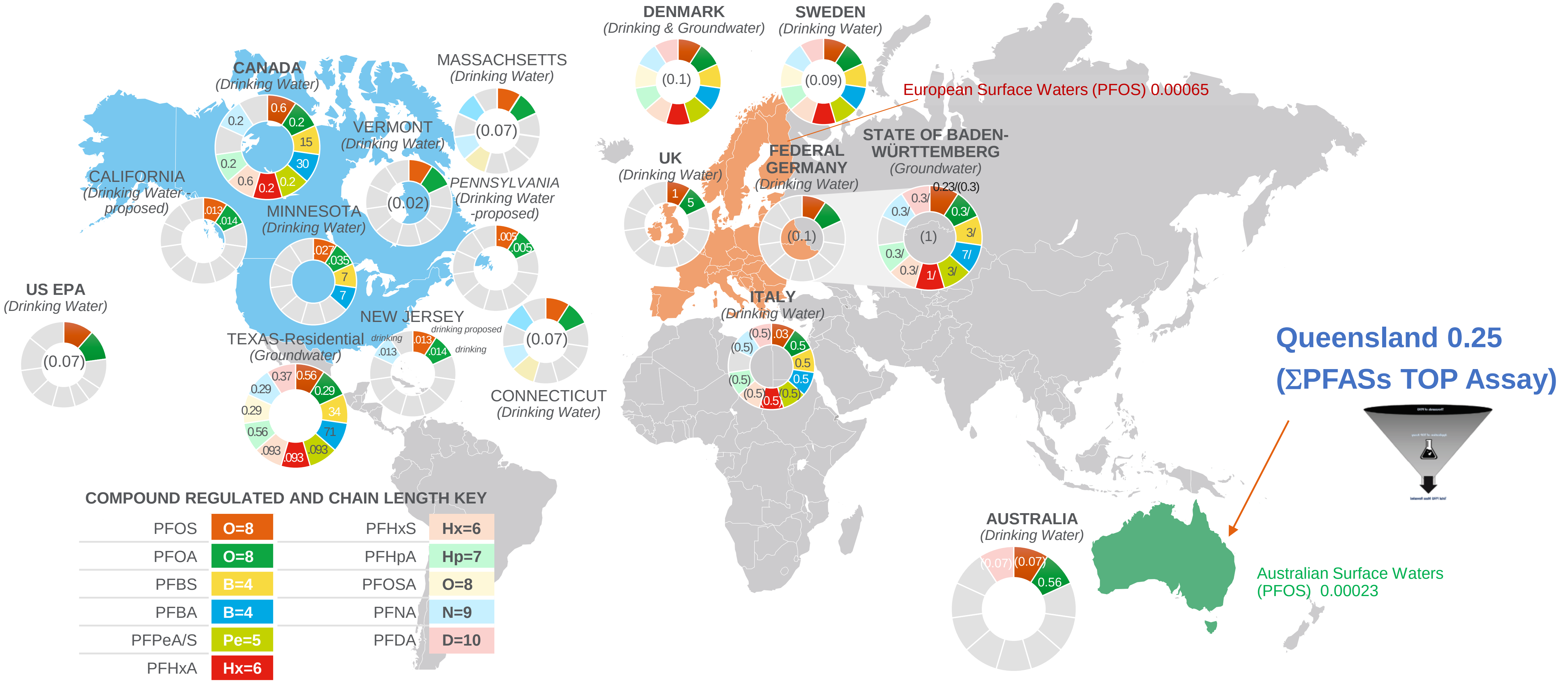


Source	TDI PFOS (ng/kg bw/day)	TDI PFOA (ng/kg bw/day)
EFSA, 2008	150	1500
EPA, 2009	80	190
Denmark, 2015	30	100
EPA, 2016 (RfD)	20	20
RIVM, 2016	in progress	12.5
Australia, 2017	20	160
ATSDR 2018 (proposed RfD)	2	3
EFSA 2018	determined	determined

http://registerofquestions.efsa.europa.eu/roqFrontend/questionLoader?question=EFSA-Q-2015-00526

PFASs

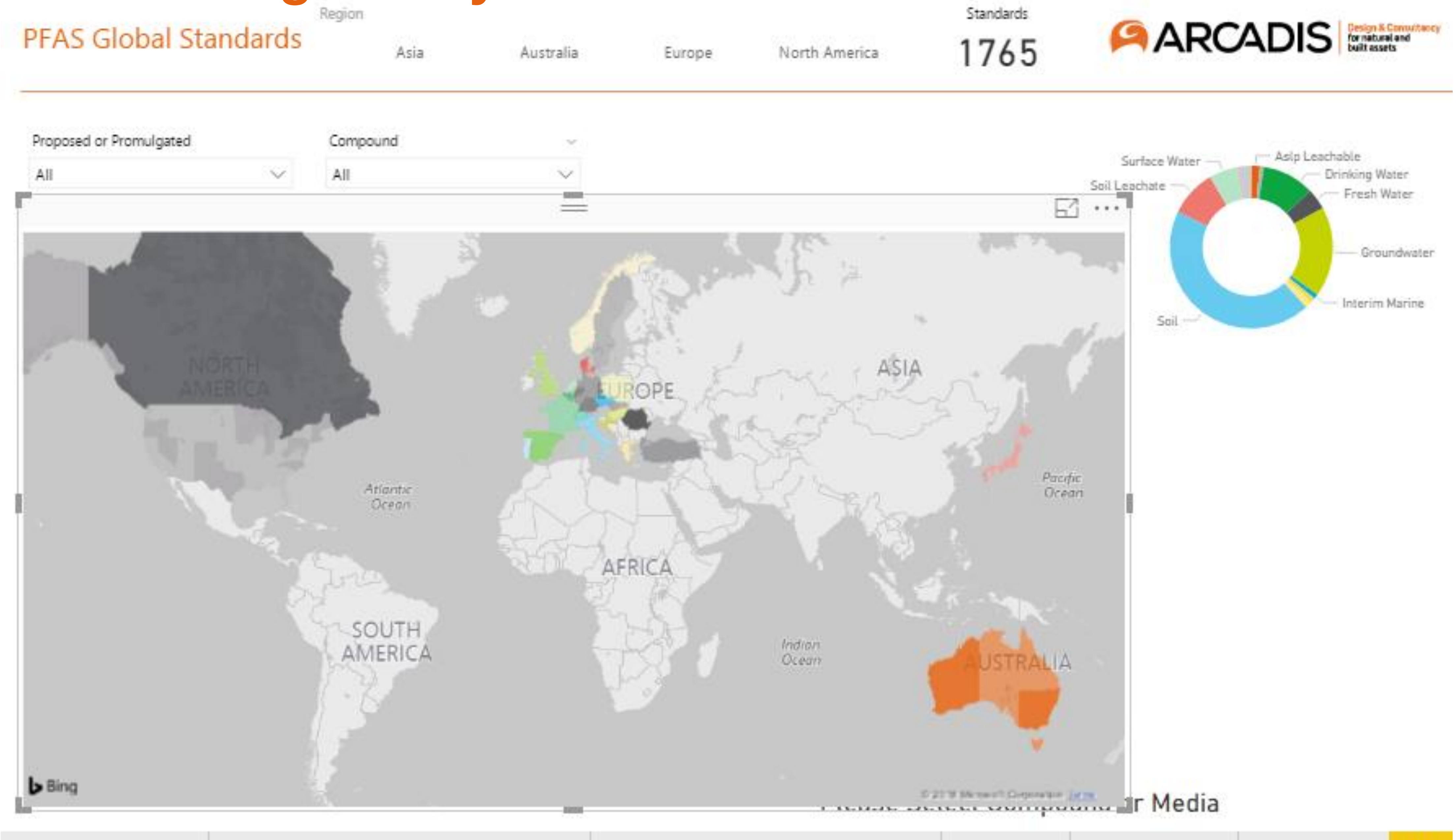
Evolving Regulatory PFAS Values



COMPOUND REGULATED AND CHAIN LENGTH KEY

PFOS	O=8	PFHxS	Hx=6
PFOA	O=8	PFHpA	Hp=7
PFBS	B=4	PFOSA	O=8
PFBA	B=4	PFNA	N=9
PFPeA/S	Pe=5	PFDA	D=10
PFHxA	Hx=6		

Global Regulatory PFAS Tracker



Human Exposure to PFASs

Long Chain Human Bioaccumulation Half Life:

PFHxS 8.5 years

PFOS 4.2 years

PFOA 3.8 years

Drinking Water
And Food

Main Exposure

House dust

Indoor air

Outdoor air

Consumer products

- Fluoropolymers inc. side chain polymers
- Fluorosurfactants
- Performance chemicals
- Product residuals

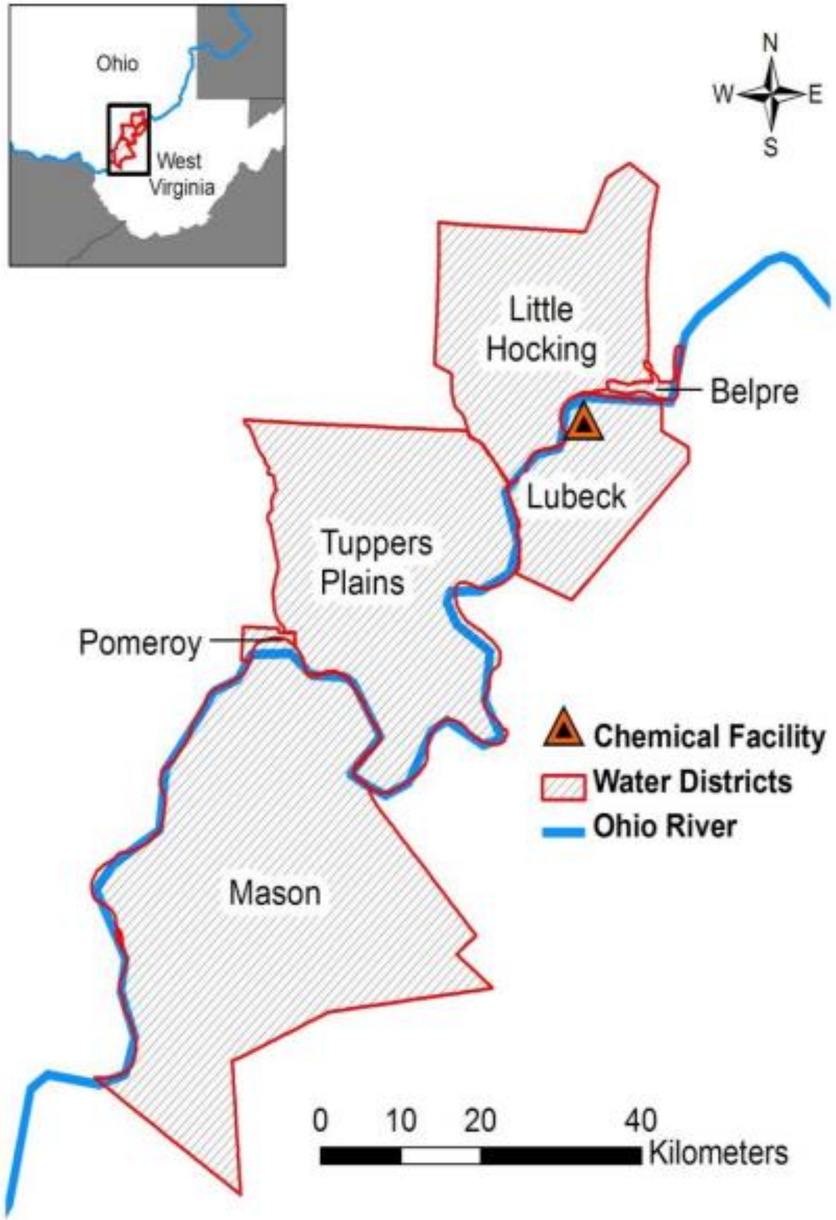
Precursor

PFAA

PFASs

C8 Science Panel

- Emissions from manufacturing plant had impacted groundwater used by municipal and private supplies
- Study commissioned by court as part of a class action against manufacturer
- Three epidemiologists studied links between PFOA and various health outcomes
- 55 health outcomes studied, 4 reports issued between 2011 and 2012.
- Information collected (69,030 individuals):
  - Blood biomarkers, 10 PFAA
  - Health questionnaire / medical records
- Study aim was to establish “Given available scientific evidence, is it more probable than not that a connection is present between C8 (PFOA) exposure and disease?”



PFASs

C8 Science Panel - Findings

- Study found mean PFOA levels of 82.9 ng/L and PFOS levels of 23.6 ng/L in serum samples.
- Probable links were identified for 6 of the 55 health outcomes.

Probable Link

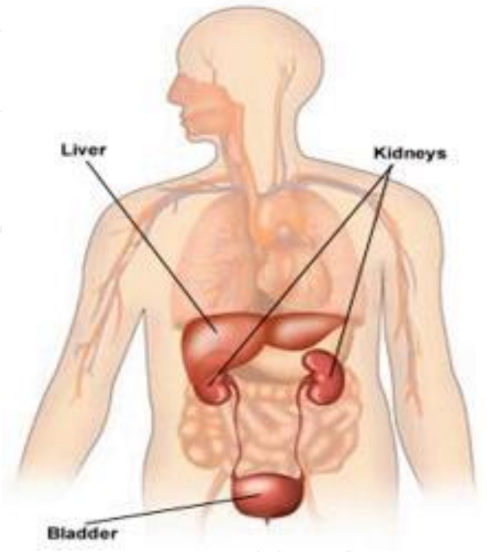
- High Cholesterol
- Ulcerative Colitis
- Thyroid Disease
- Testicular Cancer
- Kidney Cancer
- Pregnancy-Induced Hypertension

No Probable Link

- Hypertension/Coronary Artery Disease
- Chronic Kidney, Liver, Parkinson's, Autoimmune* Diseases
- Osteoarthritis
- Common Infections
- Neurodevelopmental Disorders/Stroke
- Asthma
- Birth Defects/Preterm/Low Birth Weight
- Miscarriage or Stillbirth

*rheumatoid arthritis, lupus, Type I and II diabetes, Crohn's disease, multiple sclerosis

Toxicity for Humans



- PFAS bind to proteins (not to lipids / fats) and are mainly detected in blood, liver and kidneys
- PFOS: carcinogenity "suggestive" (US EPA, 2014). PFOA: "possibly carcinogenic" (International Agency for Research on Cancer, IARC, 2014)
- Study with 656 children demonstrated elevated exposure to PFOS & PFOA are associated with reduced humoral immune response [1]
- Large epidemiological study of 69,000 persons found probable link between elevated PFOA blood levels and the following diseases: high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer and preeclampsia –C8 science panel [2]

[1] Grandjean, P.; Andersen, E. W.; Budtz-Jørgensen, E.; Nielsen, F.; Mølbak, K.; Weihe, P.; Heilmann, C. Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *JAMA* **2012**, 307, 391–397.

