

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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Ground Water and Drinking Water

Drinking Water Health Advisories for PFOA and PFOS

Health Advisories

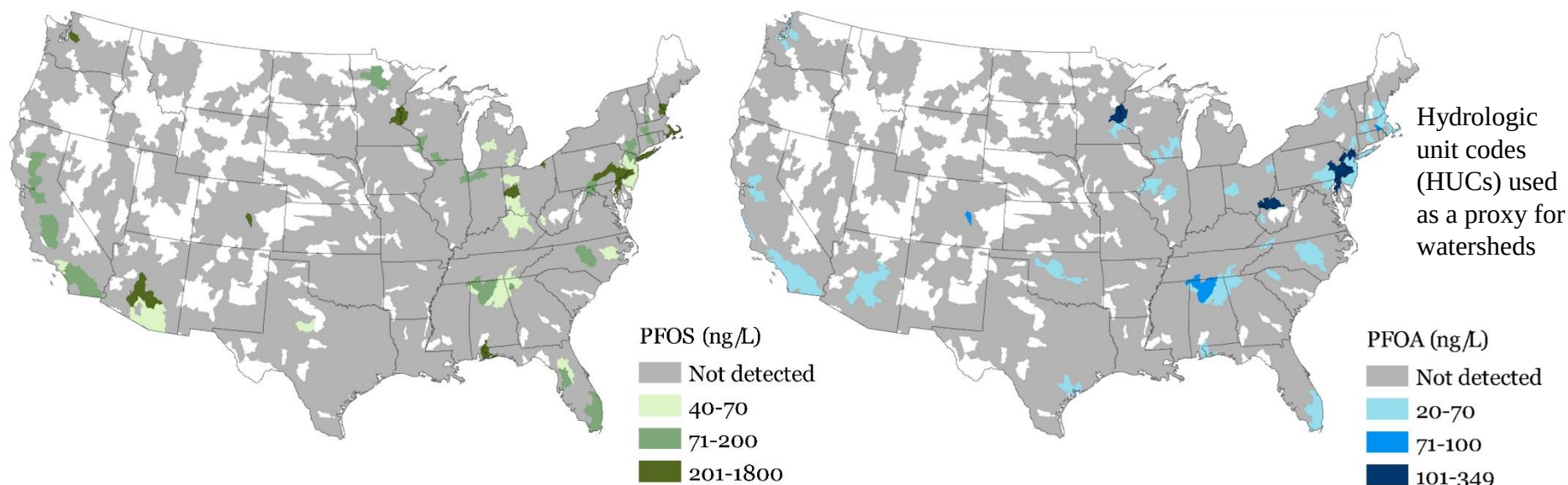
EPA has established health advisories for PFOA and PFOS based on the agency's assessment of the latest peer-reviewed science to provide drinking water system operators, and state, tribal and local officials who have the primary responsibility for overseeing public water systems, with information on the health risks of these chemicals so they can take the appropriate actions to protect their residents. EPA is committed to supporting states and public water utilities to determine the appropriate steps to reduce exposure to PFOA and PFOS in drinking water. As science on health effects of these chemicals evolves, EPA will continue to evaluate new information.

To provide Americans, including the most sensitive populations, with lifetime of exposure to PFOA and PFOS from drinking water, EPA has established advisory levels at 70 parts per trillion.

> What's a health advisory?

PFOA	70 ng/L
PFOS	70 ng/L
PFOA + PFOS	70 ng/L

A national issue? UCMR 3 Data



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Letter

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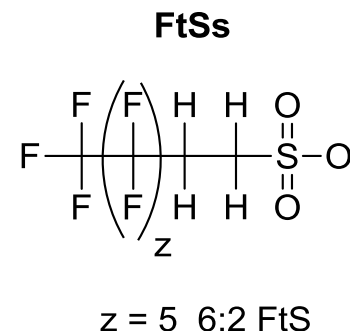
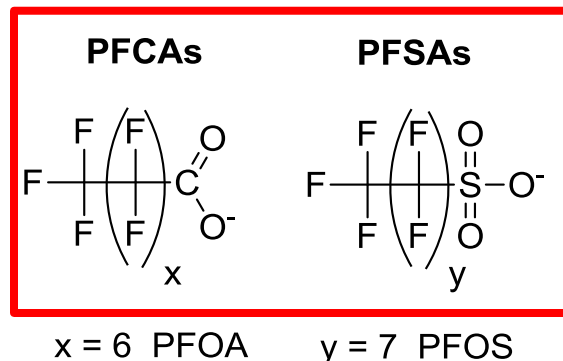
Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants

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Composition at AFFF-impacted Sites

Perfluoroalkyl acids
(PFAAs) present

- Some presumed PFAA precursors



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Discovery of 40 Classes of Per- and Polyfluoroalkyl Substances in Historical Aqueous Film-Forming Foams (AFFFs) and AFFF-Impacted Groundwater

