Efficient Sorption of Short-Chain and Ether PFAS on a Modified Clay

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June 4th, 2024

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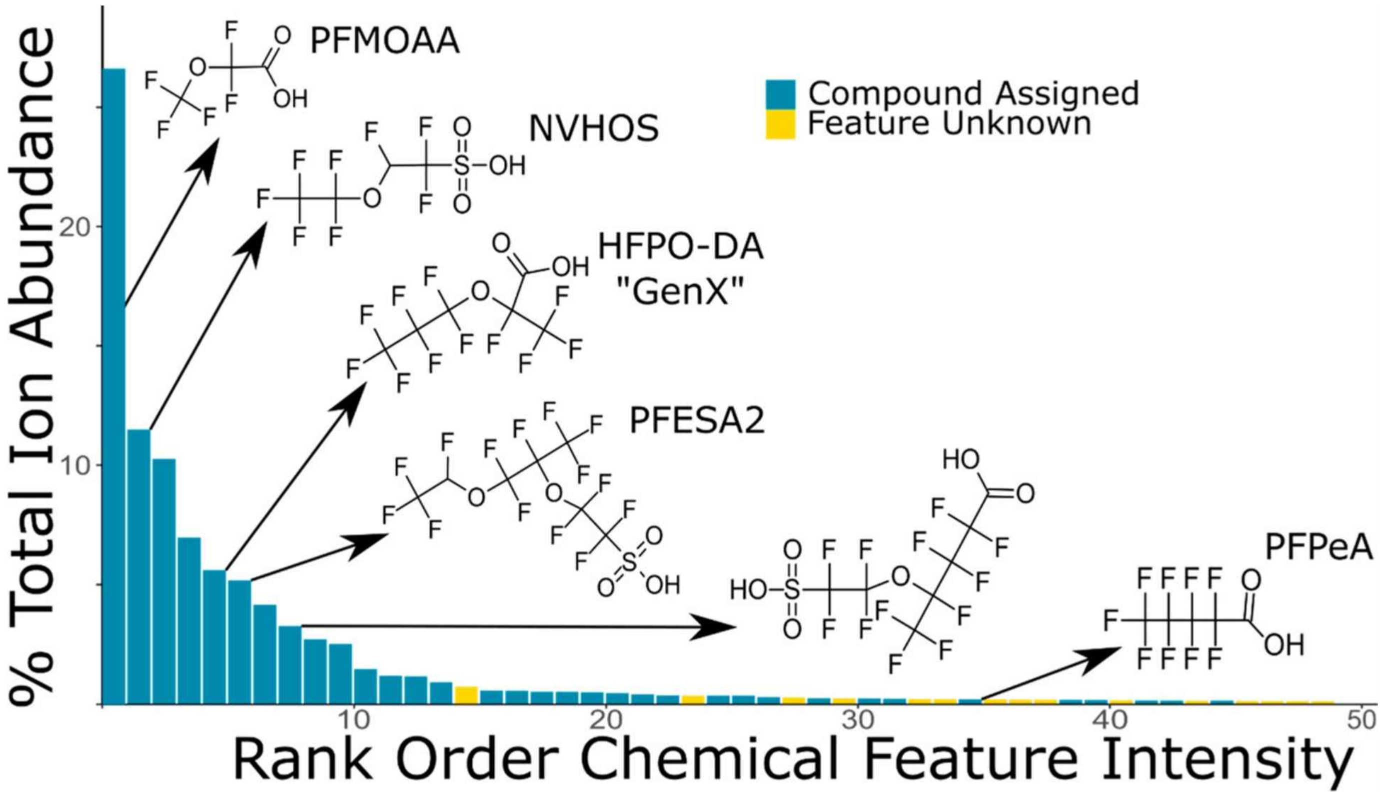
Background

Fluorinated Ether Compounds (Ether-PFAS):

- HFPO-DA (GenX) is an example but not the only one



Total ion abundance as a percentage of the sum of all chemical features of the Cape Fear River downstream of a fluorochemical manufacturer.
Environ. Sci. Technol. 2019, 53, 9, 4717–4727