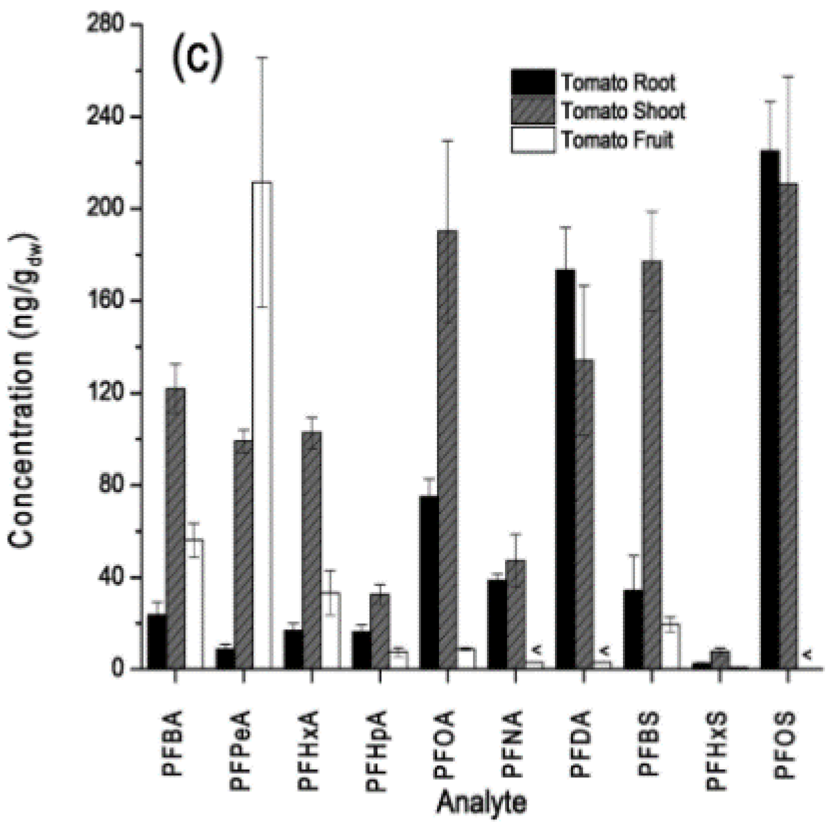
[2] http://www.c8sciencepanel.org/

PFASs

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[†,*]



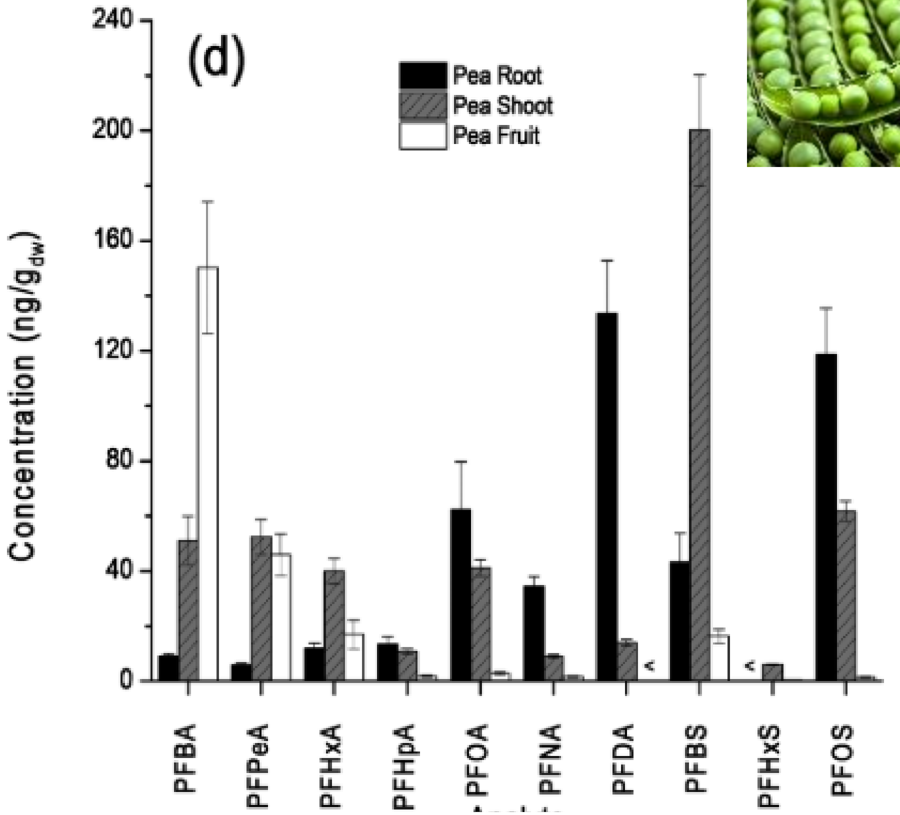


Figure 2. Concentrations of PFAAs in greenhouse radish (a), celery (b), tomato (c), and pea (d) grown in industrially impacted soil. Values for tomato fruit are from a previous study.[9] Bars represent means and standard errors of five determinations. Values less than the LOQ are denoted by <; LOQs for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

PFASs

ARCADIS Design & Consultancy for natural and built assets

Concerns over short chain PFAS - Overview

Persistent

- Based on read-across from long chain PFAS
- 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 of ecotoxicity
- Toxicity in humans to be assessed
- Potential endocrine disruptor

- Representatives of European Authorities agreed: Properties are of concern (BA-Workshop in October 2016)
- However, non-classical combination of concerns so far not covered by REACH

Umwelt Bundesamt

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

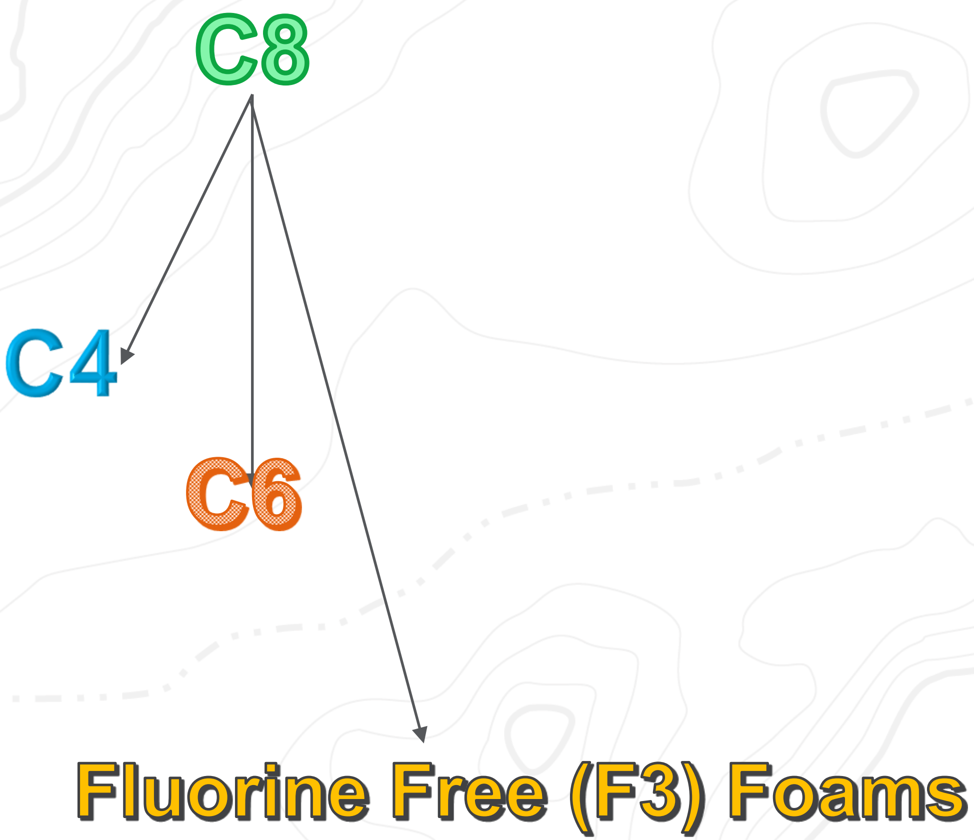
ICCE 2017 Oslo

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

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

PFAS Foams being Replaced

- C8 (PFOS and PFOA) phased-out
- C8 replaced with compounds with shorter (e.g., C4, C6) perfluorinated chains
- C4, C6 PFAS are less bioaccumulative, still extremely persistent and more mobile in aquifer systems vs C8 - more difficult and expensive to treat in water.
- Solutions for characterizing all PFAS species important to cover current and future risks / liabilities
- Regulations addressing multiple chain length PFAS (long and short) are evolving globally
- Fluorine free (F3) foams contain no persistent pollutants
- F3 foams pass ICAO tests with highest ratings for extinguishment times and burn-back resistance, so are widely available as replacements to AFFF



PFASs in Landfill Leachate

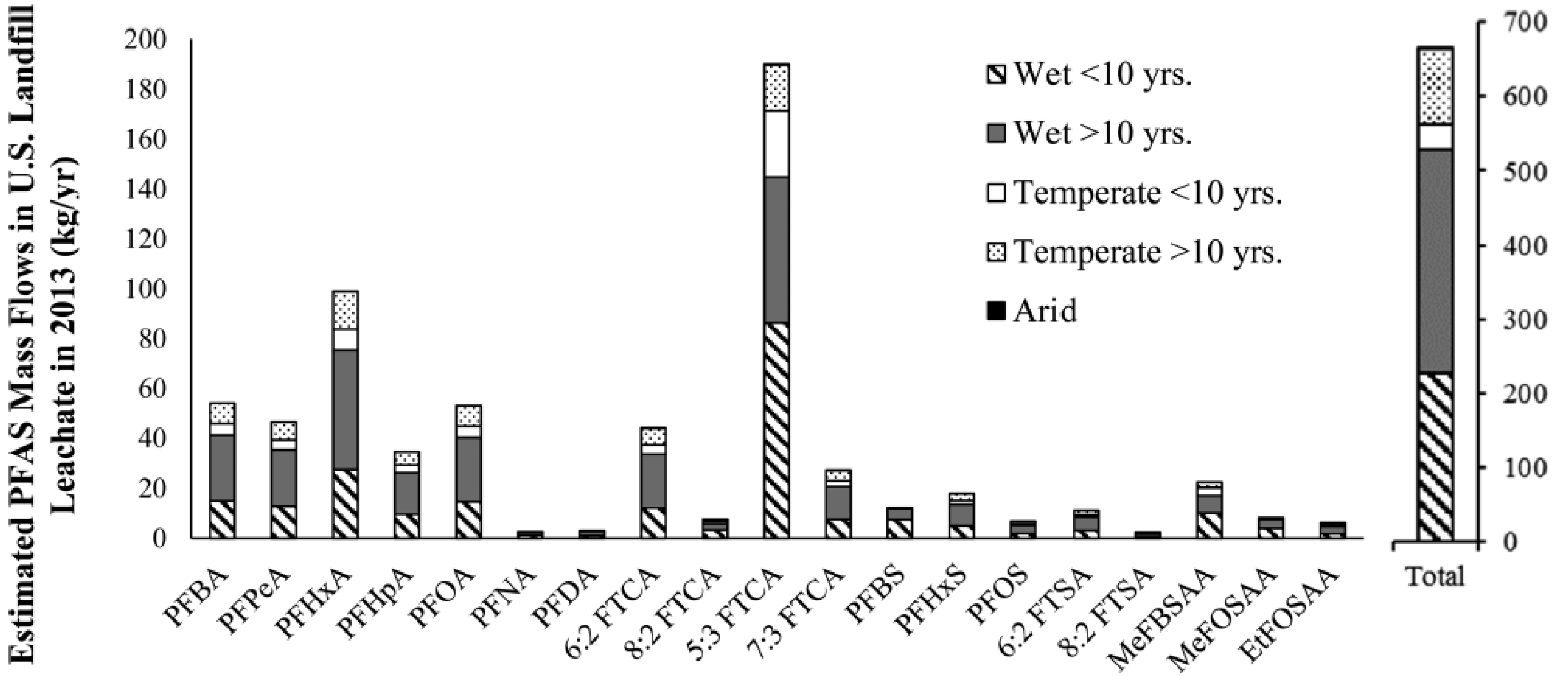


Figure 1. Group 1 PFAS release in U.S landfill leachate for 2013 demonstrating a dominance of compounds with five fluorinated carbons (PFHxA and 5:3 FTCA). Releases were calculated from mean concentrations in each climate and age category (Table 3). The individual columns are based on eq 1 while the total is based on eq 2.

Figure 1 from Lang et.al., (2017) National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate. *Environ. Sci. Technol.*, 2017, 51 (4), pp 2197–2205

PFASs

Concerns over short chain PFAS (cont.)