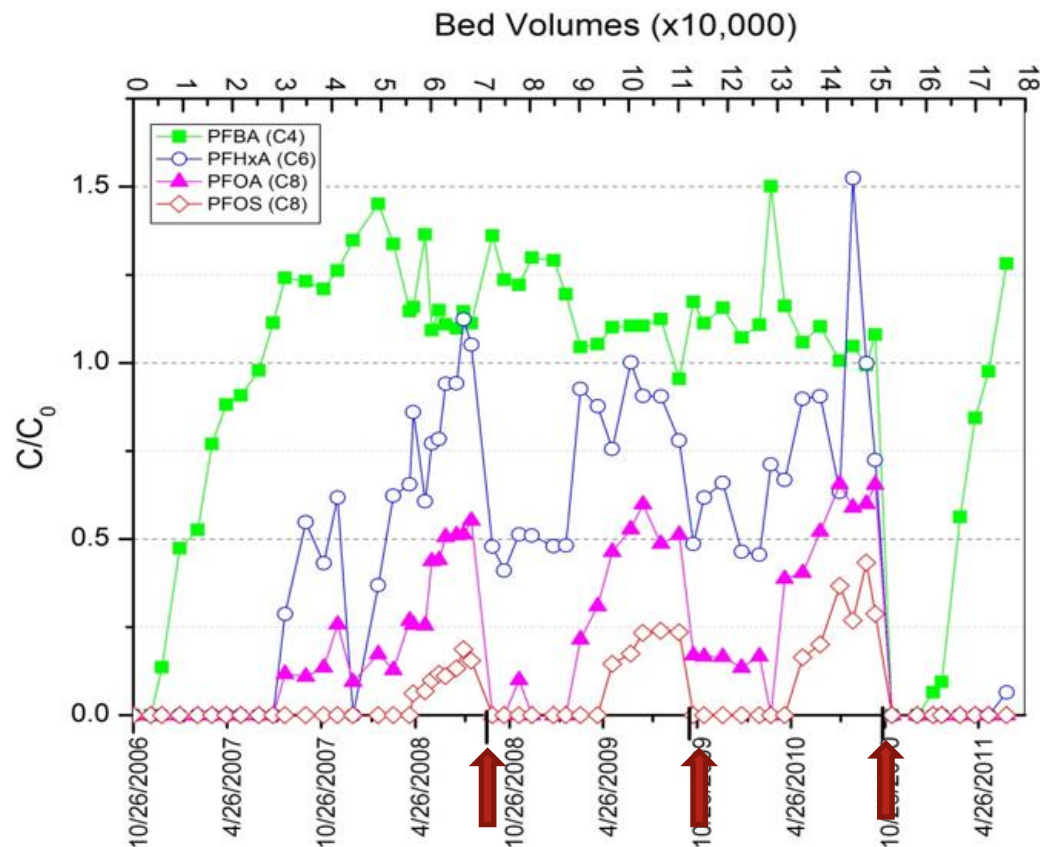
Krista A. Barzen-Hanson,[†] Simon C. Roberts,^{∇,‡} Sarah Choyke,[§] Karl Oetjen,[‡] Alan McAlees,^{||} Nicole Riddell,^{||} Robert McCrindle,[⊥] P. Lee Ferguson,[§] Christopher P. Higgins,^{*,‡} and Jennifer A. Field^{*,#}

GAC Performance for PFASs

Most utilities facing
PFOS/PFOA above HALs
are installing GAC

Horsham Township Council members inspect new water filter

A press release from Horsham Township Mar 29, 2017 Updated Mar 30, 2017



HORSHAM >> Horsham Township Council members conducted their inspection of the newly constructed granular activated carbon filter (GAC) at Well 26. They were accompanied by Horsham Water and Sewer Authority (HWSA) and township staff.

The new GAC filter will remove PFOA and PFOS from the water. Well 26 is back in service and providing filtered water to the community.

"I am very pleased that Well 26 is now providing safe, filtered...

Study Objectives

1. Evaluate what other PFASs are present in AFFF-impacted drinking water

Rationale: What's in AFFF and/or groundwater near a source zone is not necessarily what makes it to a drinking water well

2. Examine how well carbon-based treatment of an AFFF-impacted drinking water will work for these other PFASs

Rationale: Shorter-chain PFAAs exhibit earlier breakthrough, but limited data available on polyfluorinated PFASs

Study Approach

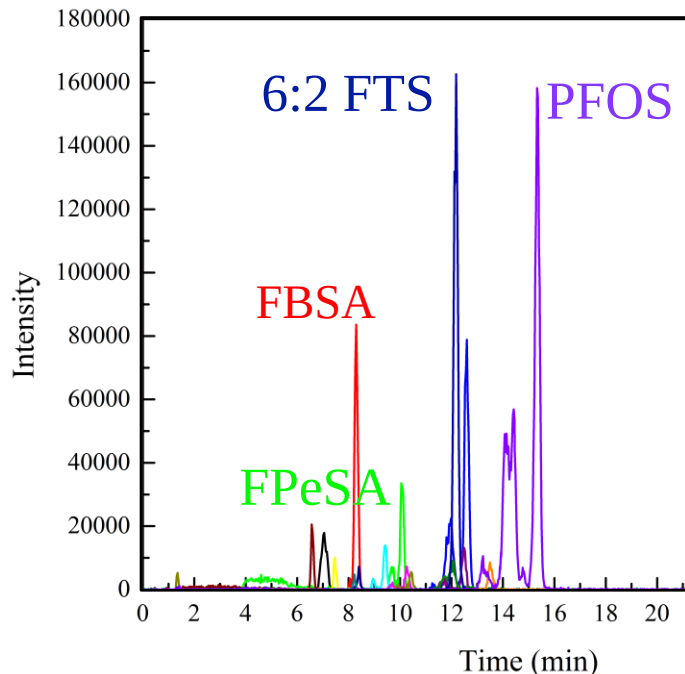
1. Evaluate what other PFASs are present in AFFF-impacted drinking water

