

An aerial photograph of Pittsburgh, Pennsylvania, showing the city skyline with several prominent skyscrapers, the Allegheny River winding through the city, and a bridge crossing the river. The image is overlaid with a semi-transparent blue filter.

Will we ever have clean water again?

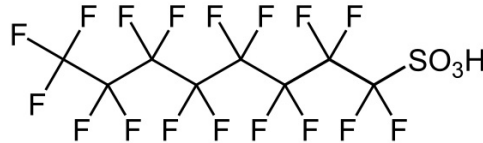
*PFAS and the challenge of mobile
persistent chemicals in water.*

A quick primer on PFAS

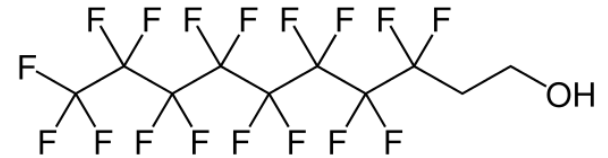
- Per and polyfluoroalkyl substances:



PFOA: C8 carboxylic acid



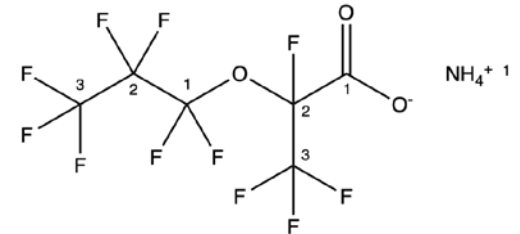
PFOS: C8 sulfonic acid



8:2 FTOH: fluorotelomer alcohol

- Digesting the acronym soup – key categories

- Long-chain (CF_n≥6) vs. short-chain (*)
- Transformable (“precursor” compounds)
- Emerging/replacement trends (short-chain, ethers)



GenX: ammonium salt of HFPO-DA

Beyond the usual suspects

The PFAS class is extremely diverse. Members from multiple sub-groups often used in a single products (e.g. AFFF).

Perfluoroalkyl acids and perfluoroalkylether acids (PFAA), e.g.

- perfluoroalkyl carboxylic acids (PFCA), $C_nF_{2n+1}-COOH$, e.g. PFOA
- perfluoroalkane sulfonic acids (PFSA), $C_nF_{2n+1}-SO_3H$, e.g. PFOS
- perfluoroalkyl phosphonic acids (PFPA), $C_nF_{2n+1}-PO_3H_2$
- perfluoroalkyl phosphinic acids (PFPIA), $(C_nF_{2n+1})(C_mF_{2m+1})-PO_2H$
- perfluoroalkylether carboxylic acids (PFCECA), e.g. $C_2F_5OC_2F_4OCF_2COOH$
- perfluoroalkylether sulfonic acids (PFESA), e.g. $C_6F_{13}OCF_2CF_2SO_3H$

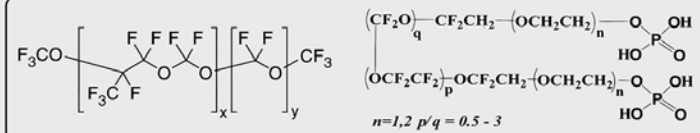
Precursors to PFAA, e.g.

- perfluoroalkane sulfonyl fluorides (PASF)
 - perfluoroalkanyl fluorides (PACF) and their derivatives, $C_nF_{2n+1}SO_2-R / C_nF_{2n+1}CO_2-R$
 - n:2 fluorotelomer-based substances $C_nF_{2n+1}CH_2CH_2-R$
 - per- and polyfluoroalkylether-based substances e.g. $C_nF_{2n+1}OC_mF_{2m+1}-R$
 - some hydrofluorocarbons (HFCs, e.g. $C_nF_{2n+1}-C_mH_{2m+1}$), hydrofluoroethers (HFEs, e.g. $C_nF_{2n+1}OC_mH_{2m+1}$) and hydrofluoroolefins (HFOs, e.g. $C_nF_{2n+1}-CH=CH_2$);
 - perfluoroalkyl ($C_nF_{2n+1}C(O)C_mF_{2m+1}$) and semi-fluorinated ($C_nF_{2n+1}C(O)C_mH_{2m+1}$) ketones;
 - perfluoroalkyl alcohols ($C_nF_{2n+1}OH$)
- side-chain fluorinated polymers e.g. (meth)acrylate, urethane, or oxetane polymers with non-fluorinated backbones and fluorinated side-chains
- non-polymers $R = NH, NHCH_2CH_2OH$, etc.

Fluoropolymers, e.g.

- polytetrafluoroethylene (PTFE), $-(CF_2CF_2)_n-$
- polychlorotrifluoroethylene (PCTFE), $-(CF_2CFCl)_n-$
- polyvinylidene fluoride (PVDF), $-(CF_2CH_2)_n-$
- fluorinated ethylene propylene (FEP), $-(CF_2CF_2)_n-(CF_2C(CF_3)F)_m-$

Perfluoropolyethers, e.g.

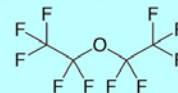


Other PFAS*, e.g.

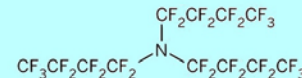
perfluoroalkanes, e.g.



perfluoroalkylethers, e.g.



perfluoroalkylamines, e.g.



* These PFAS have been less discussed in the public domain, but they meet the definition of PFAS as recommended in Buck et al. (2011) and OECD (2018). They are primarily PFAS with limited chemical reactivity.

Kwiatkowski et al.
2020 ESTL

Beyond the usual suspects

- We track a handful, but the PFAS universe is complex.

- Which are used where, in what quantity?
- Which “are” PFAS?

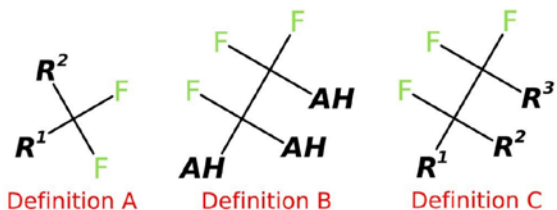


Figure 1: Schematic representation of the PFAS definitions A, B and C considered in this work. “AH” = hydrogen or any other atom; R¹, R², R³ represent any atom other than hydrogen.