ELSEVIER

Food and Chemical Toxicology

journal homepage: www.elsevier.com/locate/foodchemtox

Short communication

Internal exposure-based pharmacokinetic evaluation of potential for biopersistence of 6:2 fluorotelomer alcohol (FTOH) and its metabolites

Shruti V. Kabadi[a,*], Jeffrey Fisher[b], Jason Aungst[a], Penelope Rice[a]

[a] FDA/CFSAN/OFAS/DFCN, 5001 Campus Drive, HFS 275, College Park, MD 20740, United States
[b] FDA/NCTR, 3900 NCTR Road, Jefferson, AR 72079, United States

useful for biomonitoring purposes and toxicological evaluation. More importantly, we determined that 5:3 A is an important biomarker for assessment of long-term exposure to 6:2 FTOH as 5:3 A had the highest internal exposure and slowest clearance across species. Furthermore, we concluded that 5:3 A has the potential to reach steady state upon repeated exposure to 6:2 FTOH as its clearance was determined to reduce with increasing 6:2 FTOH exposure. We also identified specific

ChemicalWatch
GLOBAL RISK & REGULATION NEWS

FDA scientists voice concerns over metabolites of food contact substance

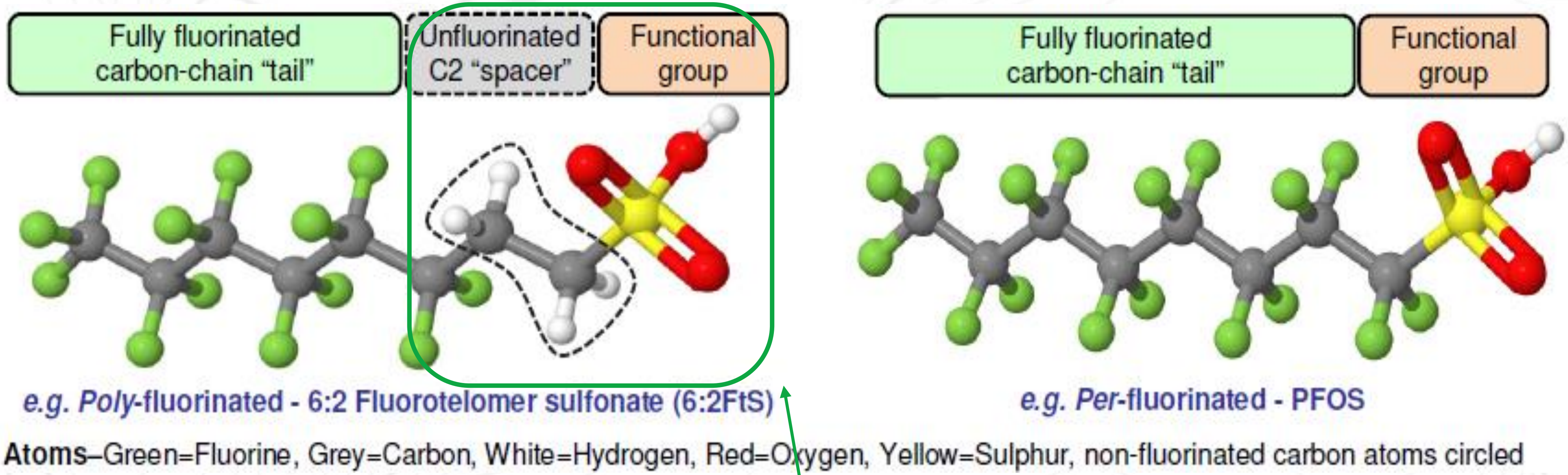
Focus on metabolites of 6:2 fluorotelomer alcohol

18 January 2018 / Academic studies, Exposure monitoring & measurement, Food & drink, PFCs, Toxicology, United States

"Our work represents the first step towards identifying the mechanism by which 6:2 FTOH, similar C6-PFCs, and its metabolites could accumulate in the body to potentially cause adverse effects," write the researchers in the journal *Food and Chemical Toxicology*.

PFASs

Polyfluorinated Compounds – PFAA Precursors



Bioactive –metabolised via reactive aldehydes and creates secondary molecule–increased toxicity vs inert PFAA

PFASs

Environment International 74 (2015) 160–169

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

ELSEVIER

ARCADIS Design & Consultancy for natural and built assets

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

Wouter A. Gebbink *, Urs Berger, Ian T. Cousins

Department of Applied Environmental Science (ITM), Stockholm University, SE 10691 Stockholm, Sweden

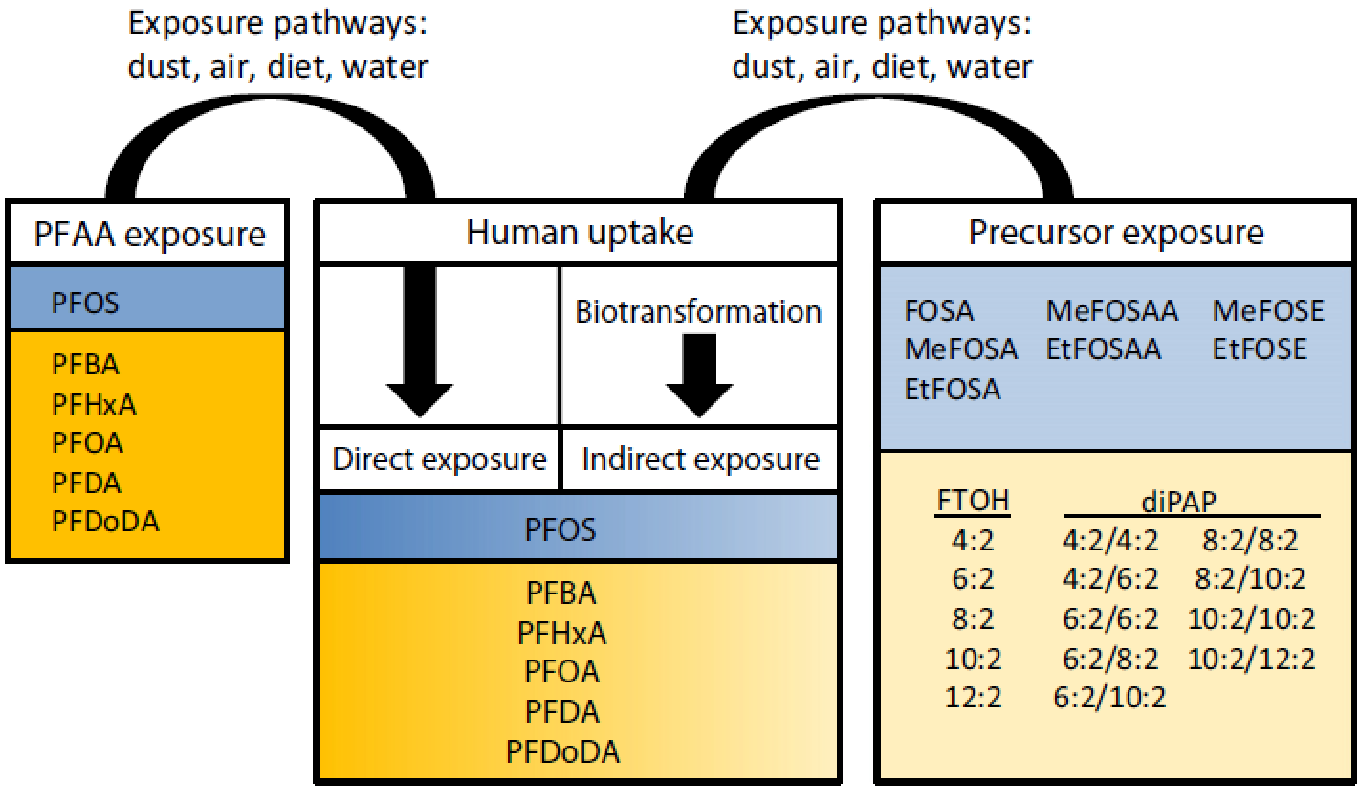


Fig. 1. Schematic of direct and indirect (precursor) exposure pathways for PFOS and PFCAs.

PFASs

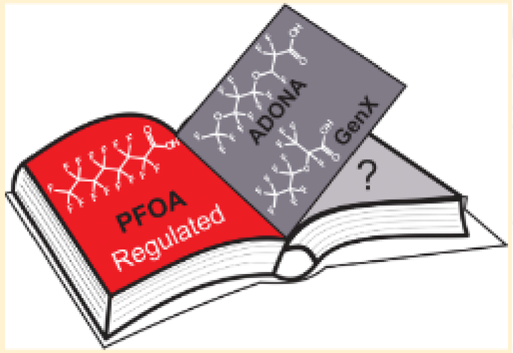
Replacement Chemistry

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

A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)?

Zhanyun Wang,[†] Jamie C. DeWitt,[‡] Christopher P. Higgins,[§] and Ian T. Cousins*[,∥]

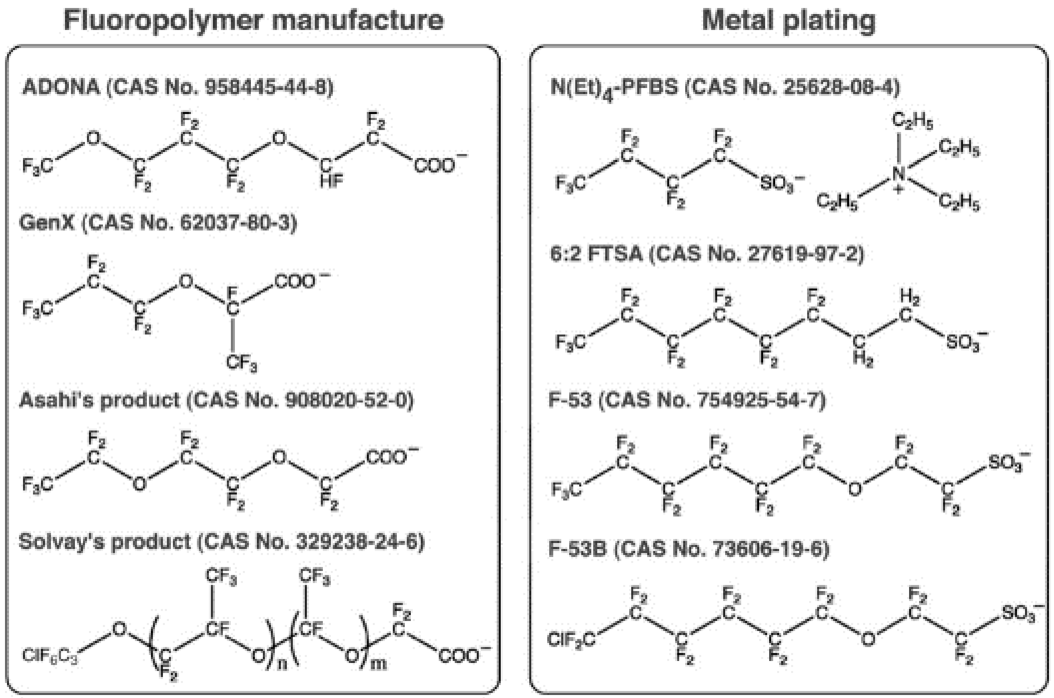
ABSTRACT: More than 3000 per- and polyfluoroalkyl substances (PFASs) are, or have been, on the global market, yet most research and regulation continues to focus on a limited selection of rather well-known long-chain PFASs, particularly perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA) and their precursors. Continuing to overlook the vast majority of other PFASs is a major concern for society. We provide recommendations for how to proceed with research and cooperation to tackle the vast number of PFASs on the market and in the environment.



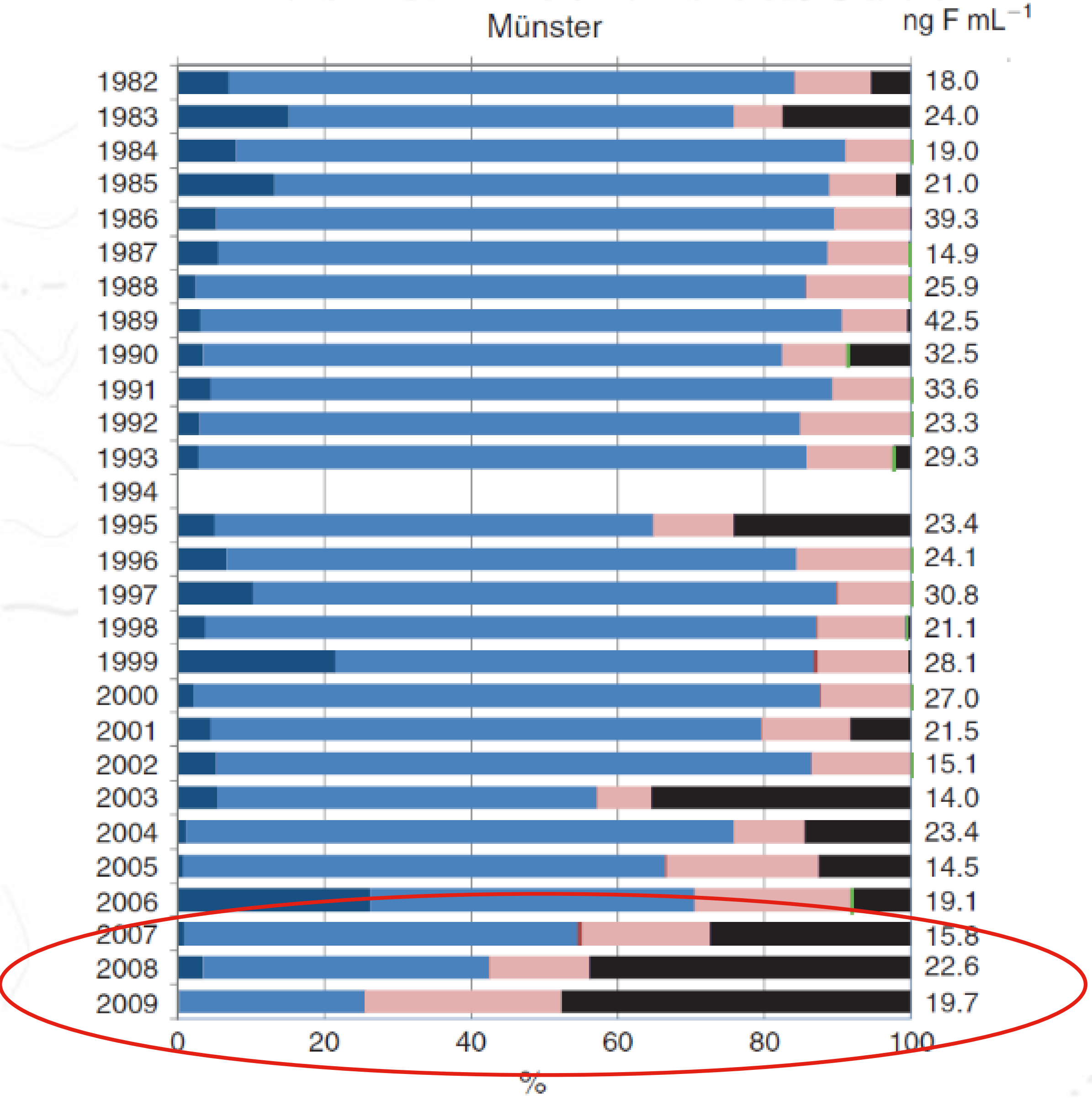
Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors

Zhanyun Wang [a], Ian T. Cousins [b], Martin Scheringer [a,*], Konrad Hungerbühler [a]

[a] Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
[b] Department of Applied Environmental Science (ITM), Stockholm University, SE-10691 Stockholm, Sweden



PFASs



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CSIRO PUBLISHING

Environ. Chem. **2016**, *13*, 102–110
http://dx.doi.org/10.1071/EN15041

Are humans exposed to increasing amounts of unidentified organofluorine?