Use newly developed LC-QToF-MS HRMS library to scan an AFFF-impacted drinking water supply for all known PFASs

2. Examine how well carbon-based treatment of an AFFF-impacted drinking water will work for these other PFASs

- 1) Develop equilibrium and kinetic parameters for PFASs present in the impacted drinking water
- 2) Use diffusion-limited model to predict PFAS breakthrough under simulated full-scale conditions

Results: PFASs present in water supply



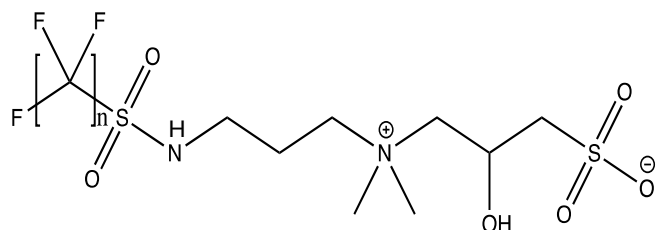
PFOS: 33 µg/L

PFOA: 11 µg/L

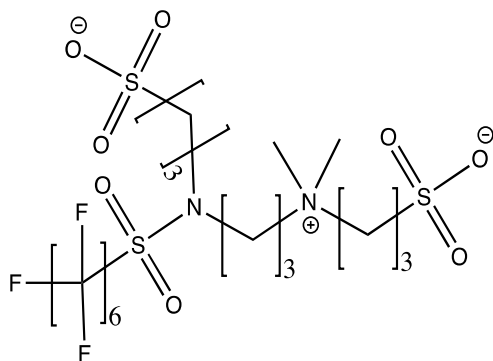
- PFASs only observed in ESI-LC-QToF-MS analysis
- 30 PFASs observed using HRMS library and/or authentic standards
 - 5 perfluorocarboxylates (C4-C8)
 - 6 perfluorosulfonates (C3-C8)
 - 2 fluorotelomer sulfonates (4:2 & 6:2)
 - 4 perfluoroalkyl sulfonamides (C3-C6)
 - 11 recently discovered polyfluorinated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

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

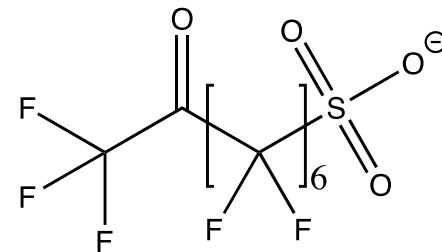
New PFASs observed



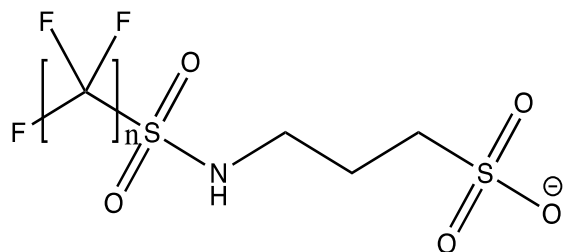
N-SHOPAmP-FASA (n=4,6)



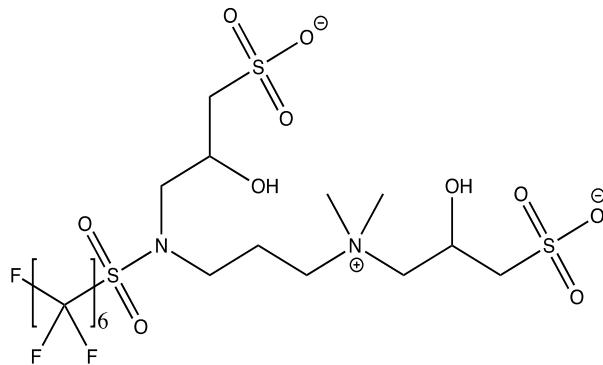
N-SPAmP-FHxSAPS



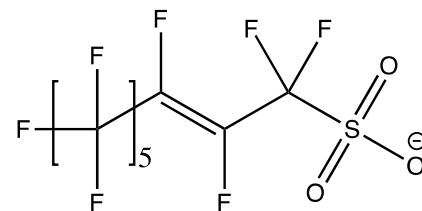
7K-PFOS



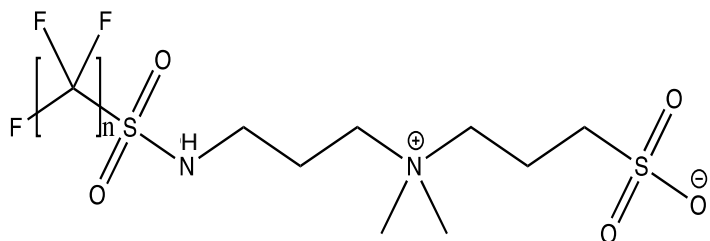
N-SPAmP-FASA (n=4,5,6)