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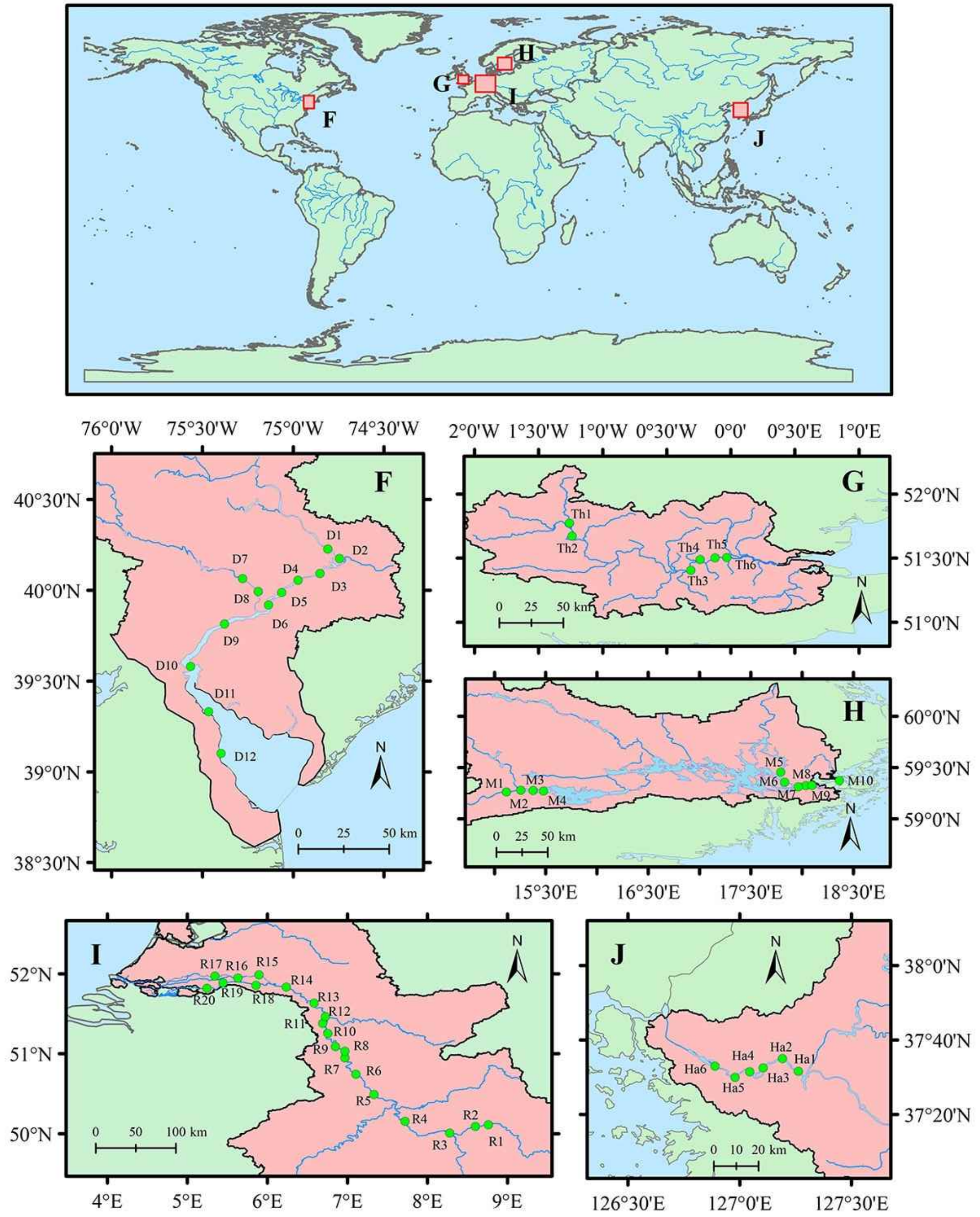
Environmental Detection:

- Found in various environmental matrices all over the world in highx concentrations