Leo W. Y. Yeung[A] *and Scott A. Mabury*[A,B]

Plasma concentrations reveal transition from identifiable PFASs to unidentified

PFOS precursor	PFSA	PFCA precursor	PFCA	PFPiA	Unidentified

PFASs

Criteria to Categorize Safety of Chemicals

- Persistence (**P**): Compounds that do not break down in the environment over long periods of time (i.e., they do not readily biodegrade).
- Bioaccumulative (**B**): Compounds that build up and are retained in organisms at a faster rate than they can be removed or expelled.
- Mobility (**M**): Compounds that can travel long distances in groundwater or surface waters from their point of release.
- Toxicity (**T**): Compounds impart an adverse health effect to an organism at a relatively low concentration of exposure.
- Biopersistence: Compounds that tend to remain inside an organism, rather than being expelled or broken down.
- Biomagnification: The increased concentration of a compound, such as a toxic chemical, in the tissues of organisms at successively higher levels in the food chain –through trophic levels.

Stockholm Convention on Persistent criteria to define persistent organic pollutants (POPs), based on **PBT**

Suggestion that other criteria are more relevant by UBA under REACH: **PMT, vPvB, vPvM**

https://www.chemicalsafetyconsulting.com/chemical-safety-news/pmt-and-vpvm-substances-under-reach-and-clp-or-ghs-report-uba-workshop
https://chemicalwatch.com/60218/german-environment-agency-updates-criteria-for-mobile-chemicals-in-water

The Precautionary Principle

Principle 15 of the Rio Declaration on Environment and Development as follows:

“Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation”

Comparisons are made to the medical Hippocratic Oath – “Do No Harm”

Multiple ways to apply this concept: Persistent Bioaccumulative and Toxic (PBT), very persistent and very bioaccumulative (vPvB), very mobile very persistent (vPvM), Persistent Mobile Toxic (PMT) or poorly reversible exposure

https://www.epa.vic.gov.au/~/media/Files/Your%20environment/Land%20and%20groundwater/PFAS%20in%20Victoria/PFAS%20NEMP/FINAL_PFAS-NEMP-20180110.pdf

Poor Reversibility of Exposure (Conceptual)

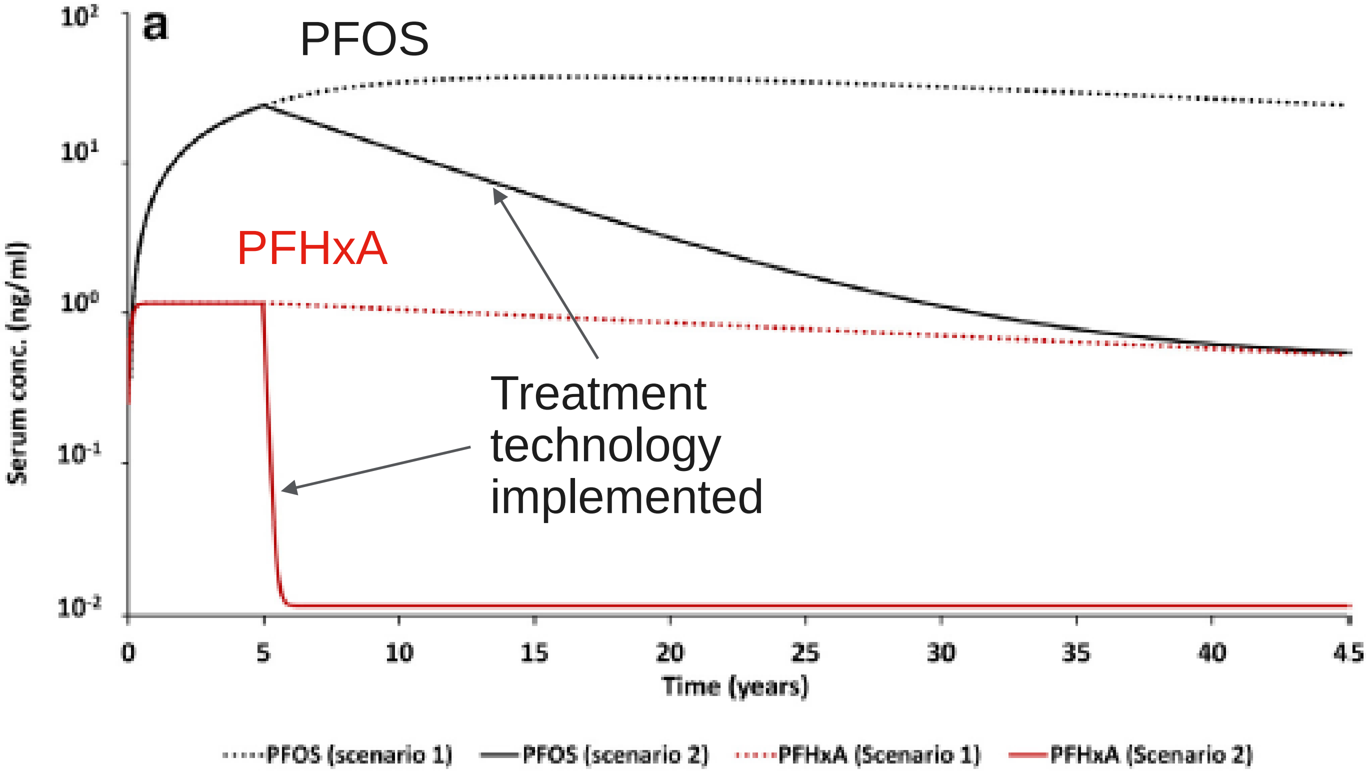
Poorly reversible exposure of a chemical can occur two ways:

- 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)



PFASs

Major Locations of PFAS Point Source Contamination

- Primary Manufacturing (e.g. PTFE)
- Secondary Manufacturing (Application of PFASs to other products) –Tanneries, Paper Mills, Firefighting Foam Blending, Metal Plating Facilities
- Fire Training Sites
    - Airports
    - Civil
    - Defence
    - Oil and Gas
    - Large Rail Yards
- Wastewater treatment plants
- Landfills



PFASs

Groundwater Risks to Receptors

Landfill Leachate
Municipal / Domestic WWTP
Industry & Manufacturing
Agricultural Land
Commercial / Domestic Products
Metal Plating
ASTs –Fuel storage (FFFP / FP)

AFFF / FFFP / FP
Fire training
Incident Response

?

?

?

Diffuse
Ground level impacts and ground/surface water

Source – Pathway – Receptor
High concentration, spill site, route via groundwater to receptor e.g. drinking water well

Grasshopper effect

via widening of source zones

e.g. concentrated plume intercepts crop spray irrigation to make secondary wider source area for more dilute plume

PFASs

Occurrence of PFAAs in UK Waters

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Environment Agency

using science to create a better place

Incidence and attenuation of perfluorinated surfactants in groundwater

Science Report – SC070002/SR

Perfluorinated chemical	Limit of detection (µg/l)
Perfluorooctane sulphonate (PFOS)	0.1
Perfluoropentanoic acid (PFC5)	0.1
Perfluorohexanoic acid (PFC6)	0.1
Perfluoroheptanoic acid (PFC7)	0.1
Perfluorooctanoic acid (PFOA)	0.1
Perfluorononanoic acid (PFC9)	0.1
Perfluorodecanoic acid (PFC10)	0.1
Perfluoroundecanoic acid (PFC11)	0.1
Perfluorododecanoic acid (PFC12)	0.1
Perfluorotetradecanoic acid (PFC14)	0.1

- Environment Agency PFAA monitoring 2008
- Groundwater sampling
  - Conducted at 219 sites in England and Wales (6.5% EA network)
  - The majority of sites were in areas of potential sources eg. airfields
  - “Low risk rural sites” comprised 5%
- Surface water sampling
  - Drinking water abstractions (42 sites)
  - “Higher risk sites” (39 sites) eg. effluents from sewage works
- Limits of detection were 0.1 ug/L so well above the new US EPA standards at 0.07 ug/L

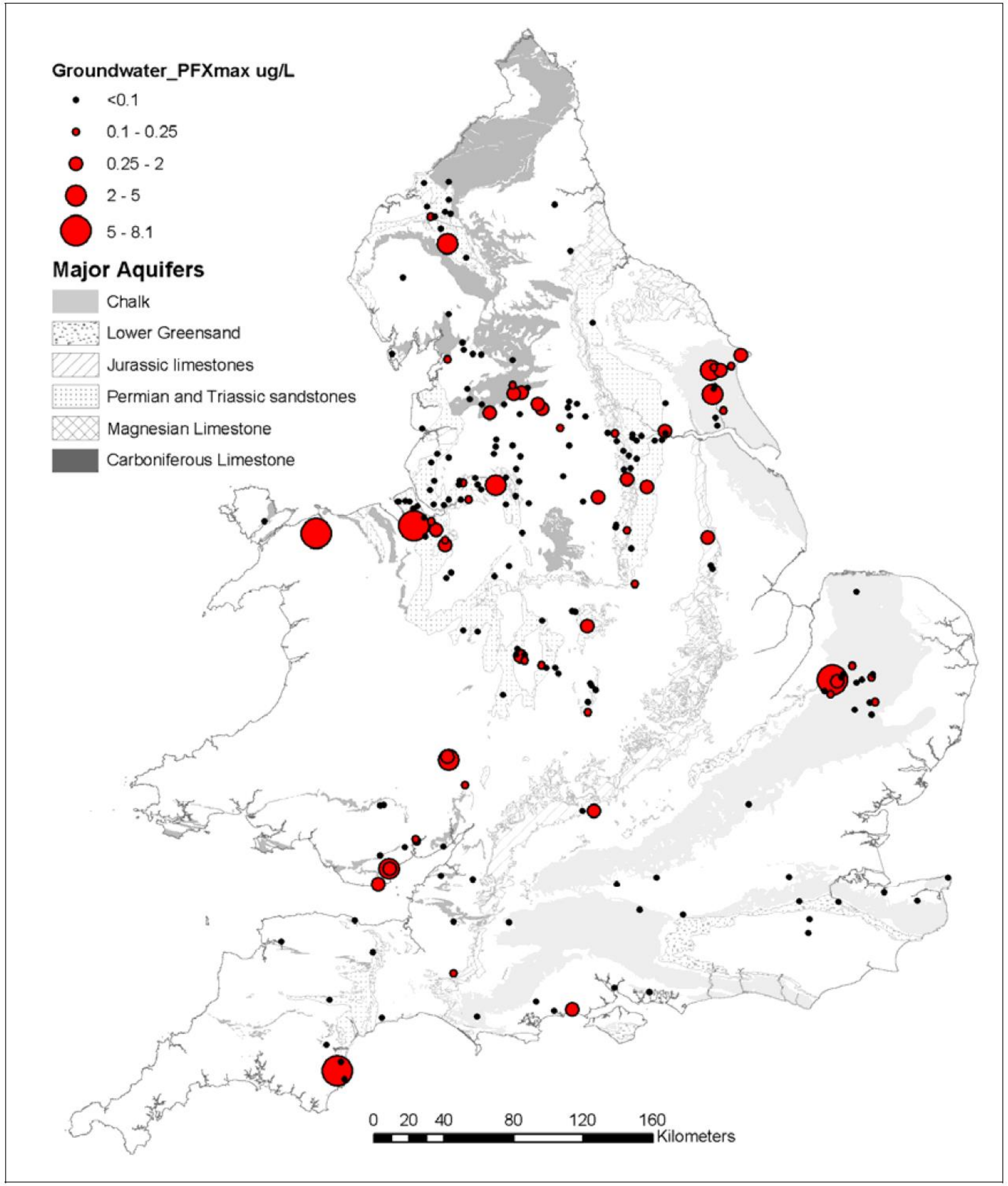

Figure 3.1 Distribution of groundwater monitoring for perfluorinated chemicals

Incidence and attenuation of perfluorinated surfactants in groundwater

Science Report – SC070002/SR

ARCADIS Design & Consultancy for natural and built assets

Groundwater

- PFCs detected in 26% of groundwater sites
- Detection even at "low risk" sites

Surface Water

- PFCs detected at 52% of surface water sites (drinking water abstractions)
- PFCs detected at 67% "high risk" sites

Table 3.1 Perfluorinated compounds in groundwater by aquifer type

Aquifer	Number of sites monitored	Sites with detected PFX		Max PFX (ug L^{-1}) excluding non detections			
		Number of sites	% sites	Min	Mean	Median	Max
Drift	6	1	16.7	0.2	0.20	0.20	0.2
Minor	75	18	24.0	0.12	1.18	0.39	6.56
Chalk	36	13	36.1	0.1	1.35	0.22	8.1
L'wer GS	3		0.0				
Jur's Lst	3	2	66.7	0.22	1.04	1.04	1.85
PT sst	72	14	19.4	0.1	1.46	0.31	7.47
Mag Lst	7	3	42.9	0.1	0.30	0.20	0.6
Carb Lst	16	6	37.5	0.12	0.39	0.45	0.64

PFAS in European Surface Waters

River	PFOS (ng/l)	Flow(m^3/s)
Scheldt (Be, NL)	154	-
Seine (Fr)	97	80
Severn (UK)	**238**	**33**
Rhine (Ge)	32	1,170
Krka (Sl)	1,371	50

Environmental Pollution 157 (2009) 561–568
Contents lists available at ScienceDirect
Environmental Pollution
journal homepage: www.elsevier.com/locate/envpol
ELSEVIER

EU-wide survey of polar organic persistent pollutants in European river waters

Robert Loos*, Bernd Manfred Gawlik, Giovanni Locoro, Erika Rimaviciute, Serafino Contini, Giovanni Bidoglio
European Commission, Joint Research Centre, Institute for Environment and Sustainability, Via Enrico Fermi, 21020 Ispra, Italy

More than 100 river water samples from 27 European Countries were analysed for 35 selected polar organic contaminants.