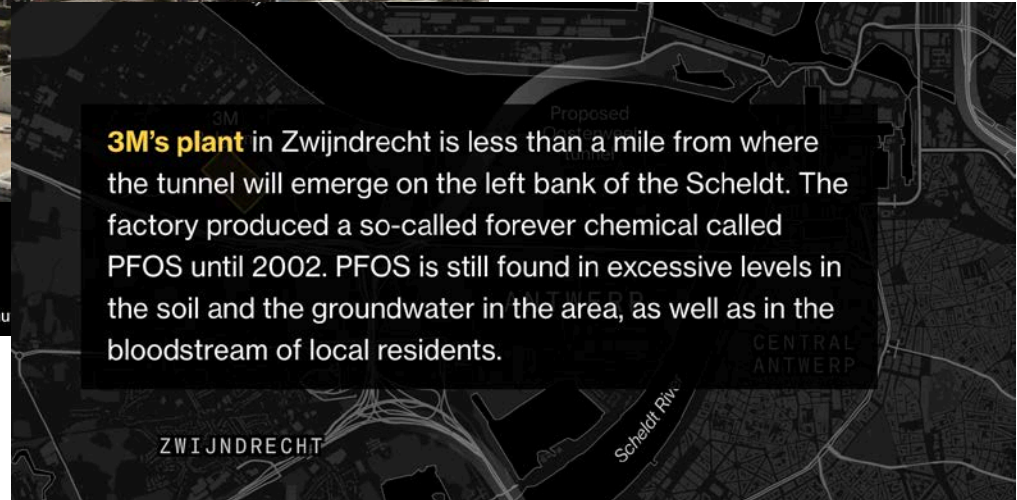
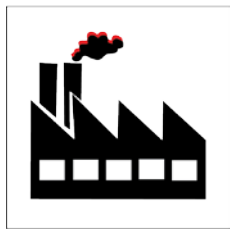
CORE: Aggregation of open access journal papers.

	Total	Not found in PFASMASTER (10,782 InChI)	Found in PFASMASTER (10,782 InChI)	Found in OECDPFAS (3,741 InChI)	Not found in PubChem*
CORE Definition A	27,058	25,446	1,612 (1686 IKFB)	944 (988 IKFB)	7,119
CORE Definition B	4,139	2,652	1,487	939	1,175
CORE Definition C	3,457	2,095	1,362	931	915
Patents Definition A	1,783,651	1,780,041	3,610	1,529	216,777
Patents Definition B	75,108	71,818	3,290	1,520	10,809
Patents Definition C	34,197	32,564	1,633	847	4,882

*Prior to deposition of the entire dataset to PubChem, to fill these gaps.

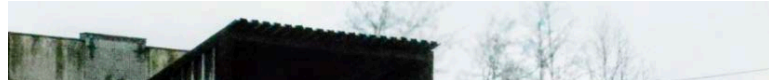
Barnabas, et al. Digital Discovery, 2022, DOI: 10.1039/D2DD00019A

How PFAS gets into our water



Direct releases from industrial activities.

How PFAS gets into our water



State investigating contamination at fire training center

March 30, 2022 5:33 pm



The **Fire Training Center** was placed on the State's Superfund site due to **water contamination from poly- and perfluoroalkyl substances, known as PFAS, which are chemicals used in firefighting applications.** The State says that the site presents a significant threat to public health and/or the environment.



Groundwater contamination.

At least 12 military bases contaminating water supply with toxic PFAS

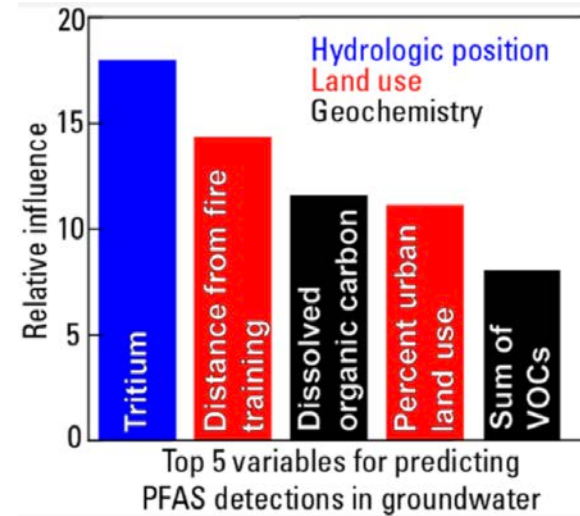
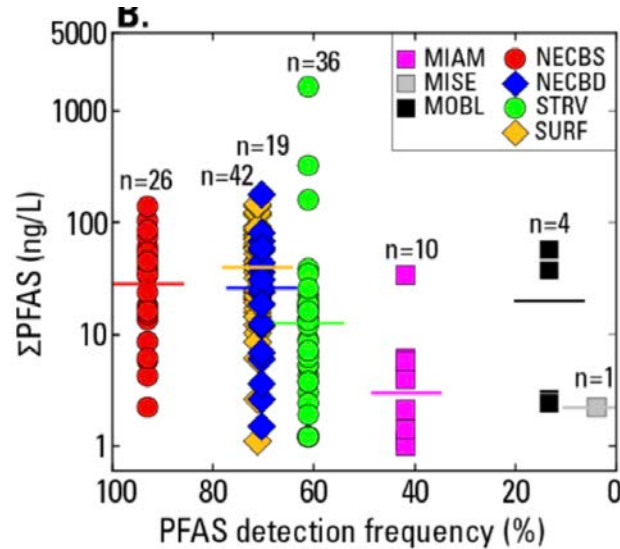
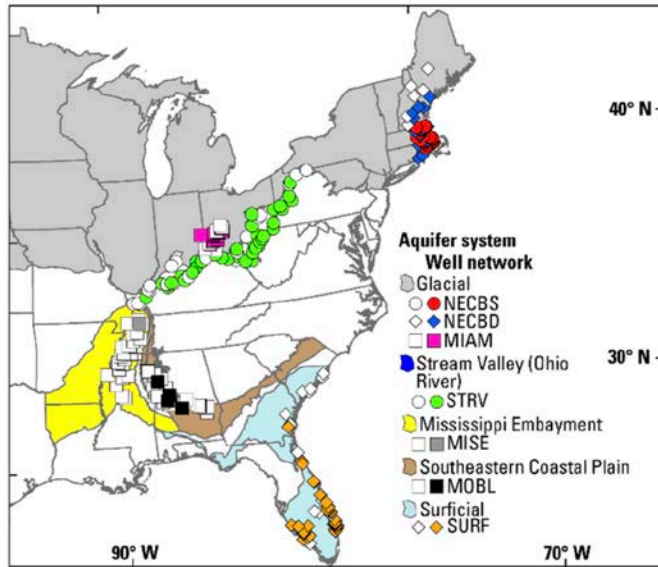
Testing by the Department of Defense revealed dangerous levels of the contaminants, drawing concern from public health advocates



PFAS are a class of about 9,000 chemicals used to make products resistant to water, stains and dirt. Photograph: Jake May/AP

Dangerous levels of toxic PFAS are contaminating water supplies in areas around at least 12 military bases, new Department of Defense testing has revealed, drawing concern from public health advocates that the DoD is not doing enough to protect the public.