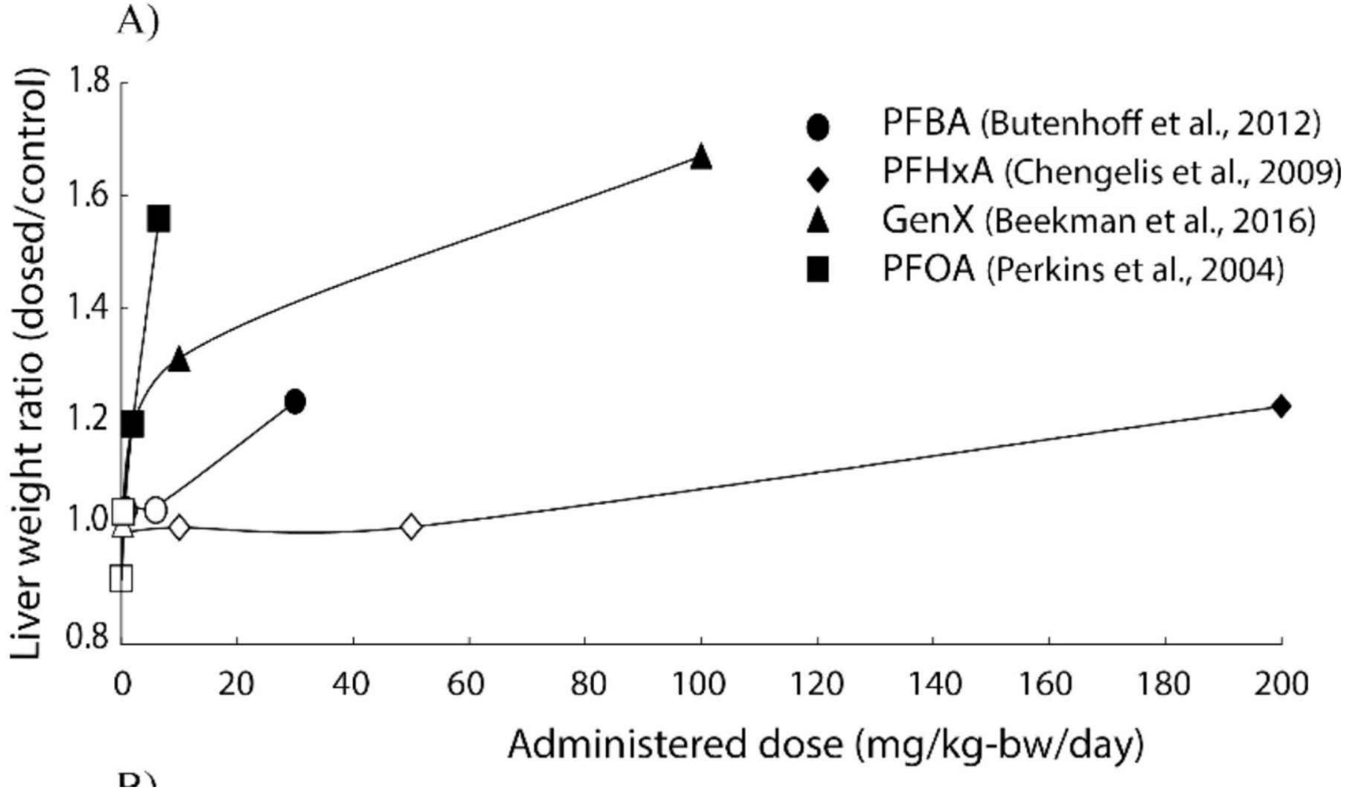


Overview of water sampling sites (F) Delaware River (U.S.A.), (G) Thames River (U.K.), (H) Mälaren Lake (Sweden), (I) Rhine River (Germany, R1–R14; The Netherlands, R15–R20), (J) Han River (Korea). *Environ. Sci. Technol. 2018, 52, 14, 7621–7629*

Background

GenX Toxicity:

- 28-day oral exposure in male mice led to liver necrosis
- Potentially more toxic to the liver than PFOA



Liver weight ratios – dosed/control – as a function of administered dose
Environ. Int. 2018, *113*, pp.1-9