Table 5.2: EQS of the European Commission for PFOS and its derivatives

Name of substance	AA-EQS* (µg/l)		MAC-EQS** (µg/l)		EQS (µg/kg)
	Inland surface waters	Other surface waters	Inland surface waters	Other surface waters	Biota
Perfluoro octane sulfonate and its derivatives (PFOS)	0,00065	0,00013	36	7,2	9,1

* AA: Annual average
** MAC: Maximum allowable concentration

PFASs

Worldwide Distribution of Novel Perfluoroether Carboxylic and Sulfonic Acids in Surface Water

Yitao Pan,[†,‡,⊥] Hongxia Zhang,[†,⊥] Qianqian Cui,[†] Nan Sheng,[†] Leo W. Y. Yeung,[§] Yan Sun,[∥] Yong Guo,[∥] and Jiayin Dai[*,†]

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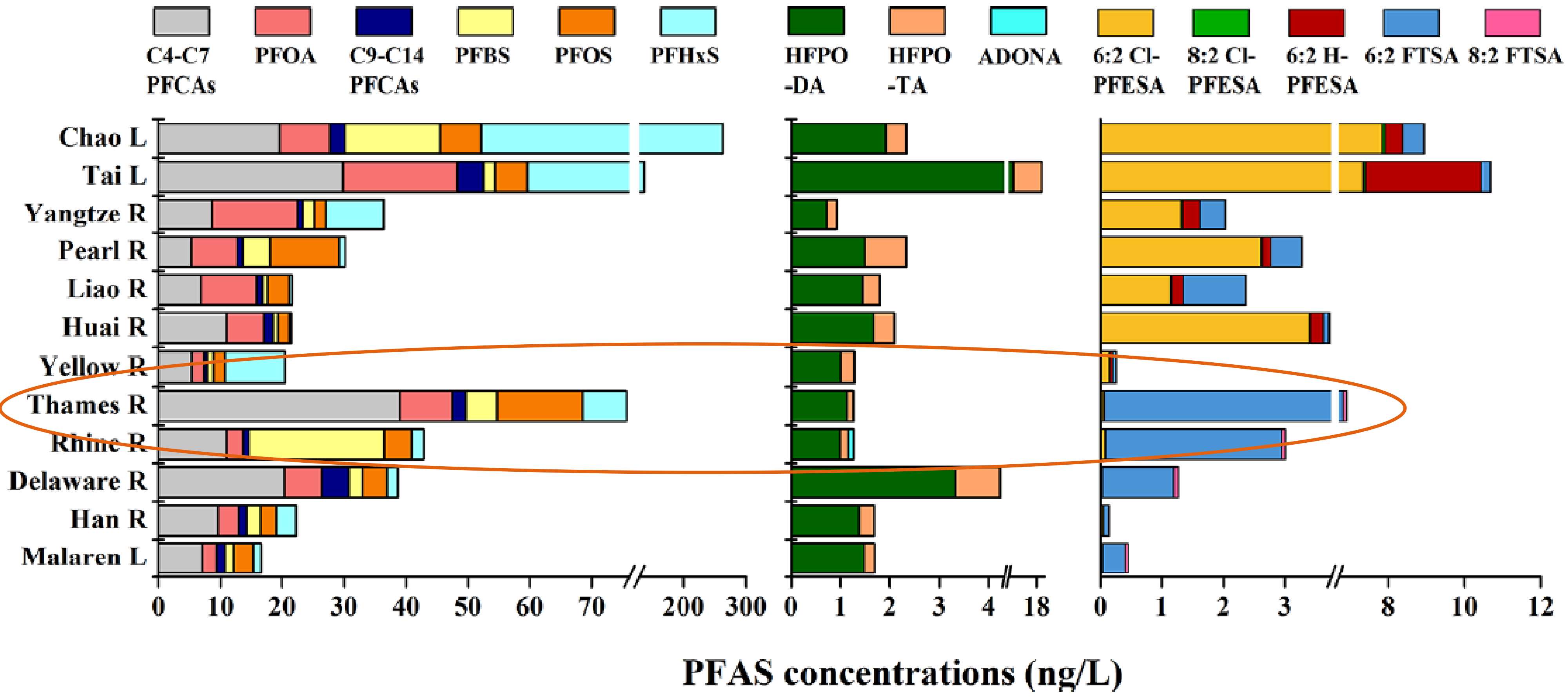


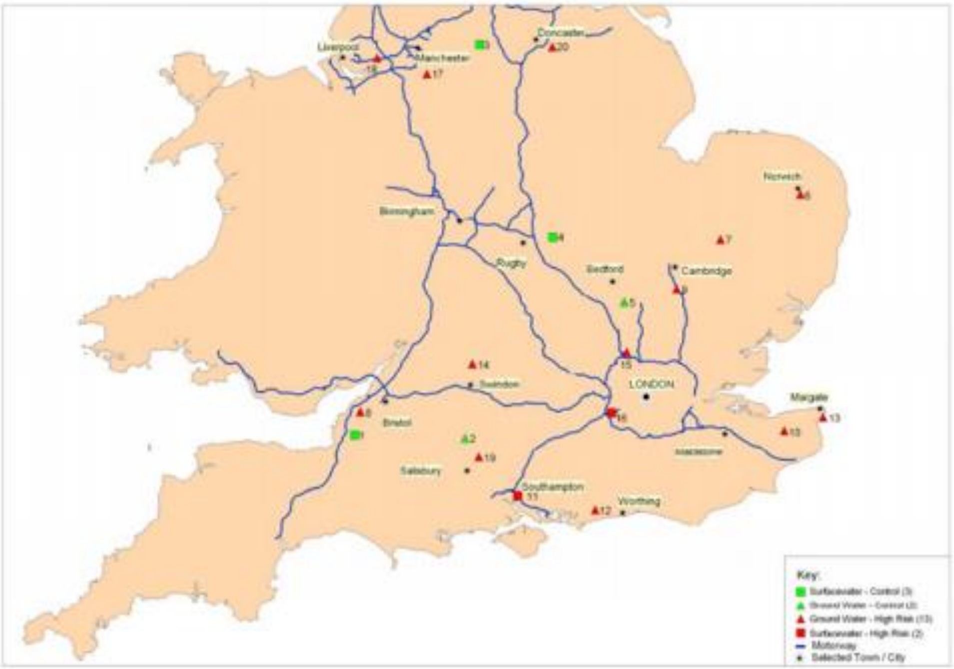
Figure 2. Mean concentrations (ng/L) of legacy PFASs (PFCAs and PFSAs) and fluorinated alternatives (PFECAs, PFESAs, and FTSAs) in the studied rivers and lakes: Chao Lake (n = 13), Tai Lake (n = 15), Yangtze River (n = 35), Pearl River (n = 13), Liao River (n = 6), Huai River (n = 9), Yellow River (n = 15), Thames River (n = 6), Rhine River (n = 20), Delaware River (n = 12), Han River (n = 6), and Mälaren Lake (n = 10).

River Thames Significantly Impacted?

Occurrence of PFCs in UK Drinking Water

SURVEY OF THE PREVALENCE OF PERFLUOROOCTANE SULPHONATE (PFOS), PERFLUOROOCTANOIC ACID (PFOA) AND RELATED COMPOUNDS IN DRINKING WATER AND THEIR SOURCES

WRc Ref: DEFRA 7585
FEBRUARY 2008



- Sampling and a data review was conducted by the Drinking Water Inspectorate in 2007
- Review found only 4 of 29 water companies had PFAS testing data to share with the DWI
- The sampling drinking water at raw, mid treatment, and final stage of process
  - Fifteen “high risk” sites based on surrounding land use (usually airfields)
  - Five lower risk “control” sites

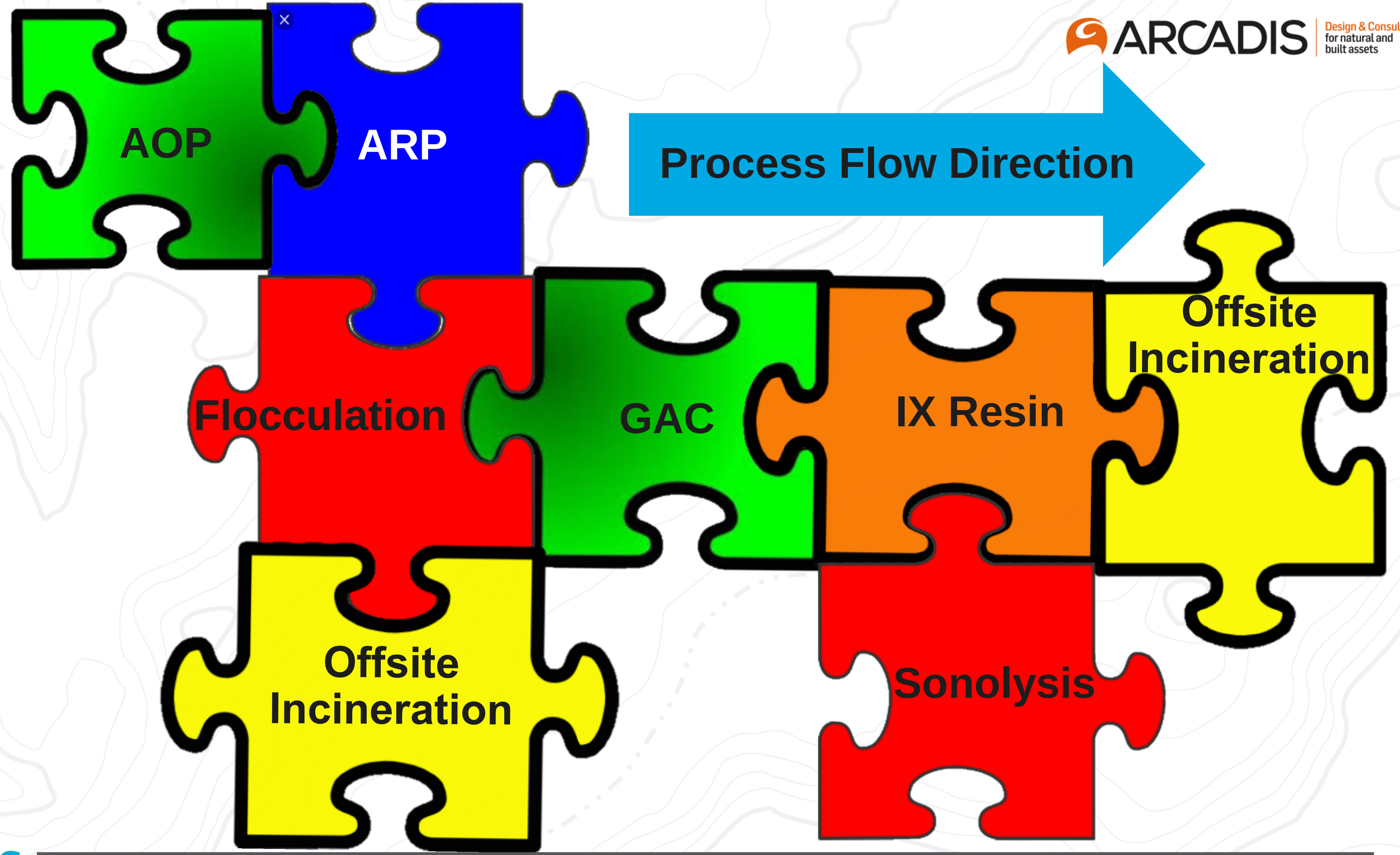
http://dwi.defra.gov.uk/research/completed-research/reports/DWI70_2_212PFOS.pdf

Table 6.2 PFOS results (in µg/l) of sampling in 2007 at the perceived higher-risk sites for all four sampling sessions.