How PFAS gets into our water



McMahon et al. *ES&T* 2022 56 (4), 2279-2288

How PFAS gets into our water

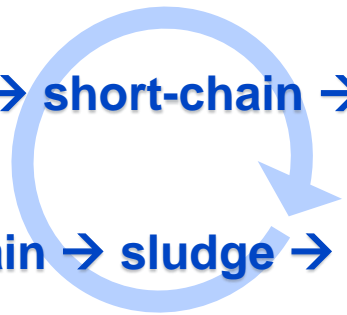


Distribution and fate of per- and polyfluoroalkyl substances (PFAS) in wastewater treatment facilities†

Elham Tavasoli,^{ab} Jenna L. Luek,^{id}^a James P. Malley Jr.^{id}^a and Paula J. Mouser.^{id}^{*a}

Precursors → short-chain → effluent

Long-chain → sludge → land



Wastewater effluent and solid waste.

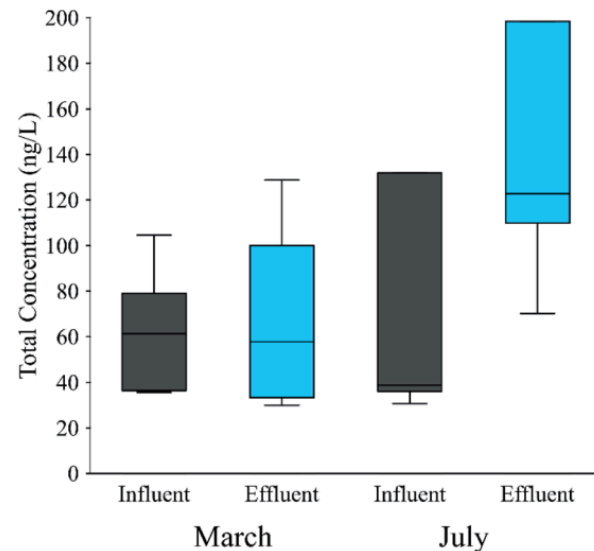


Fig. 2 Boxplot of influent and effluent Σ PFAS concentrations from all WWTFs by sampling month (March $n = 6$, July $n = 4$). Box indicates 25th to 75th percentile with median, whiskers indicate maximum and minimum values.

How PFAS gets into our water



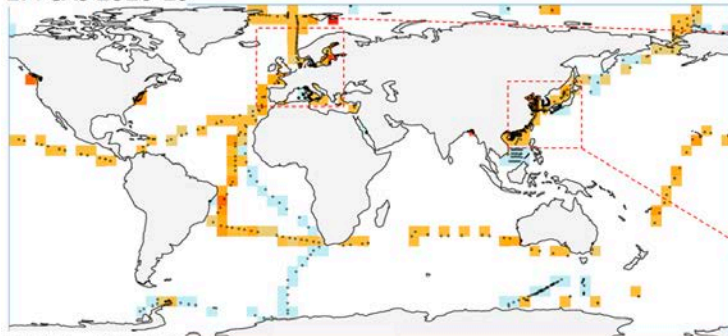
Rainwater in parts of US contains high levels of PFAS chemical, says study

Levels high enough to potentially impact human health and trigger regulatory action, which only targets two of 4,700 variants

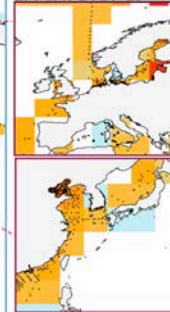


Global distribution means there is no avoiding PFAS.

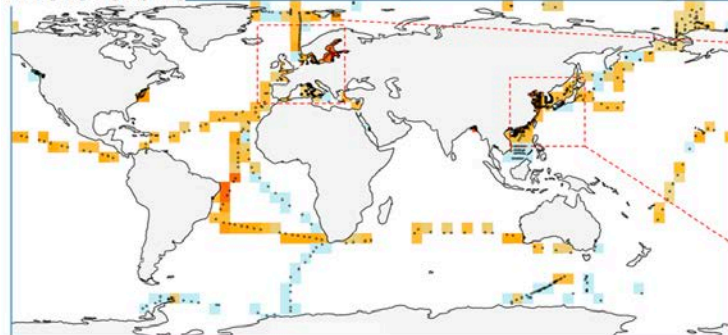
ΣPFCA_s 2010-19



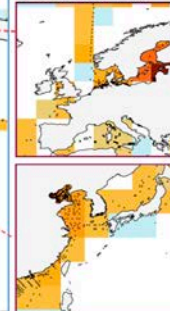
ΣPFCA_s 2010-19



ΣPFSA_s 2010-19



ΣPFSA_s 2010-19



Median concentration [ng/L]