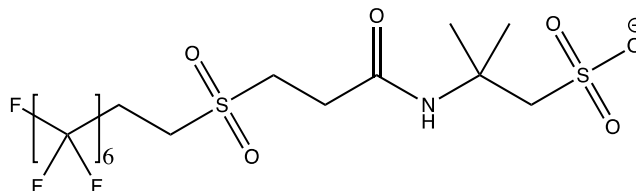
N-SHOPAmP-FHxSAHOPS



U-PFOS



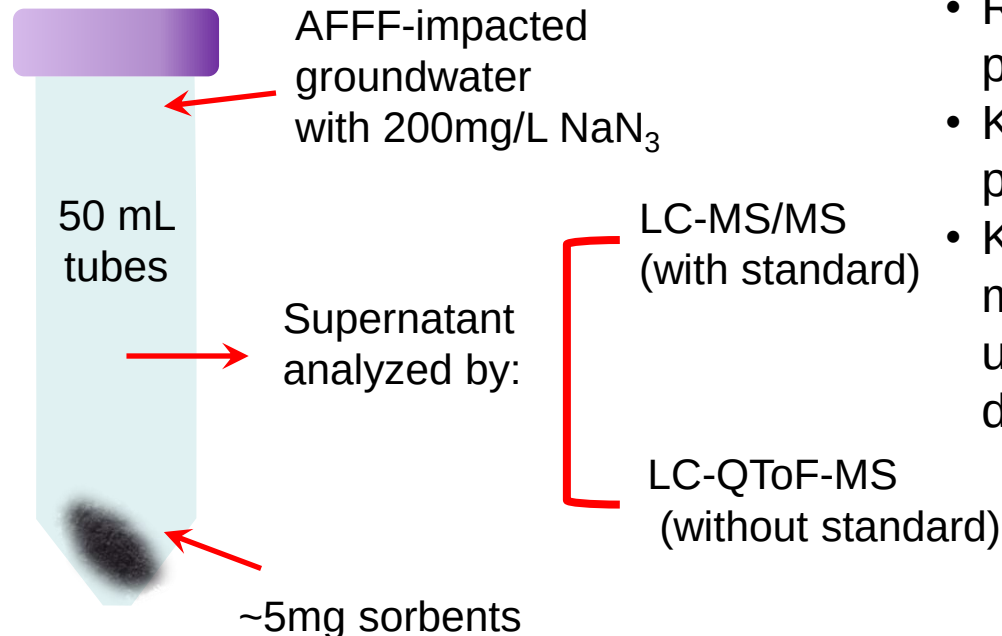
N-SP-FASA (n=4,5,6)



6:2 FHxSO₂PA-MePS

Approach for carbon tests

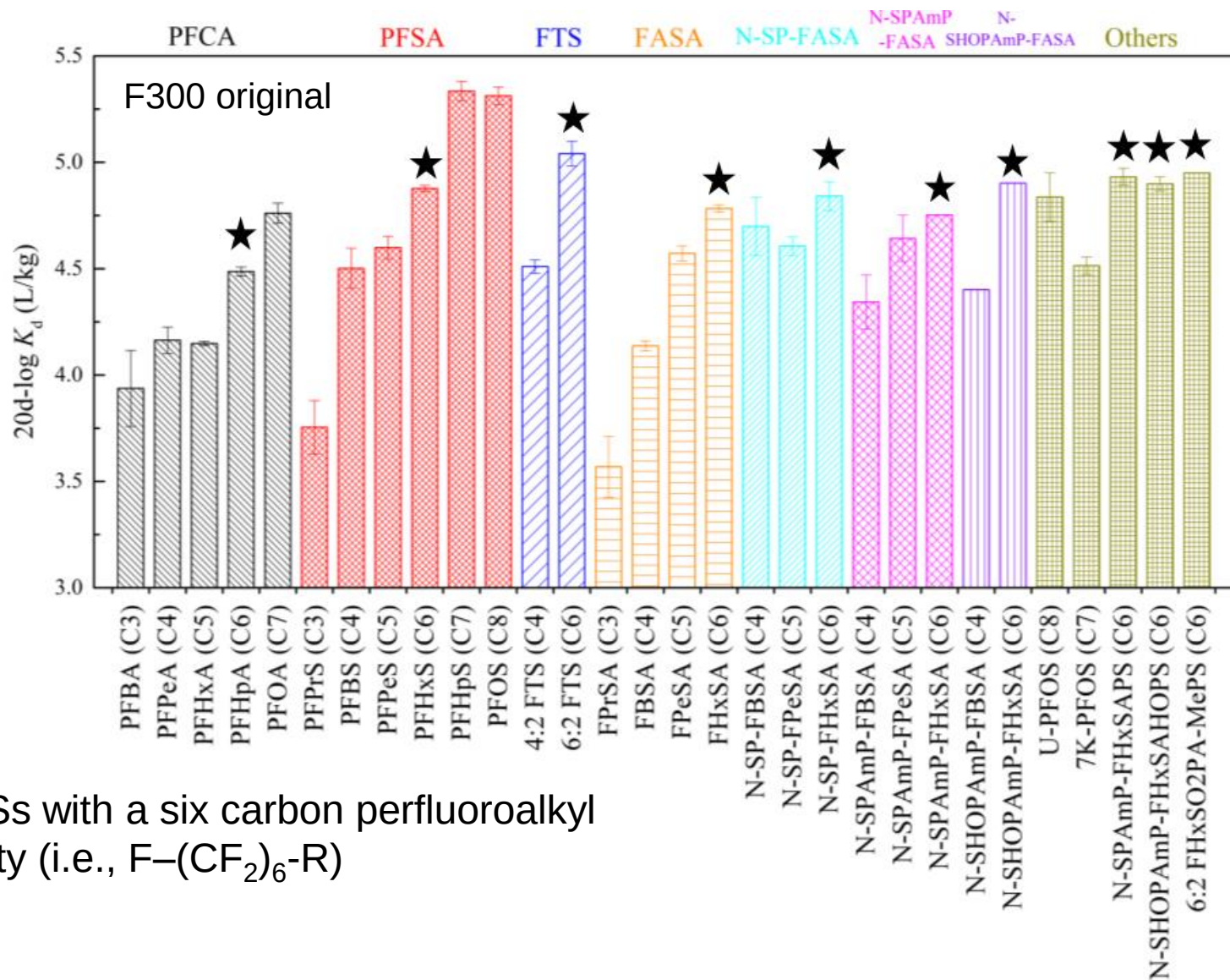
- Carbon-based sorbents examined:
 - Activated carbon: Calgon Filtersorb 300 (F300)
 - Gasification biochar: Mountain Crest Gardens (MCG)
 - Pine needle biochars under different pyrolysis temperatures: PN150, PN250, PN350, PN500, PN700
- Experimental approach:



- Relative concentrations and/or peak areas monitored over time
- K_d estimated using linearized pseudo 2nd order kinetic model
- K_d (estimated or maximum measured K_d) then used to fit τ using a non-linear intraparticle diffusion kinetic model

$$D_{app} = \frac{pD_w}{\tau[(1-p)\rho_s K_{d,Eq} + p]}$$

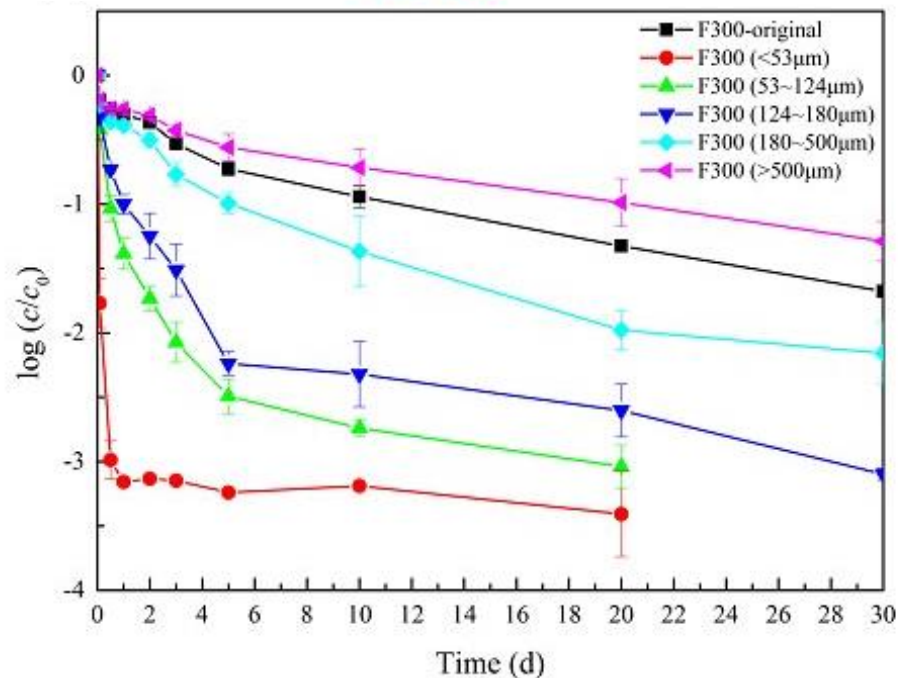
Results: Chain-length effects evident



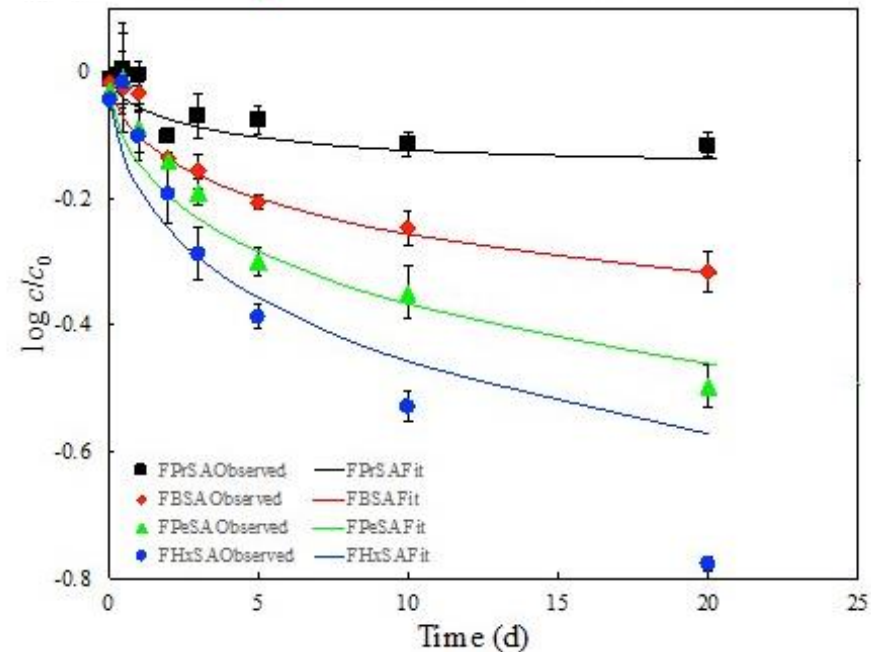
★ PFASs with a six carbon perfluoroalkyl moiety (i.e., $\text{F}-(\text{CF}_2)_6\text{-R}$)