8	Groundwater (UC)	Ultrafiltration membranes and chlorination using chlorine gas.	Airfield and industrial	Raw	0.016	0.020	<0.011	0.013
				Before last chlorination	0.016	0.023	<0.011	-
				After Cl contact tanks	0.016	0.019	<0.011	0.014
9	Groundwater (UC)	None on site: water pumped by raw water pumping main to another treatment works, which has GAC (not in operation), super chlorination using gas and dechlorination.	Airfield	Raw	0.152	0.124	0.205	0.135
				Raw	0.162	-	0.183	-
				Raw	0.154	-	0.208	-
				Final	-	-	-	0.130
15	Groundwater (UC)	GAC and chlorination by on-site electrolytic generation using food grade salt stored in HDPE. 12 GAC beds.	Large use of PFOS-containing fire fighting foam	Borehole 3	0.059	0.076	0.052	Off line
				Borehole 4	0.029	0.028	0.018	Off line
				Borehole 5	0.038	0.029	0.030	Off line
				GAC feed water	-	-	-	0.046
				GAC 1	-	-	-	0.042
				GAC 2	-	-	-	0.043
				GAC 3	-	-	-	0.044
				GAC 4	-	-	-	0.048
				GAC 5	-	-	-	0.046
				GAC 6	-	-	-	0.044
				GAC 7	-	-	-	0.046
				GAC 8	-	-	-	0.044
				GAC 9	-	-	-	0.038
				GAC 10	-	-	-	0.038
				GAC 11	-	-	-	0.039
				GAC 12	-	-	-	0.037
				Post GAC (all)	0.042	0.047	0.035	-
				After chlorine contact	0.045	0.040	0.032	0.034

Available *In Situ* Groundwater Treatment Technologies

Technology	Likelihood of Success?	Rationale
Aerobic Biodegradation	Low	Biotransformation does not proceed past PFAA
Anaerobic Biodegradation	Low	
Phytoremediation	Low	PFAA not volatile; depth limitations
Air Sparging/Vapor Extraction	Low	PFAA not volatile nor biodegradable
In-Situ Thermal Treatment	Low	Required temperature economically impractical; ex-situ waste management
Chemical Oxidation/Reduction	Moderate	Bench-tests confirm viable mechanisms exist; field evidence conflicting; potential for treatment train
Monitored Natural Attenuation	Moderate	PFAA do not biodegrade (dilution via advection, adsorption are viable mechanisms)
Groundwater Extraction and Ex-Situ Treatment	High	Presumptive remedy for PFAS to-date, focus of this discussion; ex-situ waste management
Permeable Reactive Barriers	High	Apply ex-situ sorption technologies with a funnel & gate; change outs required



PFASs

No “silver bullet” for PFAS remediation; treatment train is current state of the practice

C6 Firefighting Foam Loss

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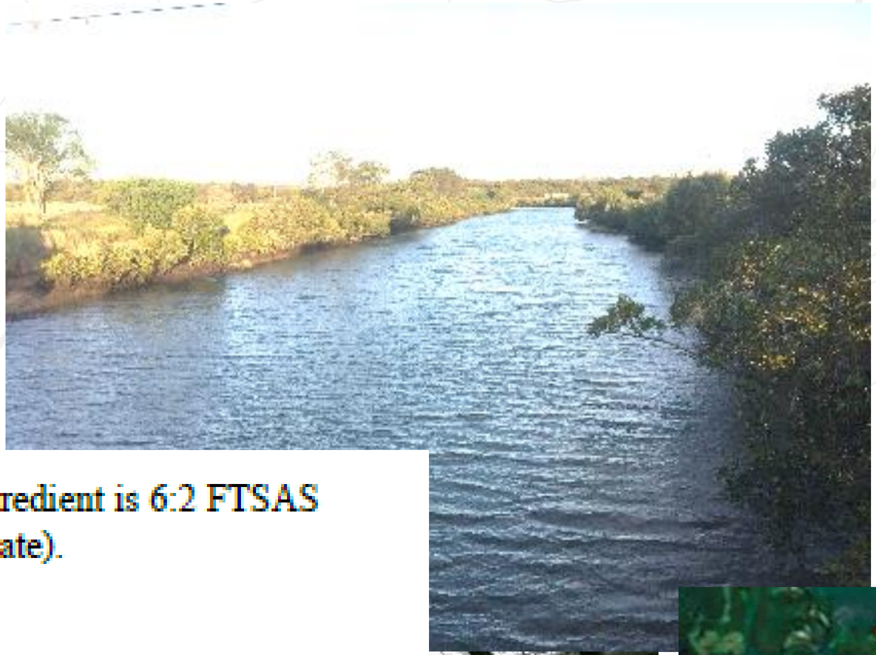
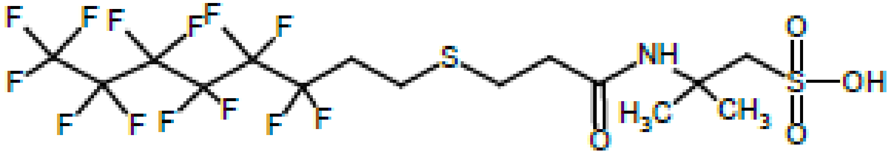
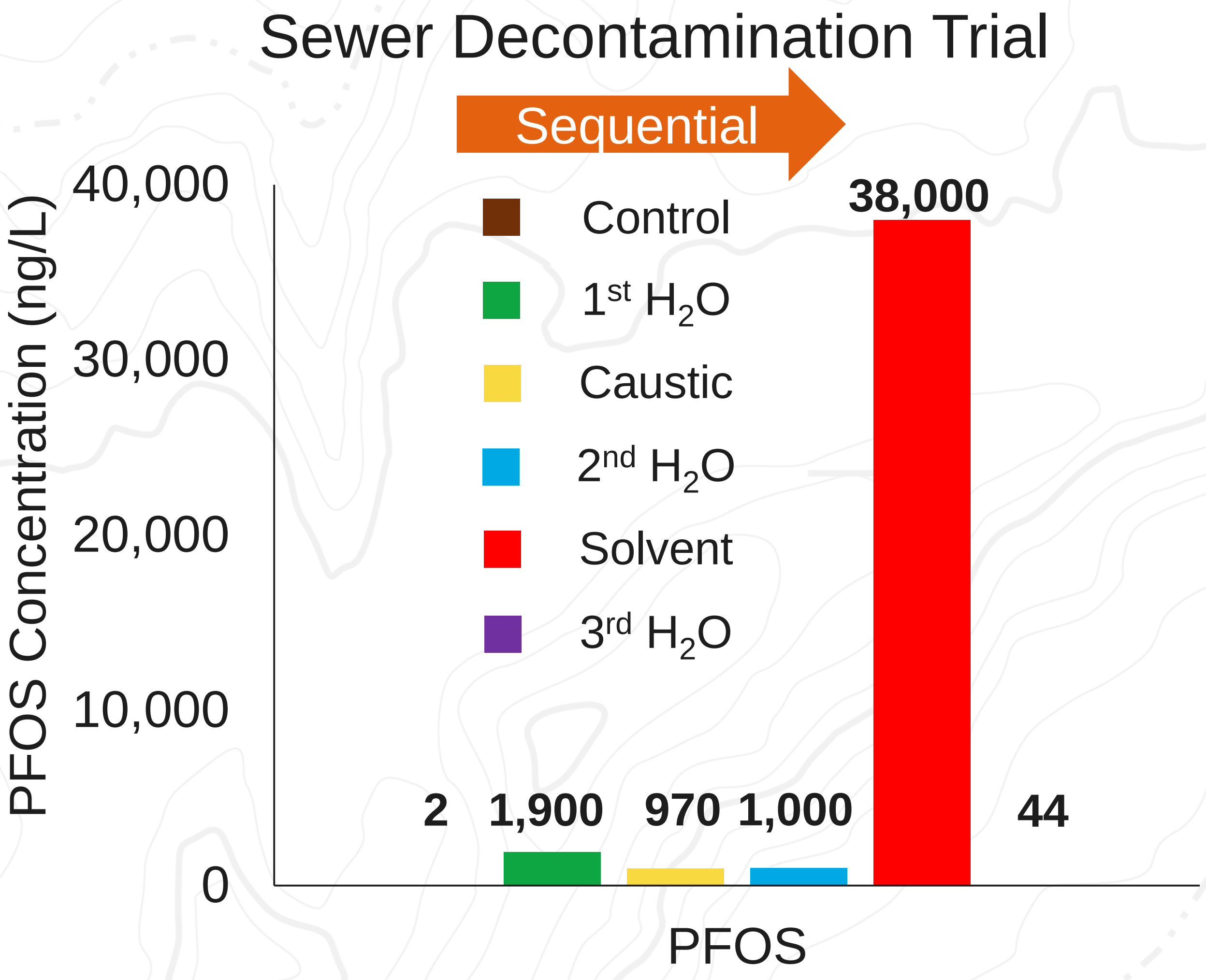


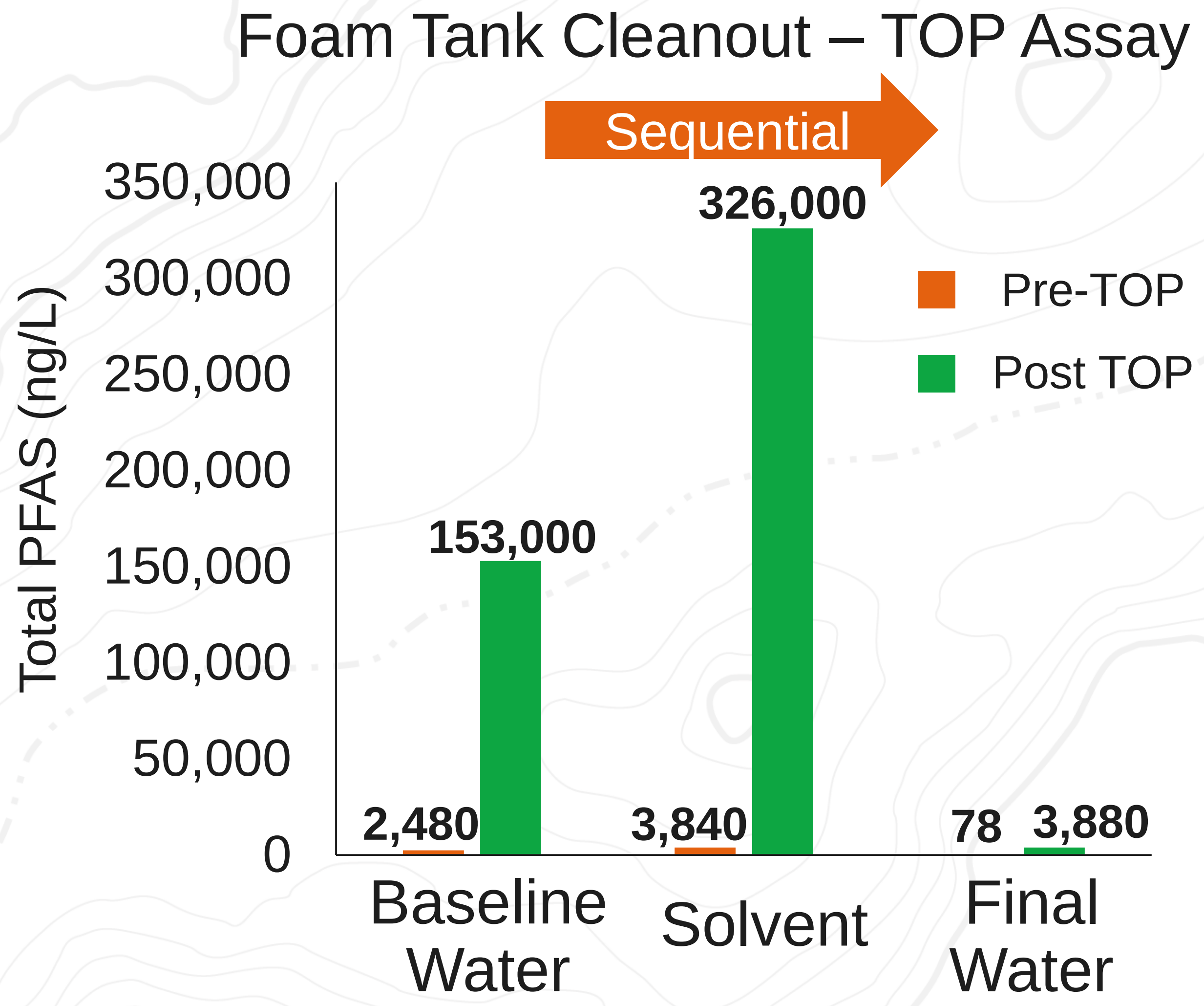
Tentatively identified PFAS as a main ingredient is 6:2 FTSAS (fluorotelomermercaptoalkylamido sulfonate).



PFASs

Foam Cleanout/Decontamination





PFASs

The Challenge

- **+ 15 ML -** Sewage, Tradewaste, Brackish Creek Water, Chemical Flush Fluids, and Stormwater
- **Emergency Response –** full-scale onsite in three weeks
- FF Foam Concentrate – Precursors, 5,000 µg/L PFAS
- Multiple Contaminants (1,500 mg/L COD)
- Small Footprint
- Treatment Objective: 0.25 µg/L sum of PFAS by TOP assay

PFASs

Emergency Response

evocra

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2 weeks permitted

Lab Scale

3 weeks system onsite

4 weeks installed

PFASs

Ozofractionation – Case Study

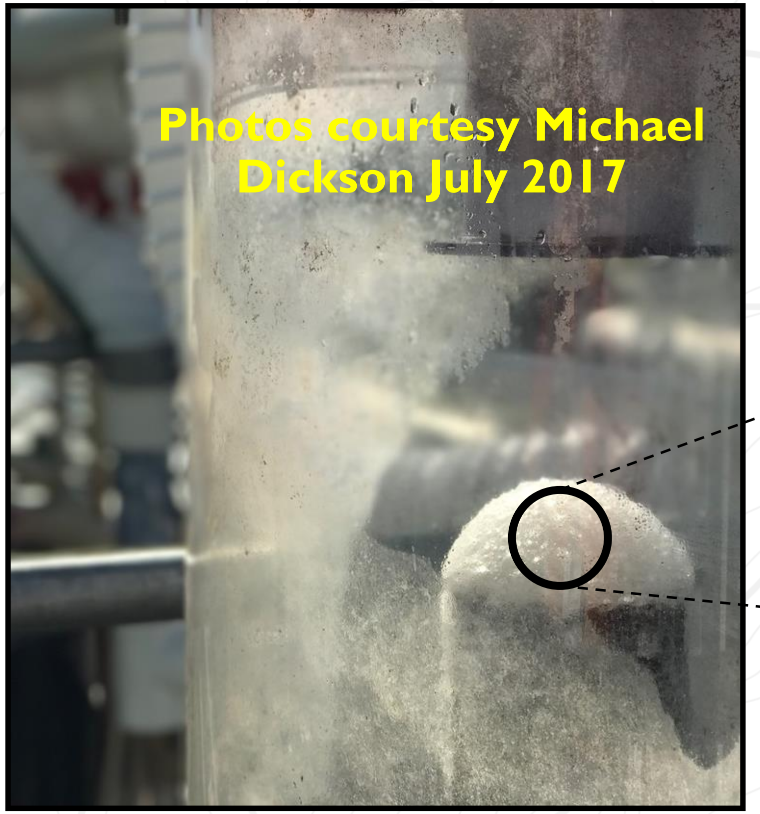
Large volume high COD, high PFAS impacted wastewater