< MDL

0 - 0.01

0.01 - 0.05

0.05 - 0.1

0.1 - 0.2

0.2 - 0.5

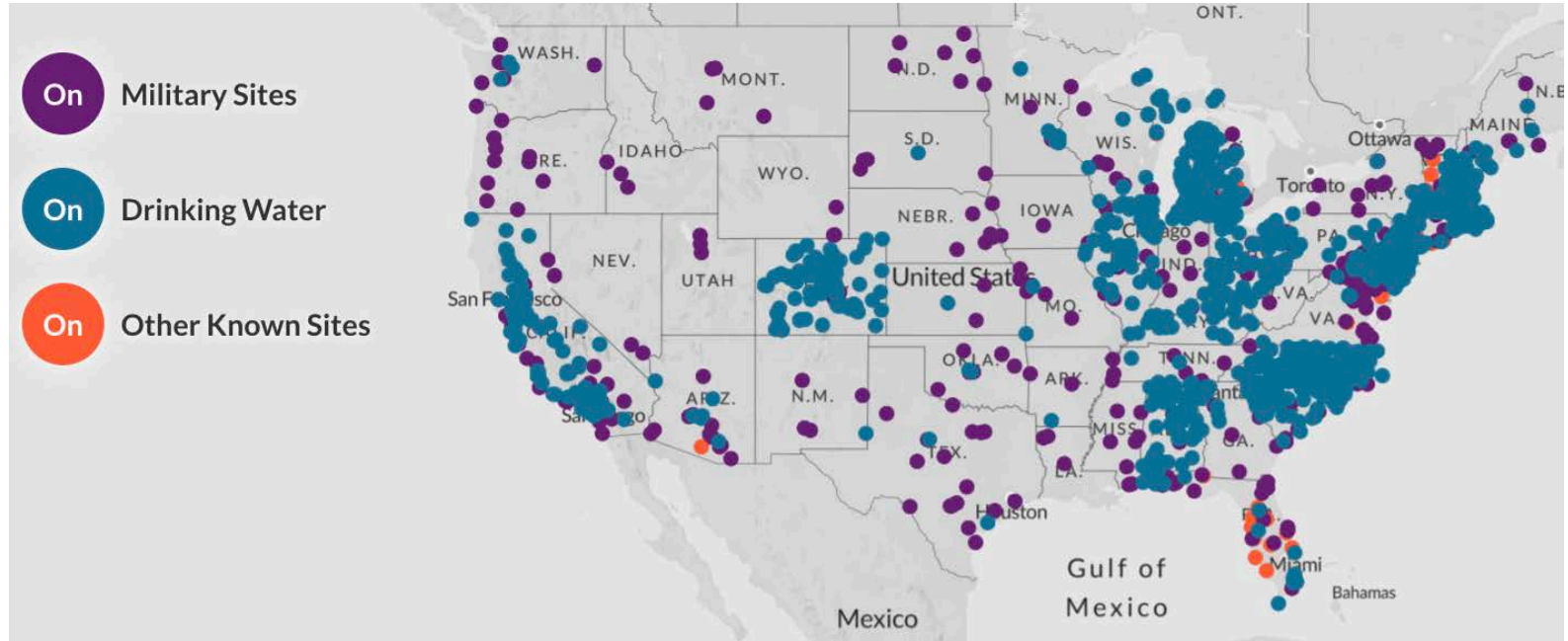
0.5 - 1.5

1.5 - 3

3 - 6

○ Site location ● stacked

In other words, PFAS are everywhere.



https://www.ewg.org/interactive-maps/pfas_contamination/map/

A surprising(?) Pittsburgh example

Part of McKeesport under water advisory

July 19, 2021 Mon Valley Independent Latest News



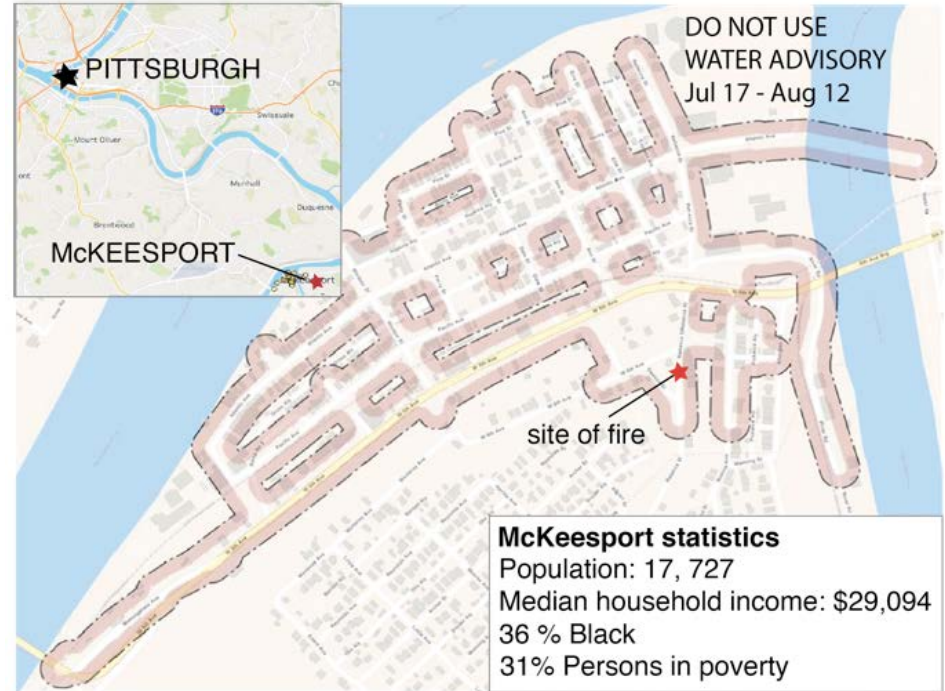
Friday's fire at McKeesport Auto Body has resulted in a water advisory being issued for a portion of the city.

Facebook 0 Tweet 0

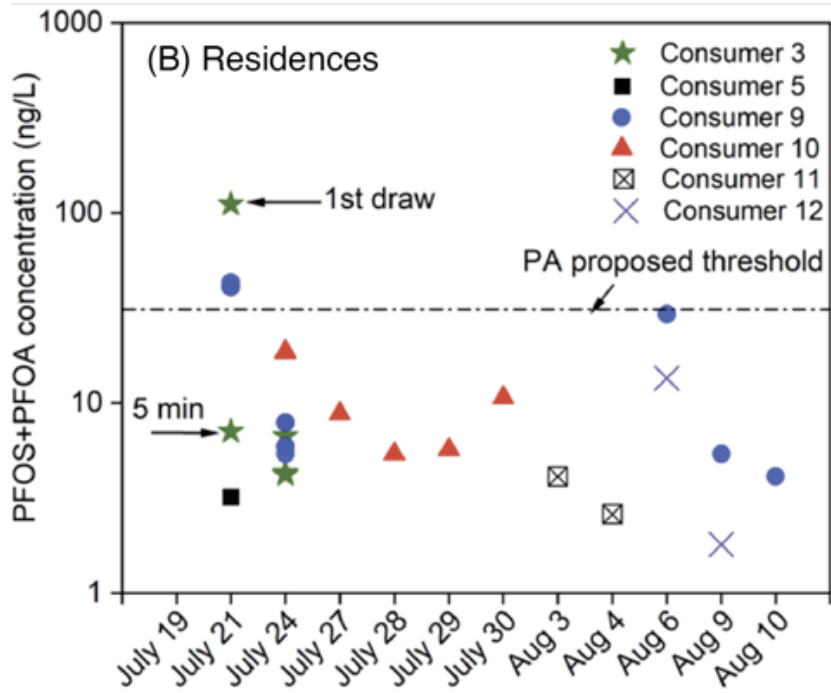
By TAYLOR BROWN

tbrown@yourmvi.com

Residents of the Lower 10th Ward in McKeesport are being asked not to use their tap water as a result of a fire in the city Friday.