Current Challenges

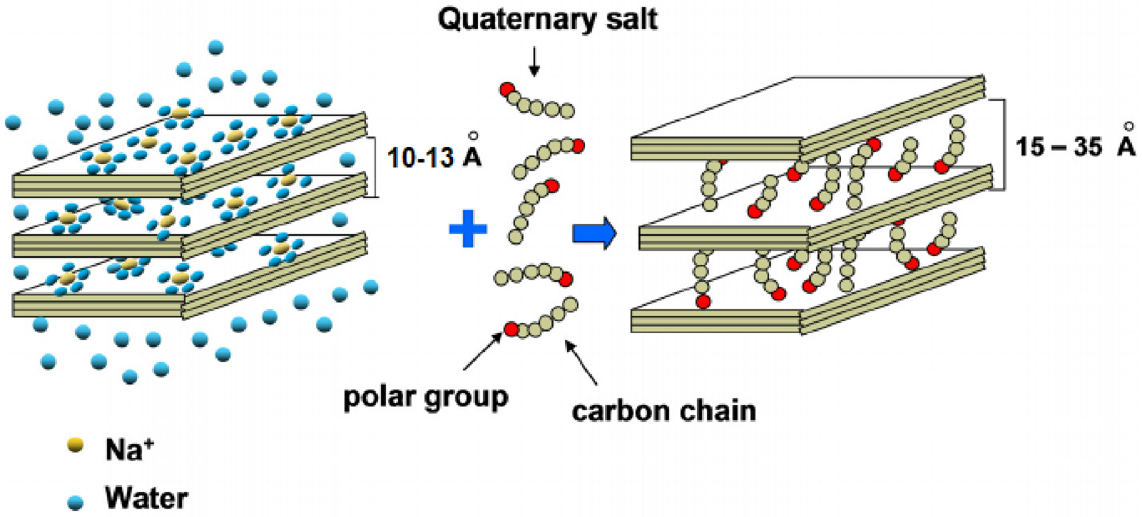
- **EPA issued final health advisories for drinking water:**
  - HFPO-DA (GenX): 10 ng/L
  - PFBS: Hazard Index of 1

$$HI\ MCL = \left(\frac{[HFPO-DA_{water}]}{[10\ ppt]}\right) + \left(\frac{[PFBS_{water}]}{[2000\ ppt]}\right) + \left(\frac{[PFNA_{water}]}{[10\ ppt]}\right) + \left(\frac{[PFHxS_{water}]}{[10\ ppt]}\right) = 1$$

- **Existing Solutions:**
  - Activated carbon: Limited for short-chain PFAS
  - Ion exchange resins: Better but costly
- **Need for Improvement:**
  - Urgent need to remove legacy and emerging PFASs from the environment

Surfactant Modified Clay

- Surfactant-modified Na-bentonite clay, organophilic, quaternary ammonium ions
- First generation (FLUORO-SORB®) has been commercialized and extensively studied, tested, and utilized in many full-scale applications including:
  - In-situ remediation
  - Ex-situ pump and treat
  - Municipal drinking water treatment systems
- Second generation (FLUORO-SORB® FLEX) is designed to work as clay-based ion exchanger
  - Intercalants likely contain a mixture of mono-quaternary and di-quaternary amines



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AWWA WATER SCIENCE

EMERGING CONTAMINANT ARTICLE | Open Access

Modified clays reduce leaching of per- and polyfluoroalkyl substances from AFFF-contaminated soils

Chenyang Wang, Bei Yan, Gabriel Munoz, Sébastien Sauvé, Jinxia Liu

molecular simulation study

Bei Yan [a], Gabriel Munoz [b], Sébastien Sauvé [b], Jinxia Liu [a]

ELSEVIER

Water Research

Volume 201, 1 August 2021, 117371

STXM-XANES and computational investigations of adsorption of per- and polyfluoroalkyl substances on modified clay

Bei Yan [a], Jian Wang [b], Jinxia Liu [a]

Jinxia Liu [a]