Results: Size Effects and Model Fits

PFOS

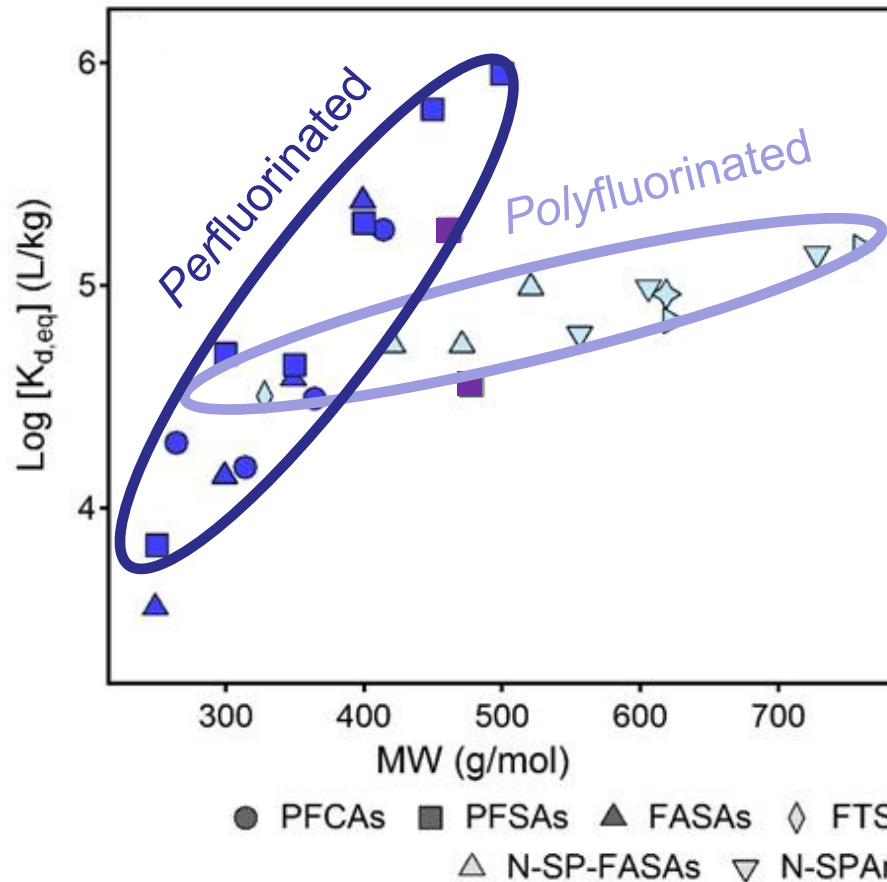


Intraparticle diffusion model fit



- Adsorption curves clearly show particle-size effects
- Intraparticle diffusion model provided good fits:
 - Apparent tortuosity averaged 4.16 (0.12 to 12.9)
 - RMSEs averaged 0.0096 (0.0011 to 0.0348)

Results



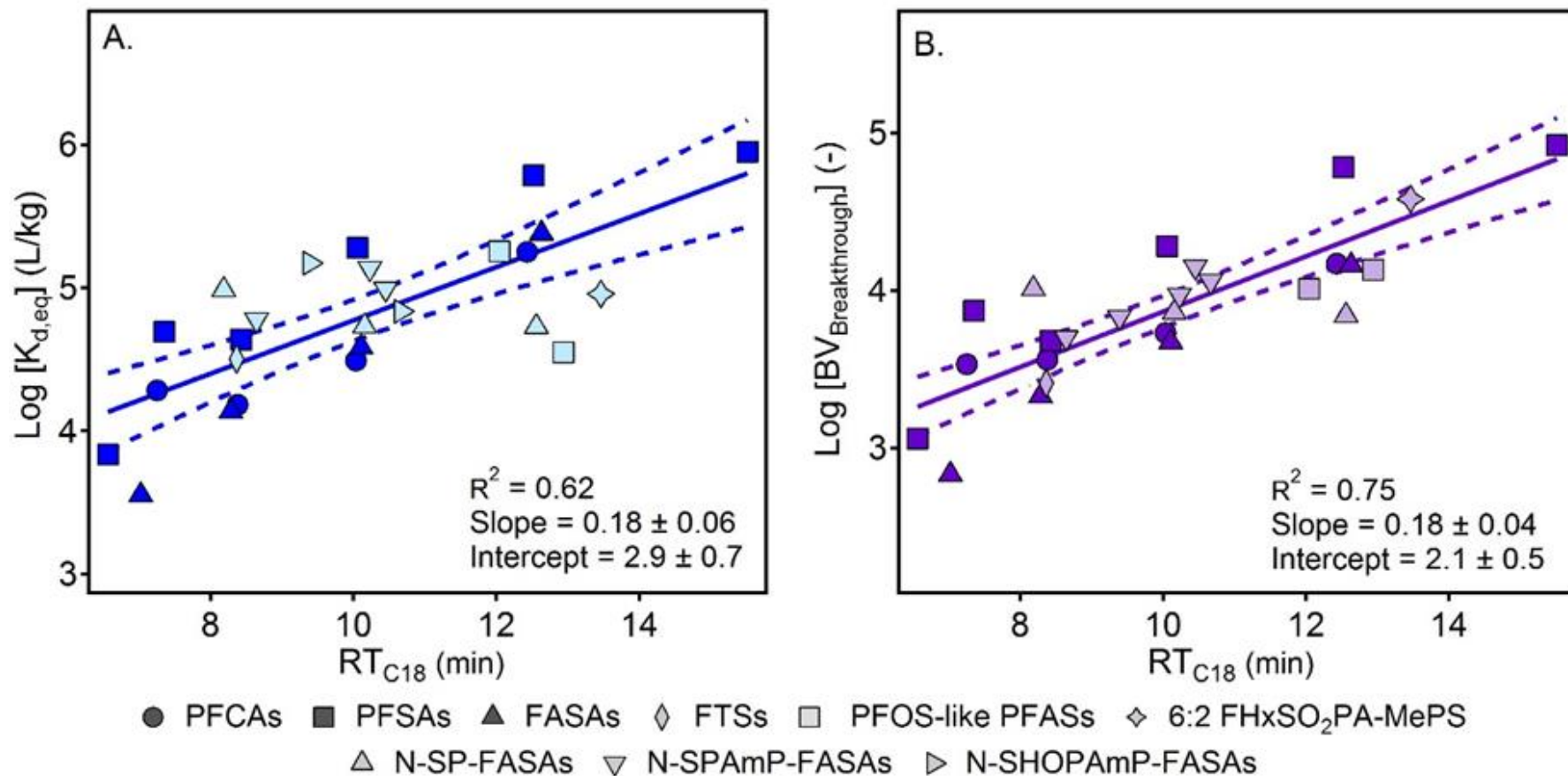
Actual PFOS breakthrough in identically sized and configured system (different GW and GAC)