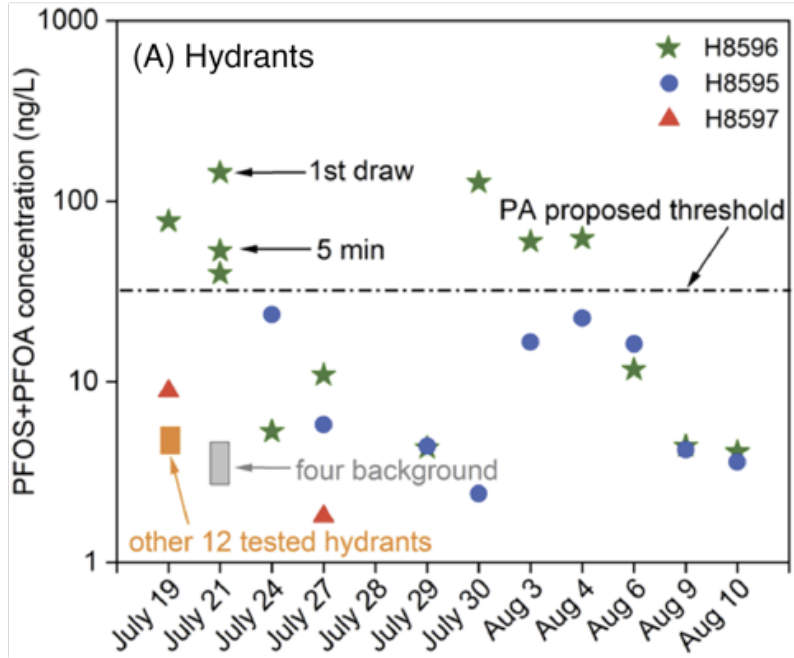


McKeesport Auto Body fire



- Testing conducted on behalf of water authority indicated varying levels, lack of consistent sampling.
- Set of targeted PFAS not necessarily appropriate for AFFF contamination.

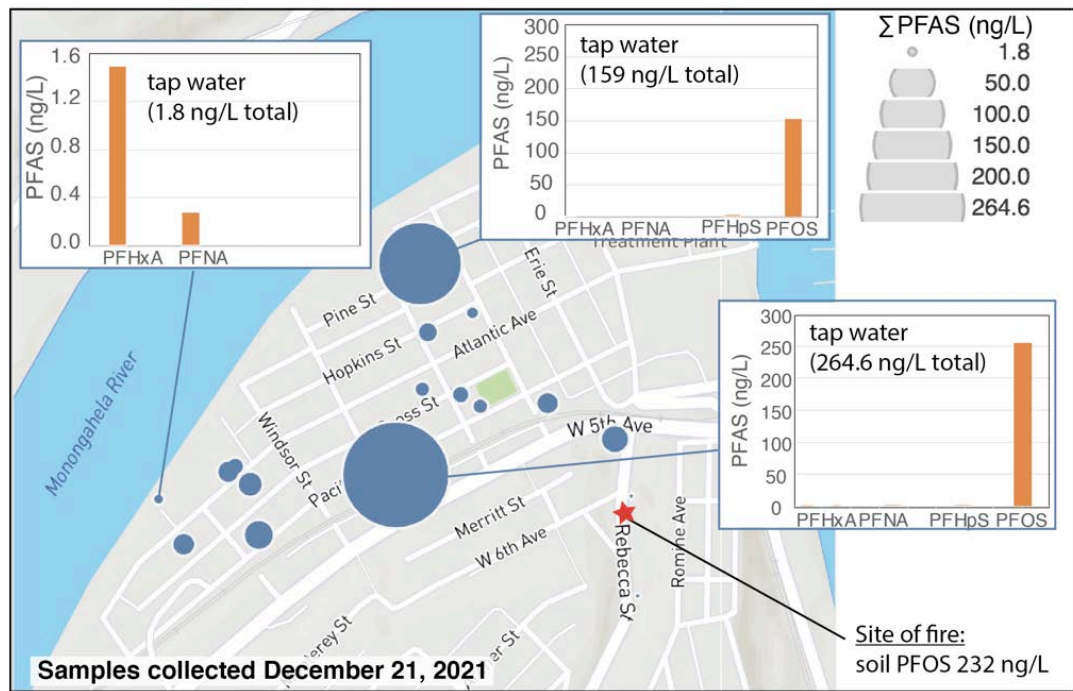
McKeesport Auto Body fire



- Hydrants were a main target of sampling as they were direct reports on levels in the distribution system.
- To our knowledge, no monitoring of environmental fate was carried out.

Drinking water, six months later

- Working with Women for a Healthy Environment (WHE), sampled drinking water across the affected part of the community.
- Tested for long- and short-chain perfluoroalkyl acids.
- Two households had one high sample each, dominated by PFOS (>150 ng/L).
- PFOS was still high in soil around fire site (232 ng/L).



What can be said of the surrounding landscape?

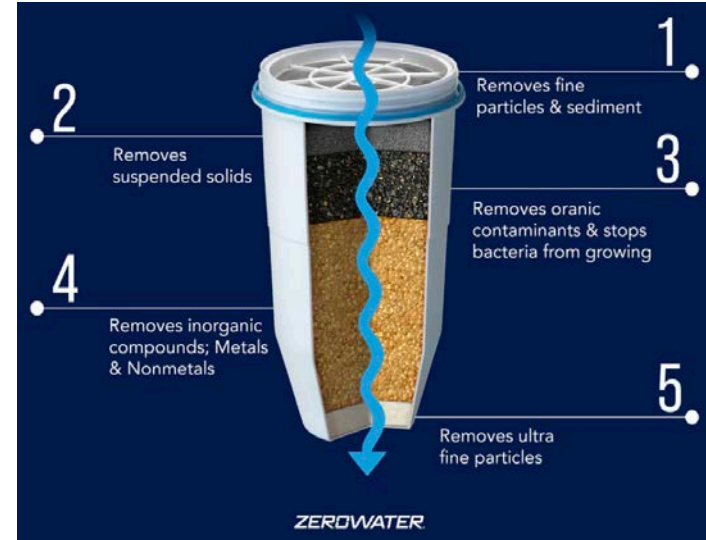
- The primary strategy to clear PFAS contamination in the distribution system was flushing of affected hydrants.
- In one case a hydrant had to be replaced because of persistent contamination.
- Where did the flushed PFAS go?



Treatment options ...