Objective of the Study

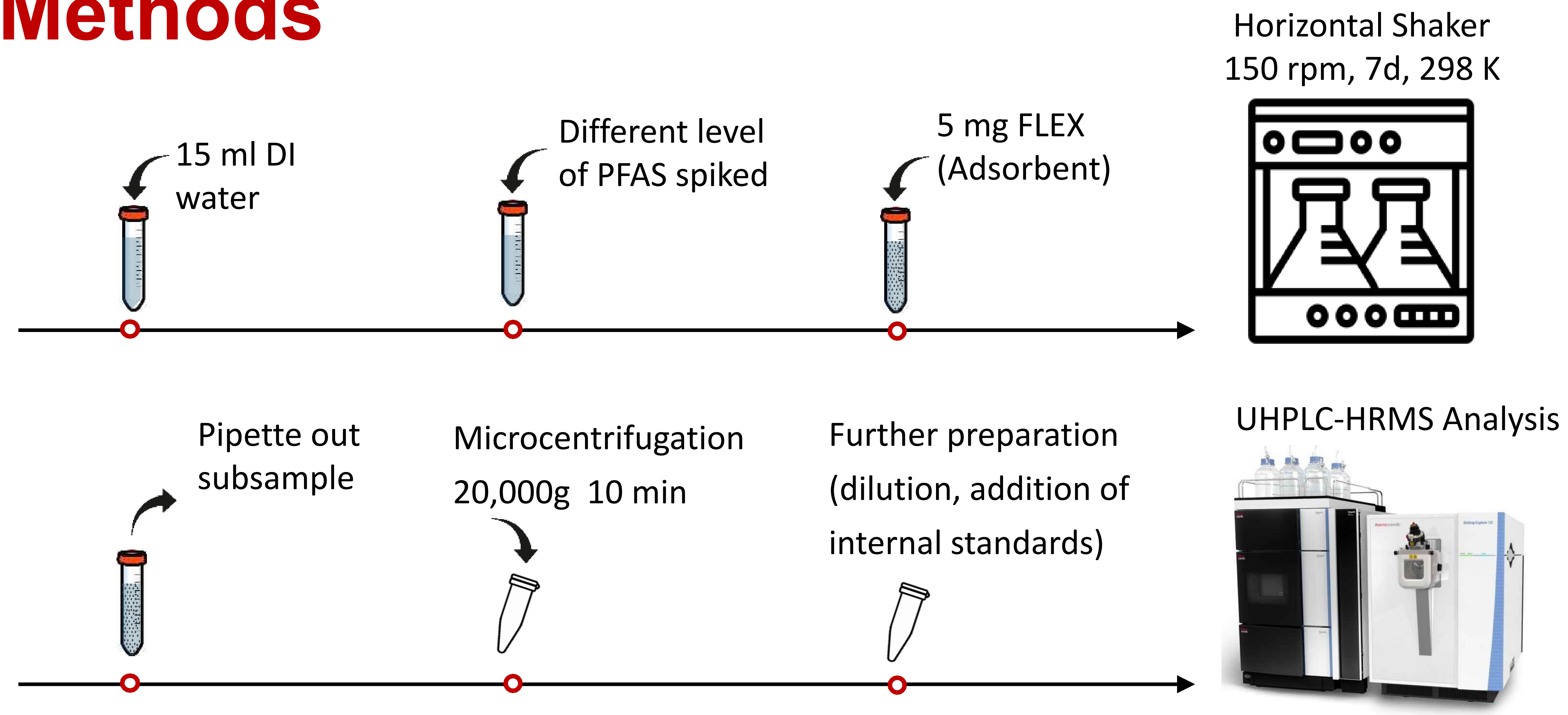
Evaluate performance of FLEX for short-chain PFAS and Ether-PFAS