Treating for PFOS
or PFOA likely **not**
protective for *most*
other PFASs

- Full-Scale GAC simulation:
 - Two 28.5 m³ vessels in series at 1.5 m³/min (each with 2.7 m of F300)
 - Empty-bed contact time (EBCT) of 13 min (26 overall)
 - Forward model from Ulrich *et al.* applied to predict 10% breakthrough

Predicting GAC breakthrough



- C18 retention time (RT_{C18}) appears to be a decent predictor of breakthrough for PFASs

Conclusions & Implications

- For AFFF-impacted water supplies, it's not just about PFOS and PFOA
 - *Most* PFASs not currently examined
 - Concentrations likely lower, but no standards available
 - Significant lack of toxicity data for other PFASs
- GAC for treatment of AFFF-impacted water will work, but:
 - *Most* PFASs will likely breakthrough before PFOA
 - Can use short-chain PFCAs or PFSAAs as indicators, but GAC changeout much more costly

Do we need to treat for the known unknowns?

Acknowledgements



Colorado School
of Mines

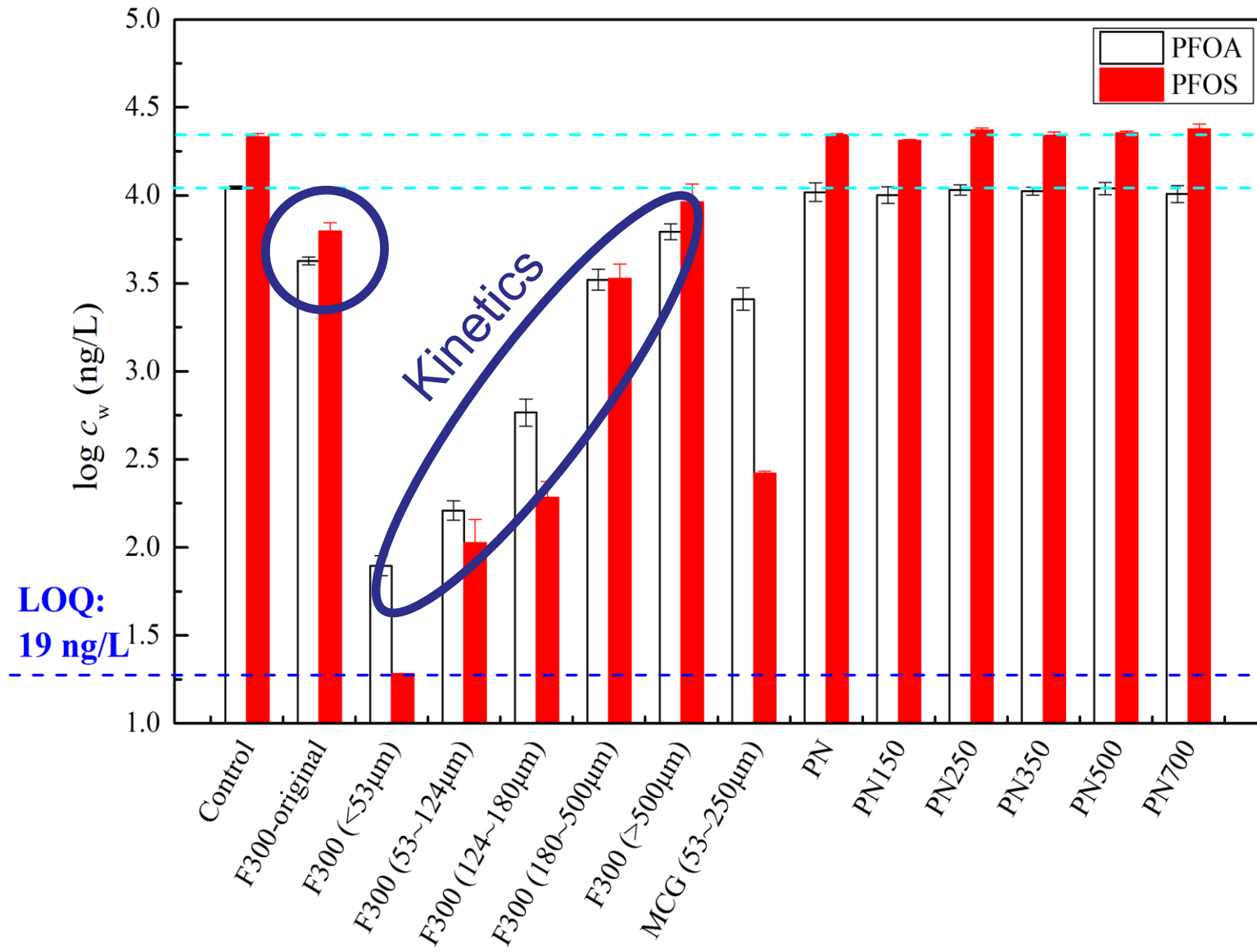


Zhejiang
University



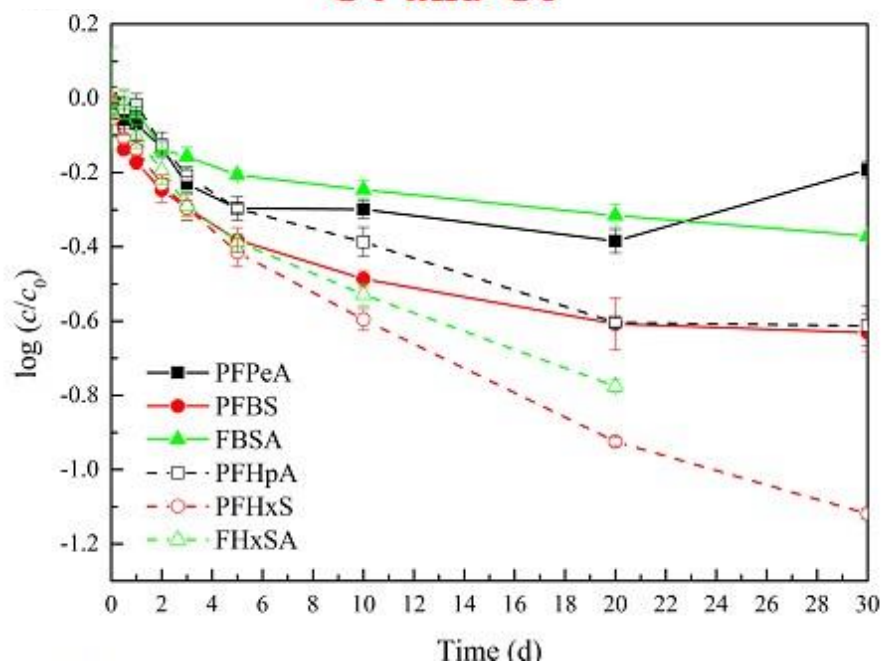
China Scholarship
Council

Results: 5-day screening - GAC works

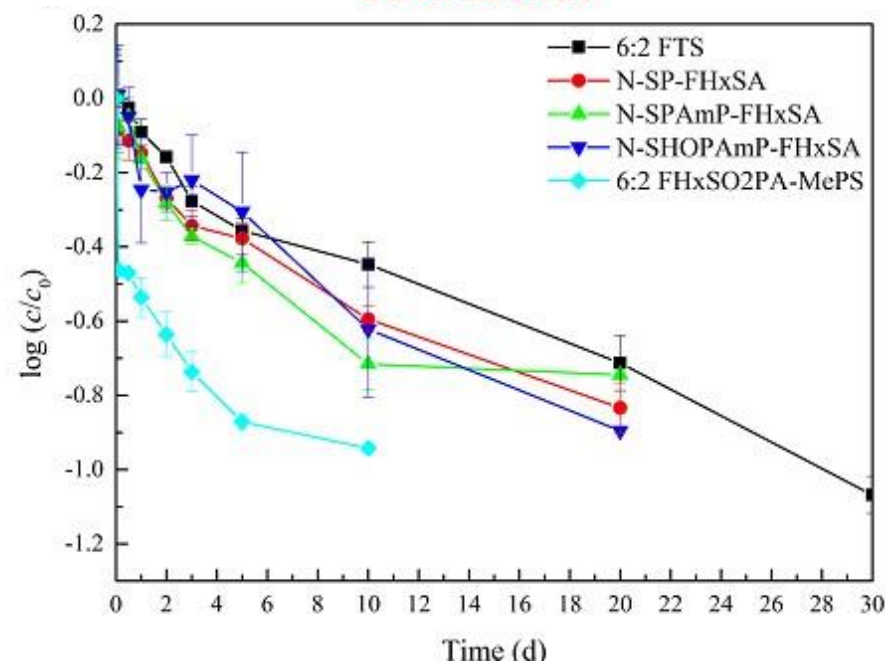


Results: Kinetic profiles

C4 and C6



Precursors



- Adsorption curves clearly show chain-length effects as well
- Most *poly*fluorinated chemicals displayed similar kinetics