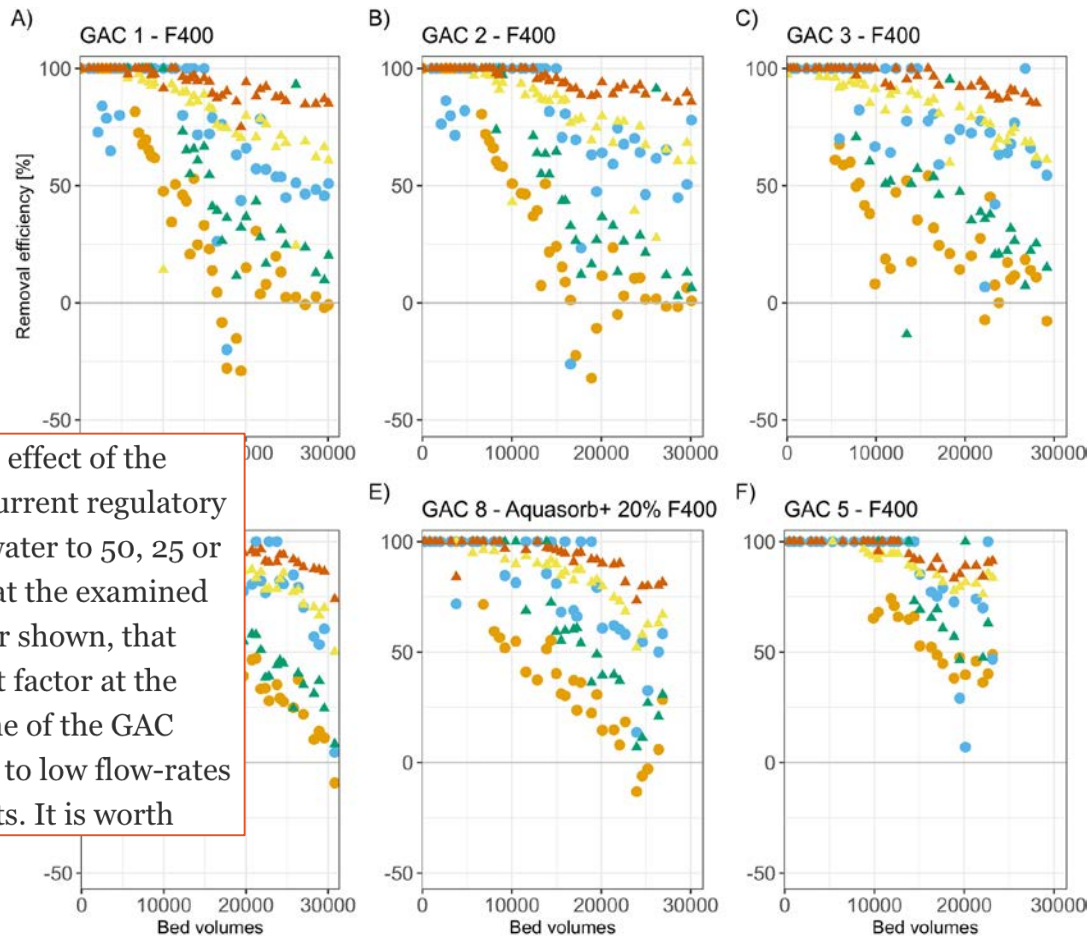
- At McKeesport, active community members working with WHE distributed pitcher filters to provide ongoing water treatment after the advisory was lifted.
- Filters that use a combination of activated carbon and ion exchange show better performance than carbon alone and are effective at removing long-chain PFAS like PFOS.
- Over the next two years, we will be using water, filters and soils to understand the fate and transport of this AFFF spill.

WOMEN
for a Healthy
ENVIRONMENT



Treatment options ...and limitations

A subsequent cost analysis indicated an overwhelming effect of the treatment goals on unit cost. A decrease of Sweden's current regulatory guidelines of accepted 90 ng L^{-1} in finished drinking water to 50, 25 or even 10 ng L^{-1} would increase annual operations cost at the examined DWTP by 21, 135 and 314%, respectively. It was further shown, that regeneration cost is the dominant PFAS treatment cost factor at the Bäcklösa DWTP. Prolonging the overall service life time of the GAC filters by adopting a operations strategy of adjustment to low flow-rates at the end of service life could decrease operations costs. It is worth



Where the policy landscape is taking us

Environmental Toxicology and Chemistry—Volume 40, Number 3—pp. 550–563, 2021

Received: 31 May 2020 | Revised: 19 August 2020 | Accepted: 20 August 2020

550

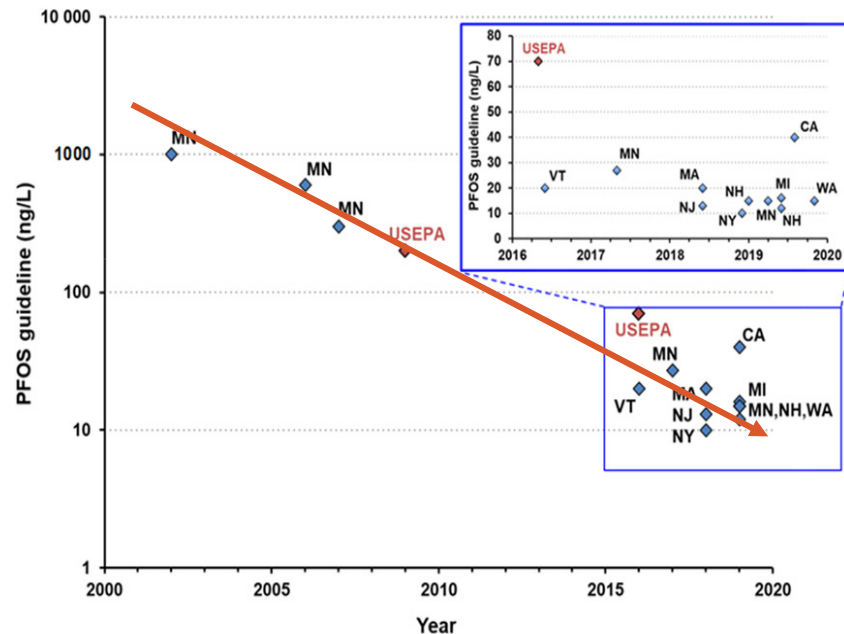
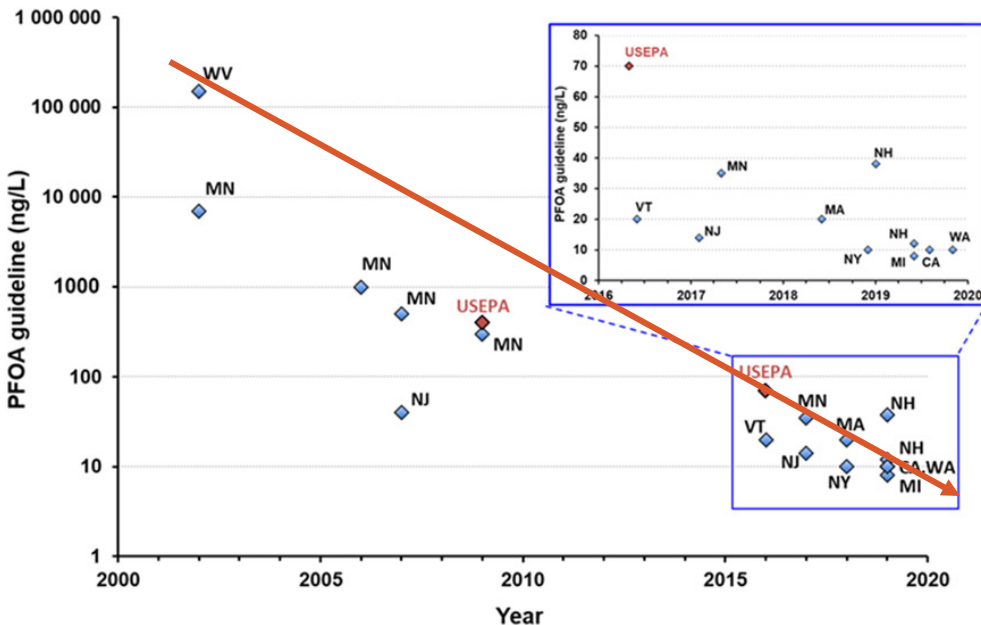
Critical Review