Compare FLEX with Fluoro-Sorb, activated carbon, and ion exchange resins

Assess impact of water chemistry and co-contaminants

Elucidate sorption mechanisms

Methods

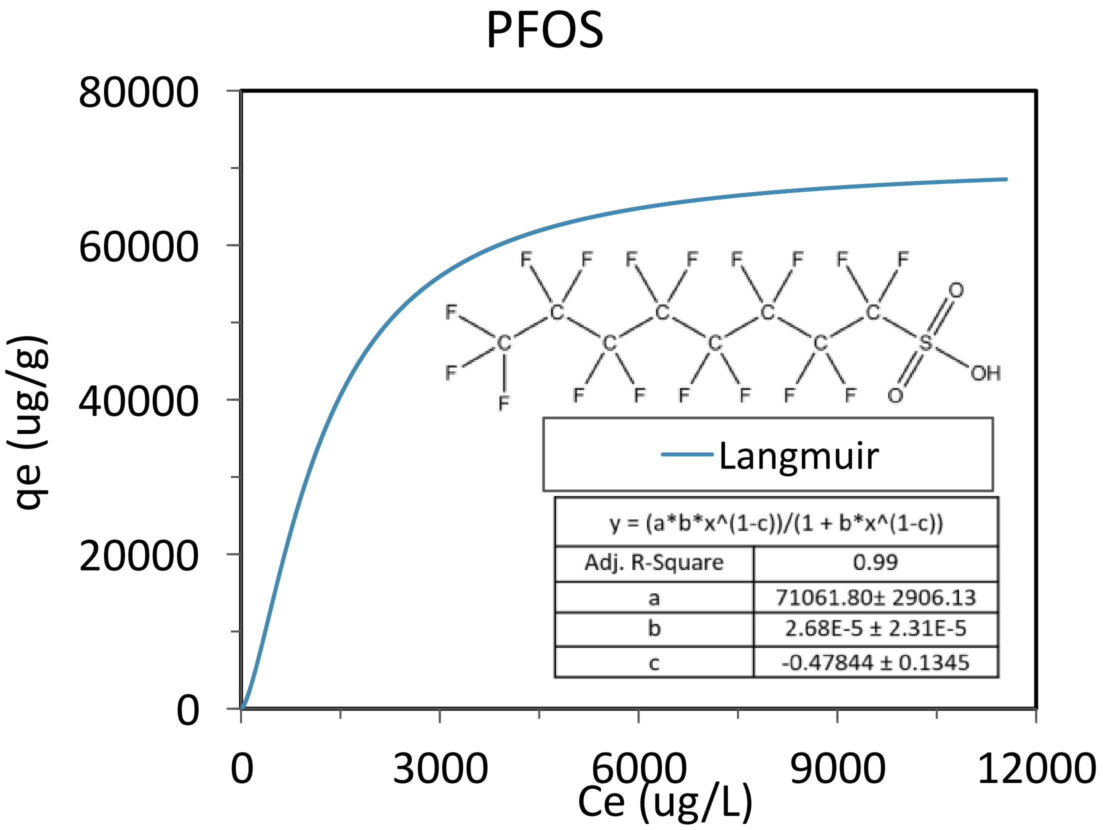


15 ml DI water
Different level of PFAS spiked
5 mg FLEX (Adsorbent)
Horizontal Shaker
150 rpm, 7d, 298 K
Pipette out subsample
Microcentrifugation
20,000g 10 min
Further preparation (dilution, addition of internal standards)
UHPLC-HRMS Analysis

Adsorption Isotherm

- Seven compounds were tested PFOS, PFBS, PFOA, PFBA, PFMPA, HFPO-DA and HFPO-TA
- Langmuir-Freundlich model was a good fit for the sorption isotherm of all seven compounds tested.

Langmuir-Freundlich model: $q_e = \frac{q_m * b * C_e^{1-c}}{1 + b * C_e^{1-c}}$



	PFBS	PFOS	PFBA	PFOA	PFMPA	HFPO-DA	HFPO-TA
q_m (mg/g)	20	71	13	40	21.8	50	62
q_m (umol/g)	66.6	142	60.7	96.6	50.2	142.8	123