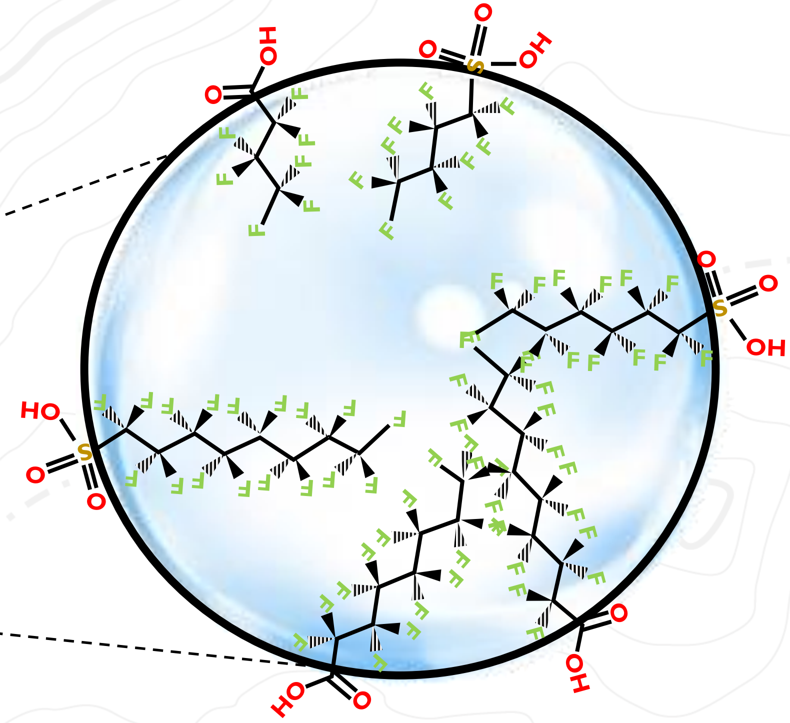
- ~3.6 million gallons of water
- Total [PFAS] ~ 3,950 µg/L; targeted discharge [PFAS] = <1 µg/L
- Laboratory analysis includes total oxidizable precursor (TOP) assay per country-specific regulations

Treatment train operation selected

- Ozofractionation with engineered polish
- Polish necessary for low discharge limit
- Foam concentrate to be thermally destroyed offsite

Ozofractionation - Concept





PFASs

Ozofractionation – Case Study

Ozofractionation highly effective at removing PFOS, PFOA, and C6 PFAA precursors.

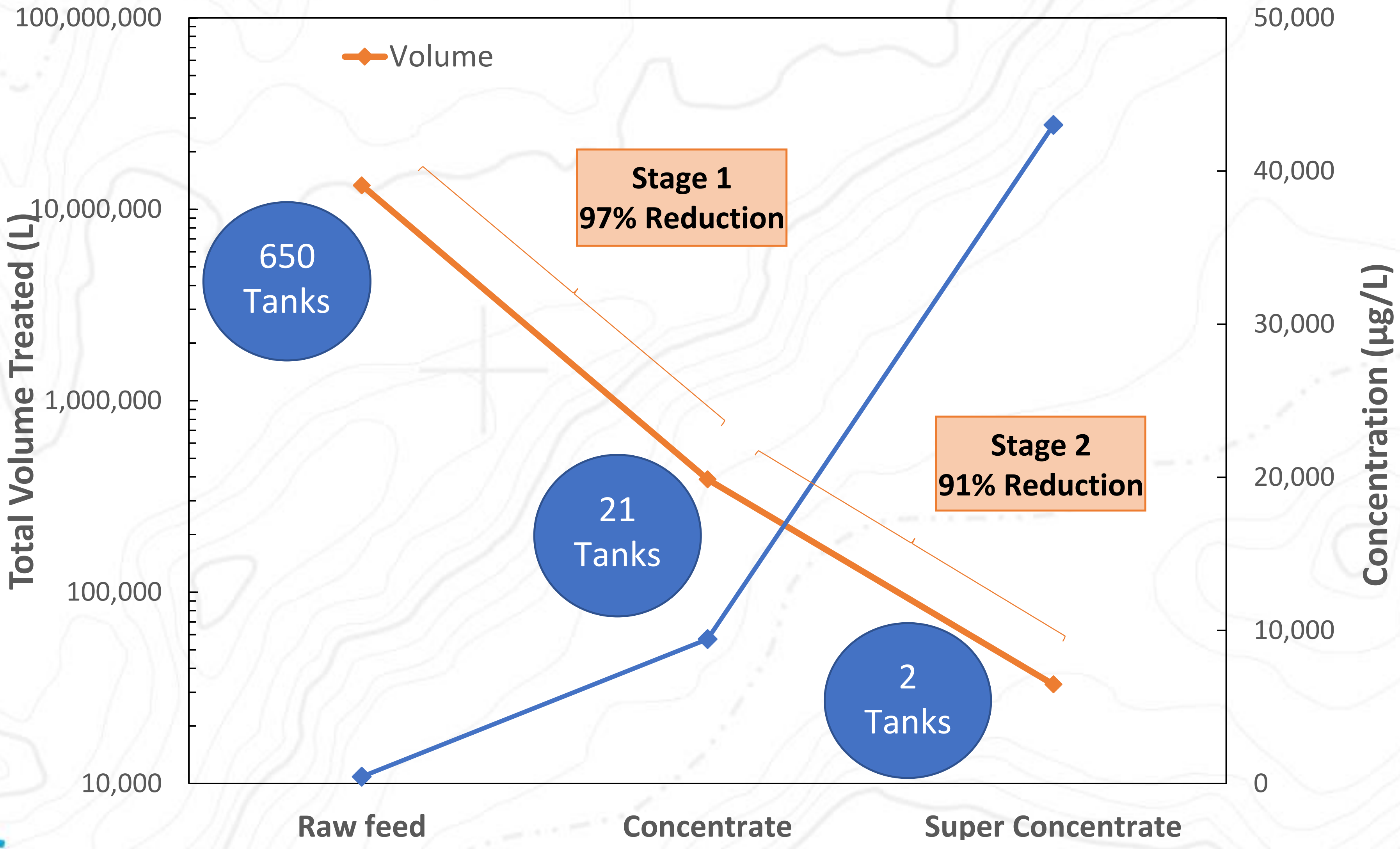
Ozofractionation converted some C6 precursors to PFHxA, PFPeA – net production of these compounds

Polishing adsorption stage was effective at removing PFHxA and, to a lesser extent, PFPeA; PFBA was not detectable in these samples

Identification	Influent (µg/L)	Ozofraction % Removal	Adsorbent % Removal	Treated Water (µg/L)	Total % Removal
PFOS	2.61	98.2%	81.3%	0.009	99.7%
PFOA	1.37	97.4%	94.4%	0.002	99.9%
6:2 FtS	87.4	95.6%	89.2%	0.416	99.5%
PFPeA	2.08	-66.3%	83.4%	0.575	72.4%
PFHxA	6.91	-66.4%	99.7%	0.034	99.5%
Sum PFAS	103	78.8%	95.1%	1.07	99.0%
Total PFAS, TOPA	**3,950**	**99.6%**	**89.6%**	**1.76**	**99.96%**

Ozofractionation and engineered polish achieve 99.96% PFAS removal, post TOP

Reconcentrate



PFASs

Sonolysis

Applicability:

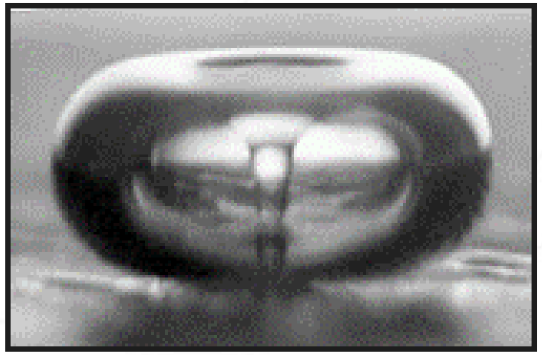
- Ultrasound applied to water results in successive rarefaction/compression of microbubbles ultimately yielding cavitation with extremely high temperatures on the surfaces of the bubbles resulting in pyrolysis of PFAS.

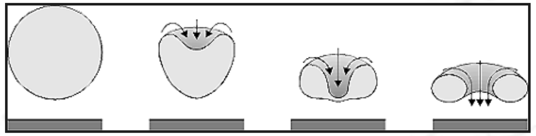
Benefits:

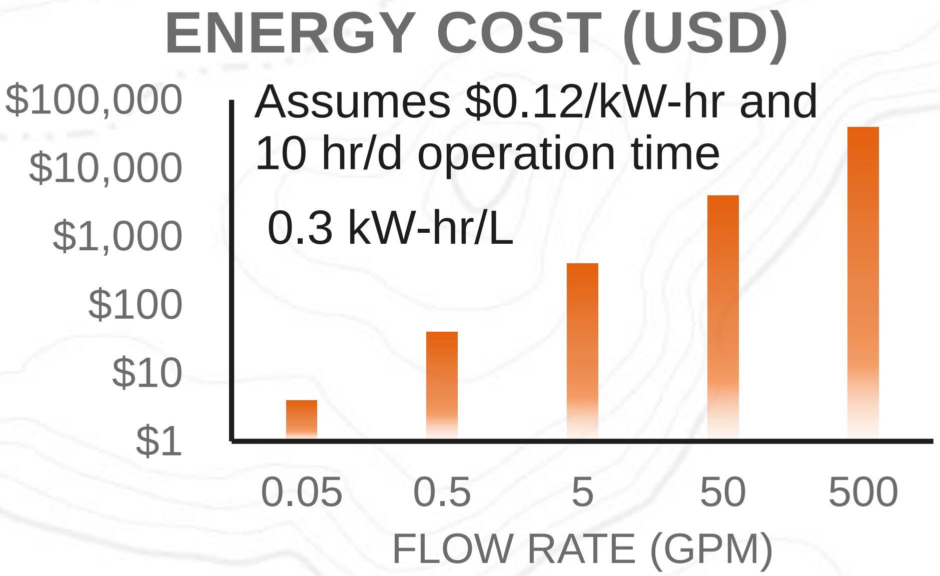
- Can reliably destroy concentrated PFAS waste streams with literature supported fluoride mass balance.
- Opportunities to use green energy sources as technology develops (i.e., solar power).

Limitations:

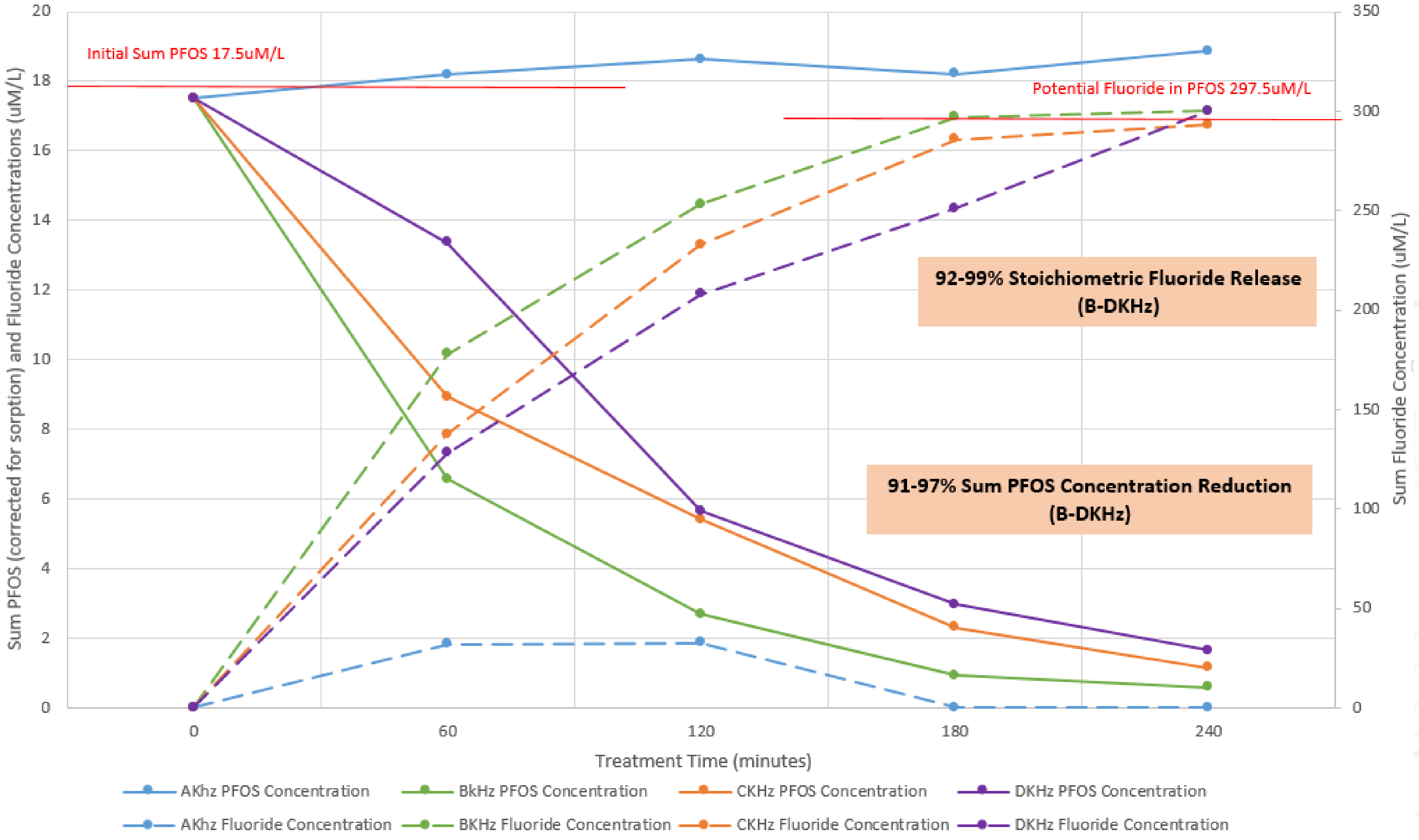
- PFOA rate > PFOS rate. PFOS will require longer residence times and/or more energy. Effective below 10,000 ppt?
- Requires specialized equipment and skilled implementation.
- High energy consumption and low flow rates.