Recent US State and Federal Drinking Water Guidelines for Per- and Polyfluoroalkyl Substances

Gloria B. Post*

New Jersey Department of Environmental Protection, Trenton, New Jersey, USA

Where the policy landscape is taking us

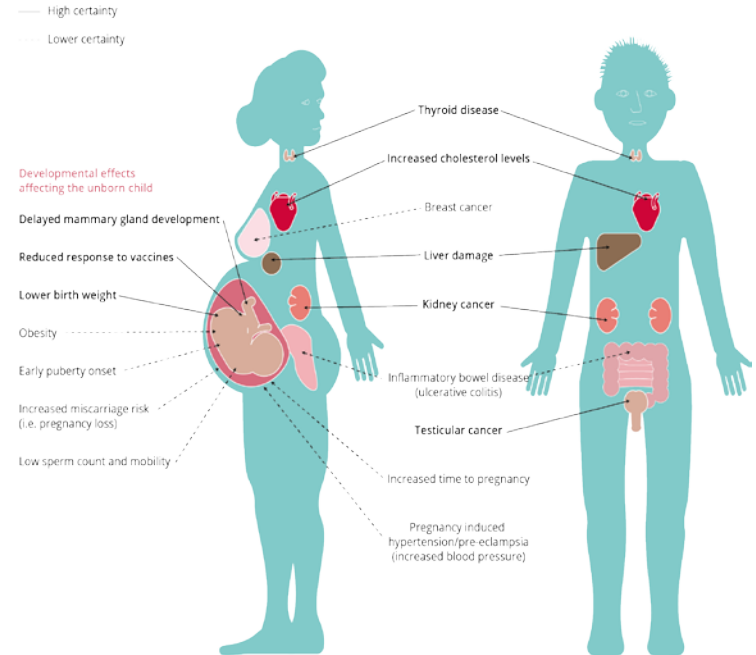


Other PFAS are added (state-by-state basis) including short-chain PFAS.

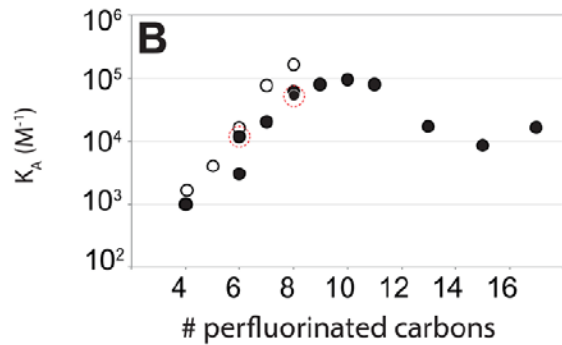
The search for novel sorbents

- What can be done about short-chain PFAS?
- Reverse osmosis is effective but expensive and energy intensive.
- GAC/IX are less effective and require regeneration/disposal of large volumes.

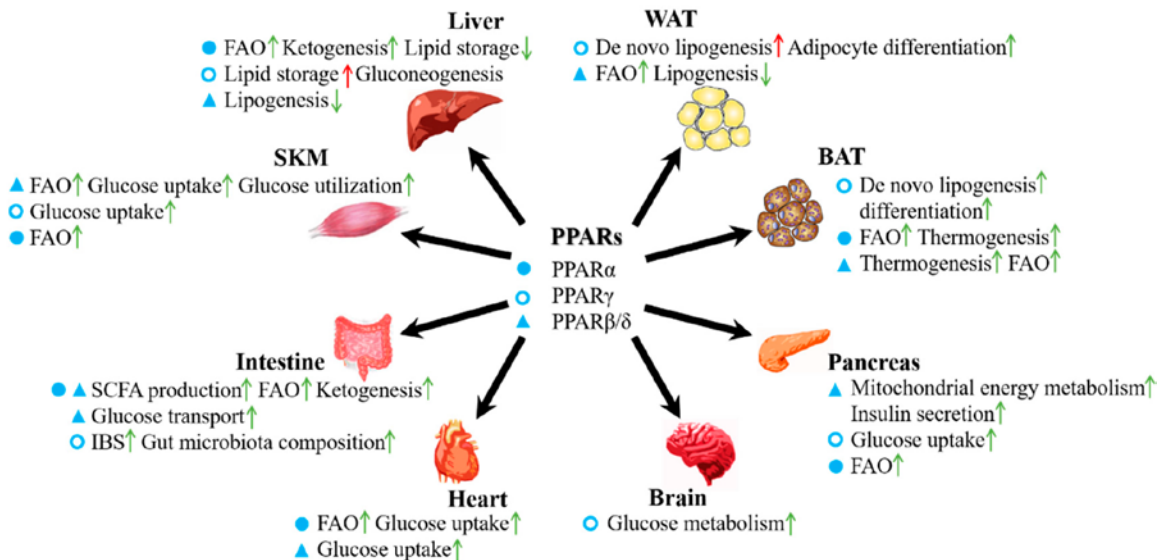
Toxicology: Problem... and clue to solution?