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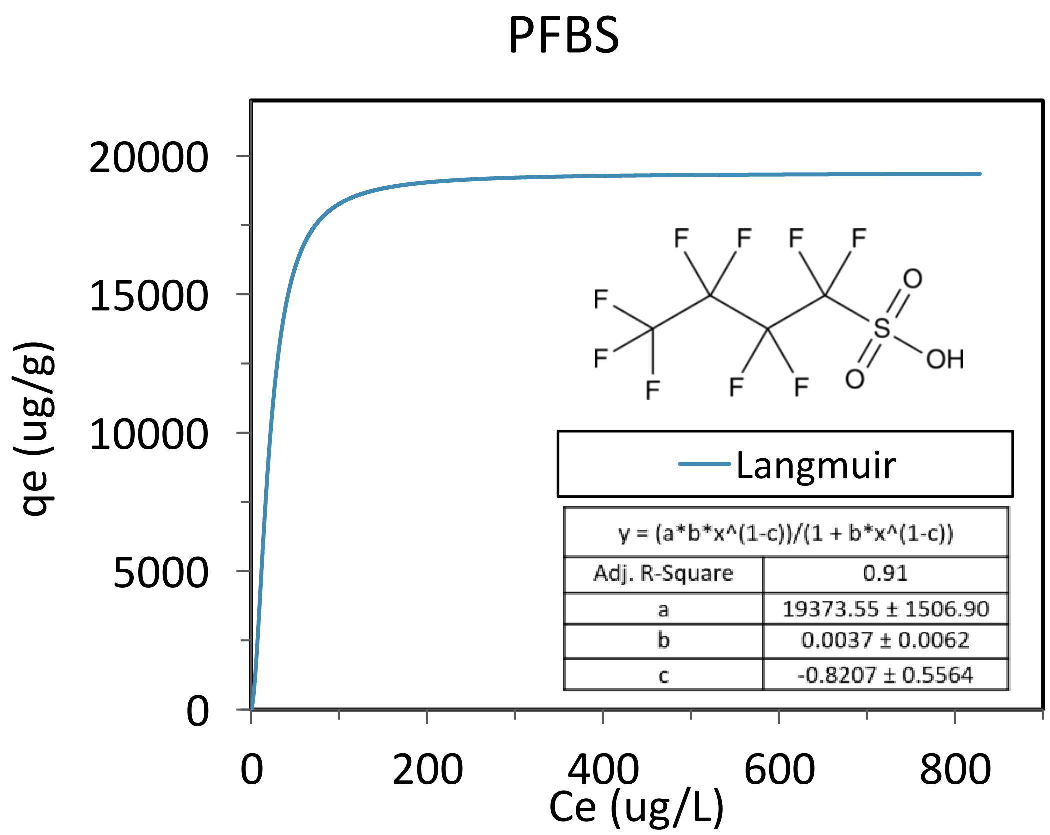

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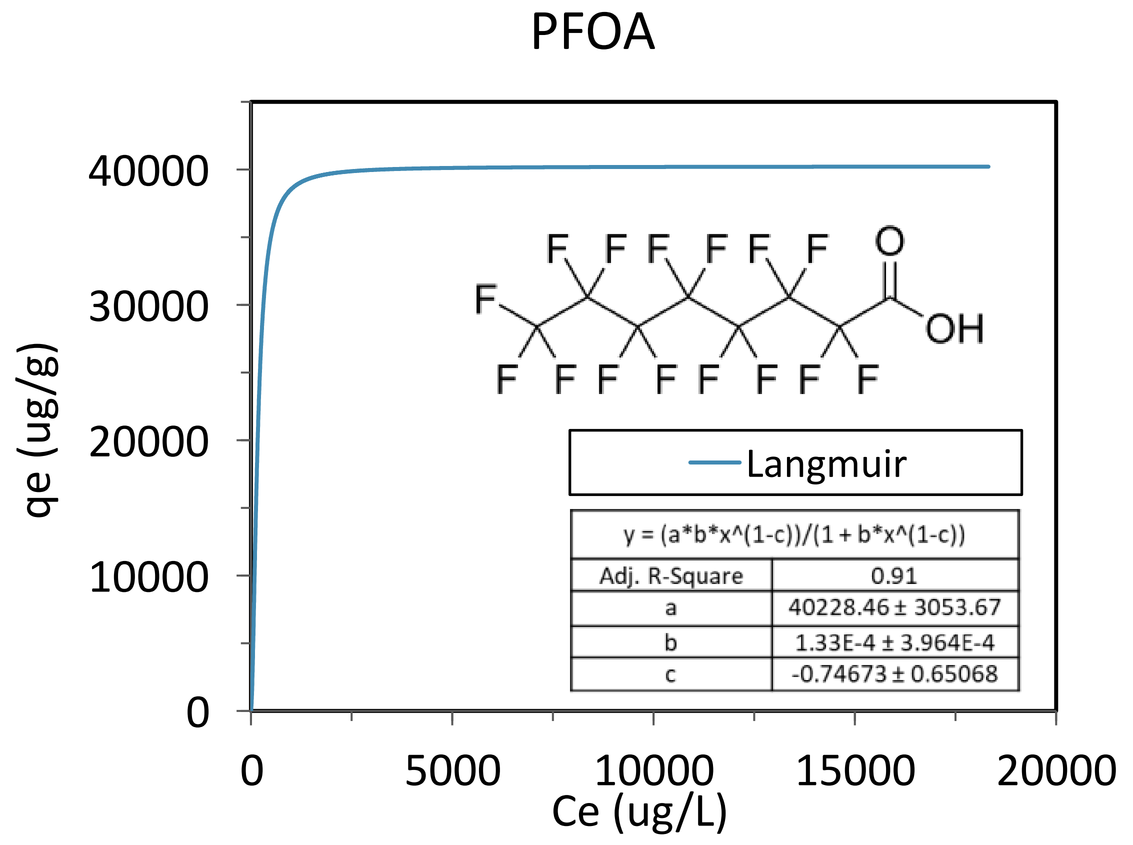