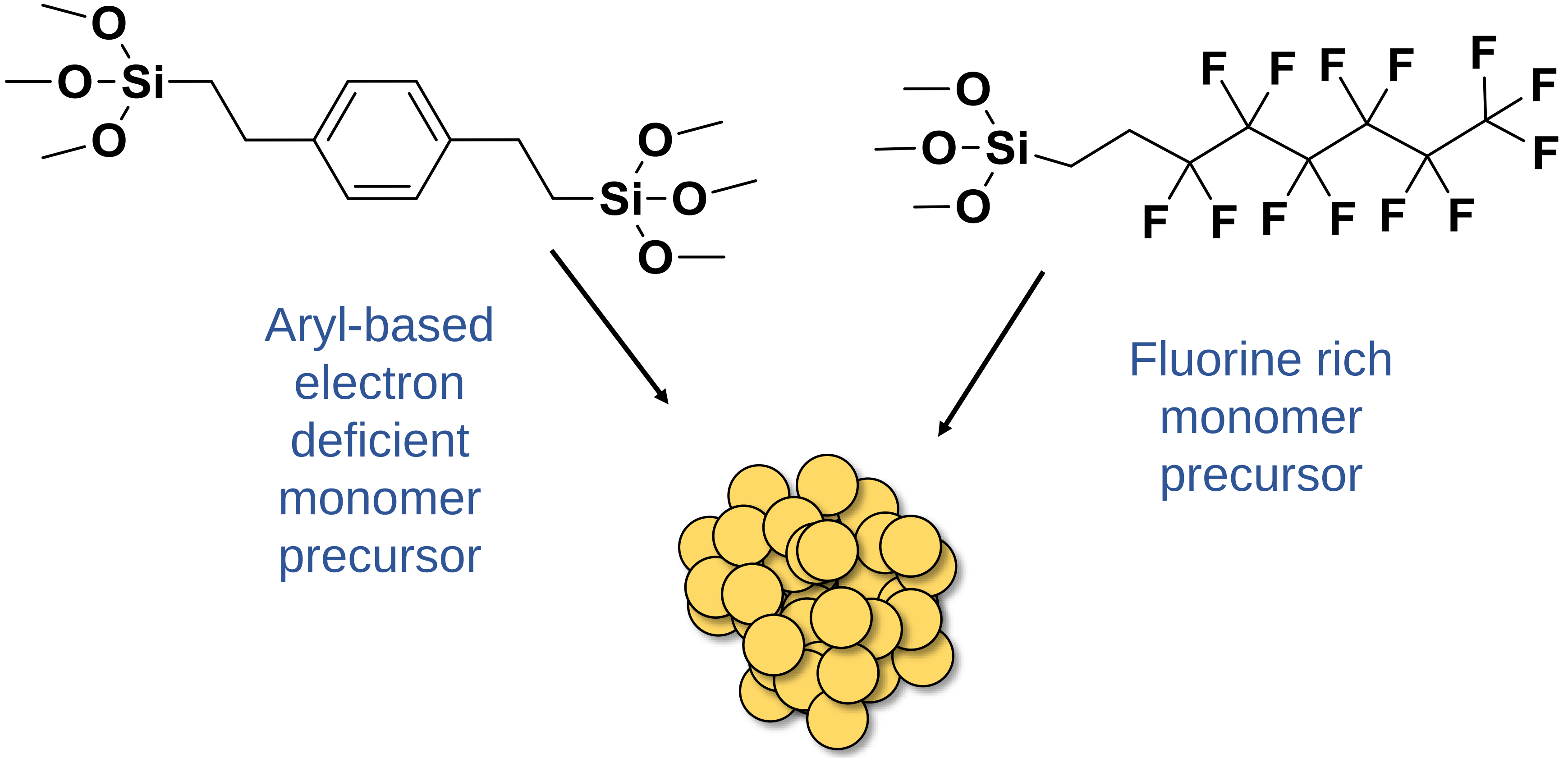


Sonolysis – Proof of Concept Testing



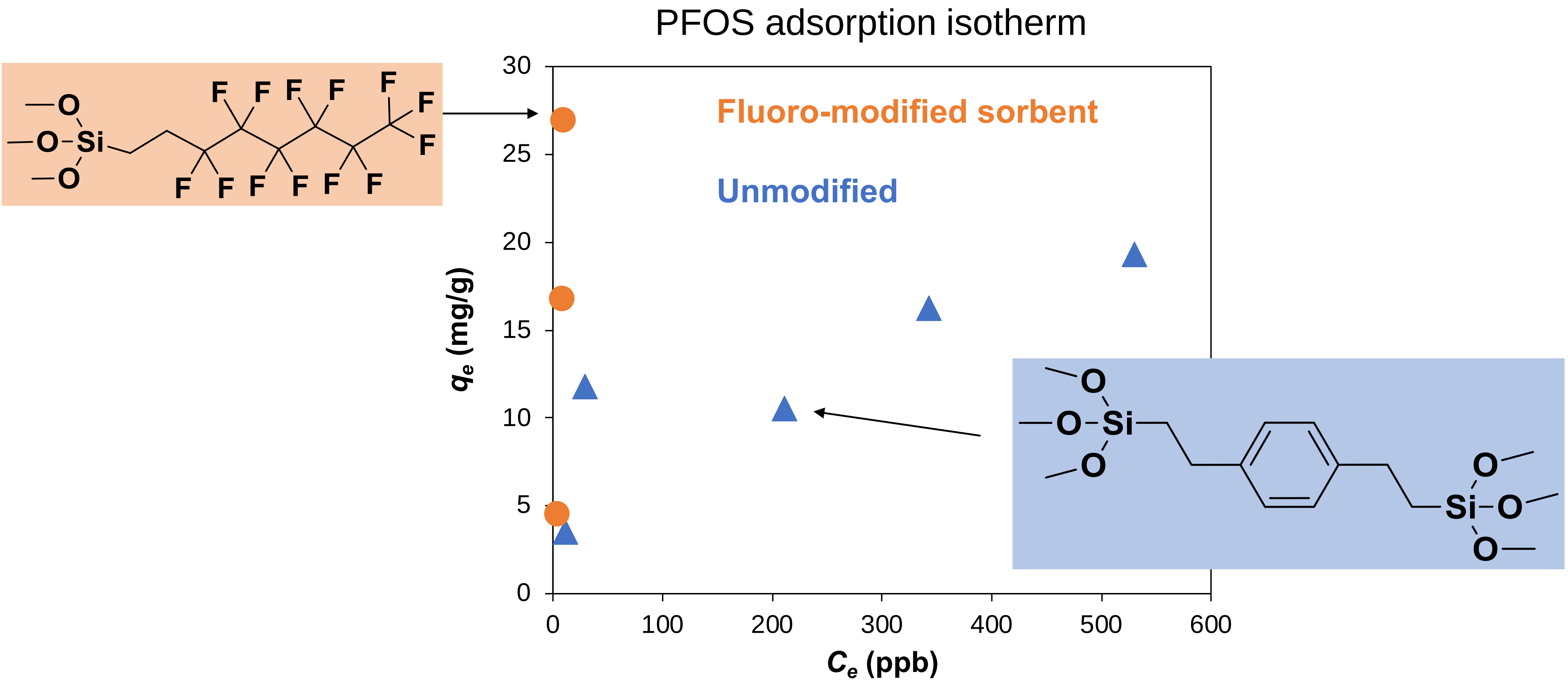
PFASs

Engineered Regenerable Sorbents to Selectively Remove PFASs SERDP Research 2018



Silica-based porous solids with aryl and fluoro groups will lead to effective adsorption sites for PFASs by **interaction with the the fluoroalkyl chain**.

Engineered Regenerable Sorbents to Selectively Remove PFASs SERDP Research 2018



RESULTS: PFOS ADSORPTION ISOTHERM (90 BTEB / 10 TDF-TMS)

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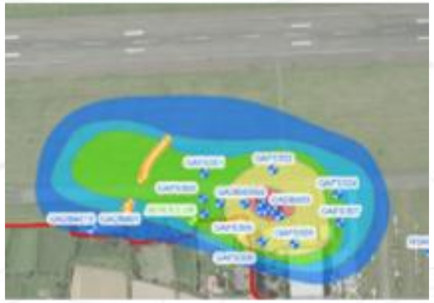
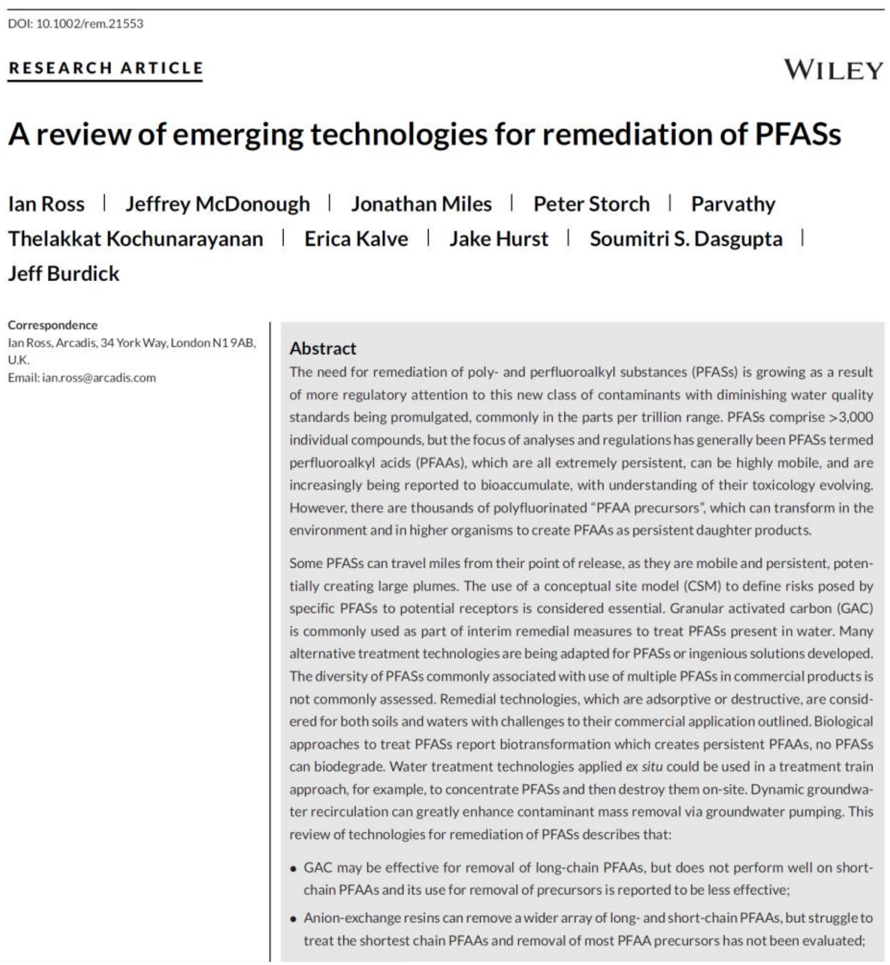
Summary

- Significant press attention & public concern on PFASs as a result of impacts to drinking water
- Significant decreases in drinking water standards globally
- Site assessment with TOP assay redefines the PFASs CSM
- How to apply the precautionary principle to be protective of human health & the environment, proportionate and sustainable?
- Risk based contaminated site management essential
- Emerging remedial technologies provide ingenious solutions for PFASs



PFASs

Some Recent Publications



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RESEARCH ARTICLE WILEY

A review of emerging technologies for remediation of PFASs

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Abstract

The need for remediation of poly- and perfluoroalkyl substances (PFASs) is growing as a result of more regulatory attention to this new class of contaminants with diminishing water quality standards being promulgated, commonly in the parts per trillion range. PFASs comprise >3,000 individual compounds, but the focus of analyses and regulations has generally been PFASs termed perfluoroalkyl acids (PFAAs), which are all extremely persistent, can be highly mobile, and are increasingly being reported to bioaccumulate, with understanding of their toxicology evolving. However, there are thousands of polyfluorinated "PFAA precursors", which can transform in the environment and in higher organisms to create PFAAs as persistent daughter products.

Some PFASs can travel miles from their point of release, as they are mobile and persistent, potentially creating large plumes. The use of a conceptual site model (CSM) to define risks posed by specific PFASs to potential receptors is considered essential. Granular activated carbon (GAC) is commonly used as part of interim remedial measures to treat PFASs present in water. Many alternative treatment technologies are being adapted for PFASs or ingenious solutions developed. The diversity of PFASs commonly associated with use of multiple PFASs in commercial products is not commonly assessed. Remedial technologies, which are adsorptive or destructive, are considered for both soils and waters with challenges to their commercial application outlined. Biological approaches to treat PFASs report biotransformation which creates persistent PFAAs, no PFASs can biodegrade. Water treatment technologies applied *ex situ* could be used in a treatment train approach, for example, to concentrate PFASs and then destroy them on-site. Dynamic groundwater recirculation can greatly enhance contaminant mass removal via groundwater pumping. This review of technologies for remediation of PFASs describes that:

- GAC may be effective for removal of long-chain PFAAs, but does not perform well on short-chain PFAAs and its use for removal of precursors is reported to be less effective;
- Anion-exchange resins can remove a wider array of long- and short-chain PFAAs, but struggle to treat the shortest chain PFAAs and removal of most PFAA precursors has not been evaluated;