Proteins as biological sorbents

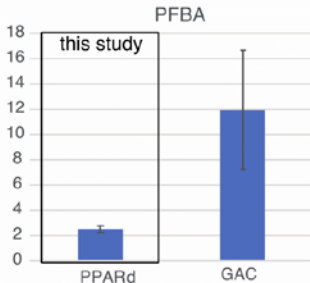
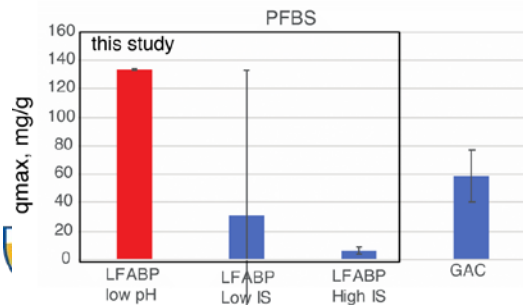
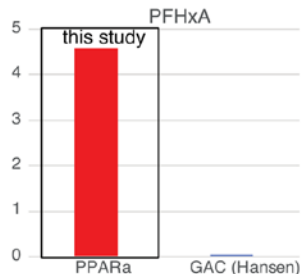
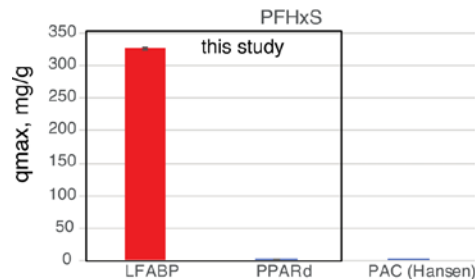
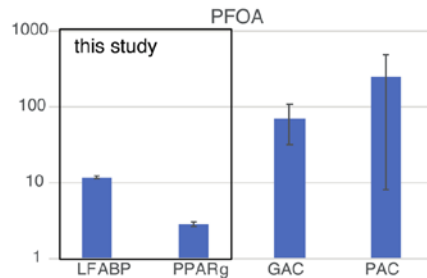
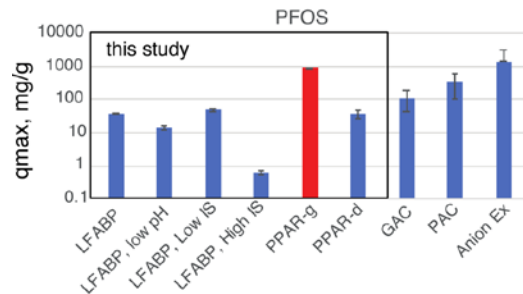


Some PFAS bioaccumulate due to binding to proteins like FABP and serum albumin.



Short-chain PFAS are less bioaccumulative, but their toxic impacts indicate they may still have strong interactions with specific receptors.

Proteins as biological sorbents



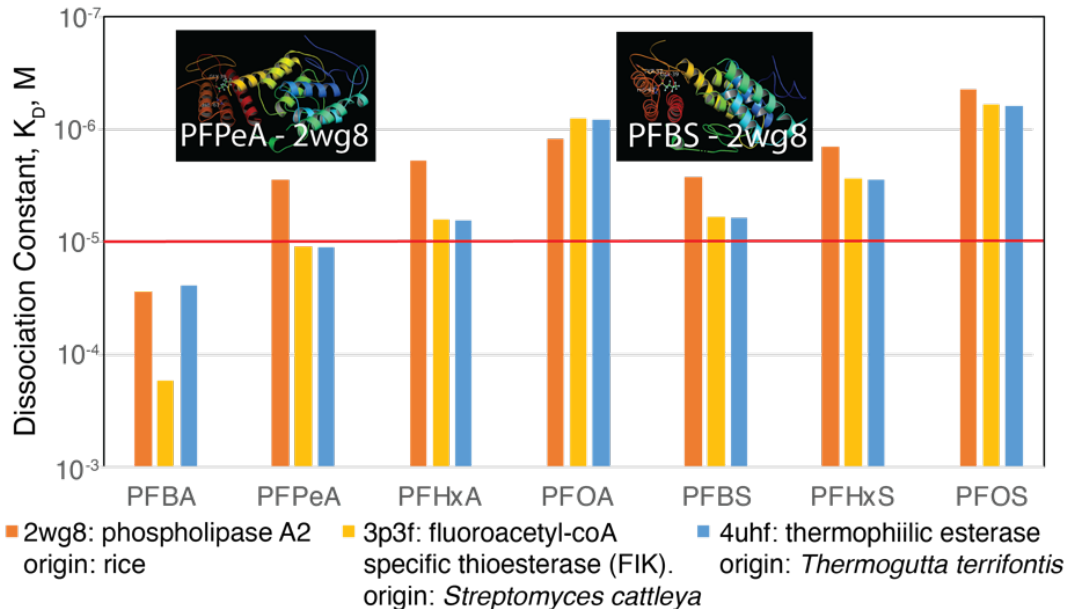
Proteins evaluated by dialysis compare favorably with activated carbon, particularly for short-chain PFAS.

We found better performance for PFHxS, PFHxA and PFBS.

PPAR- γ at least as good as anion exchange, better than activated carbon for PFOS.

The bad news: Implications for toxicity?

Using molecular modeling to screen for potential sorbents



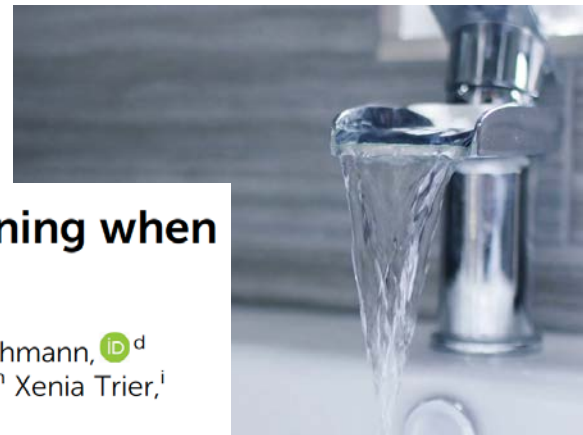
We use a combination of protein database screening with molecular docking simulations to identify potential sorbents.

Screening criteria are relevant endogenous ligands, small size, and potential for ease of extraction or production.

Next phase: Complementary in vitro methods for evaluation of binding affinity, column studies.

First, do no harm: the need to turn off the PFAS tap.

Even with these strategies, we will not solve the major issue with these chemicals: their ***extreme persistence***.



Cite this: DOI: 10.1039/c9em00163h

The concept of essential use for determining when uses of PFASs can be phased out

Ian T. Cousins,^{†*}^a Gretta Goldenman,^b Dorte Herzke,^c Rainer Lohmann,^d Mark Miller,^e Carla A. Ng,^f Sharyle Patton,^g Martin Scheringer,^h Xenia Trier,ⁱ Lena Vierke,^j Zhanyun Wang^k and Jamie C. DeWitt^l



Cite this: *Environ. Sci.: Processes Impacts*, 2019, 21, 781

Why is high persistence alone a major cause of concern?

Ian T. Cousins,^a Carla A. Ng,^b Zhanyun Wang^c and Martin Scheringer^{*d}

Questions?

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