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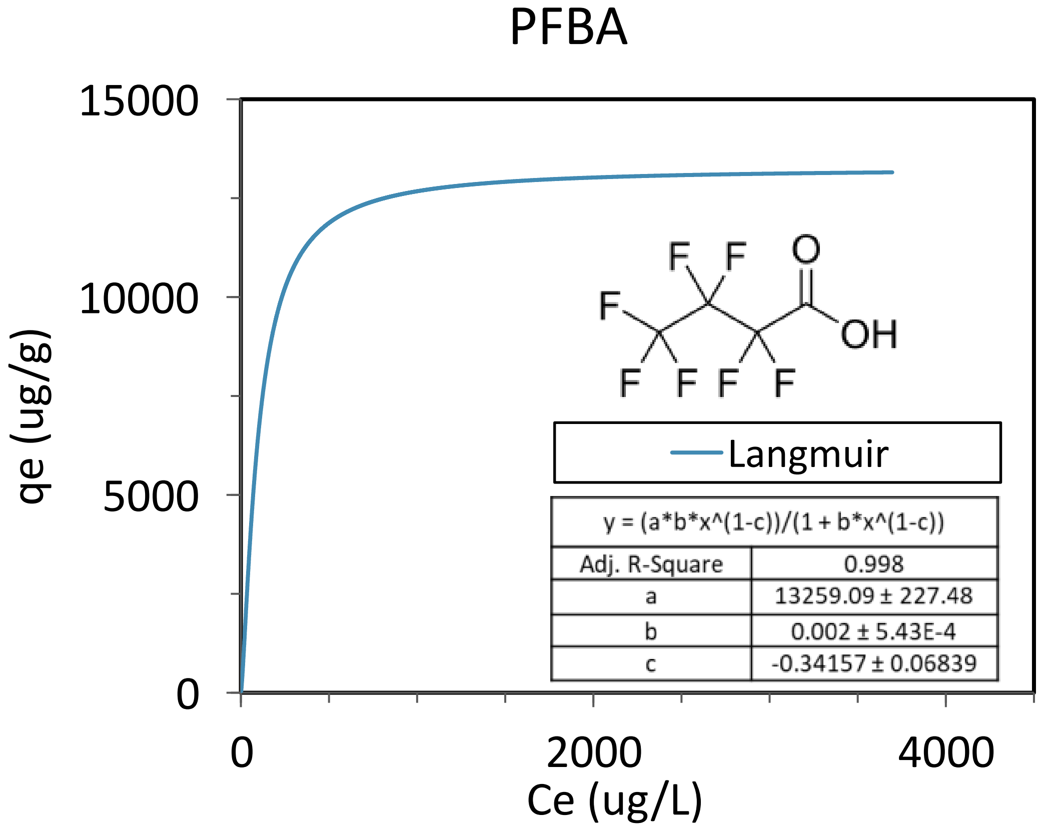

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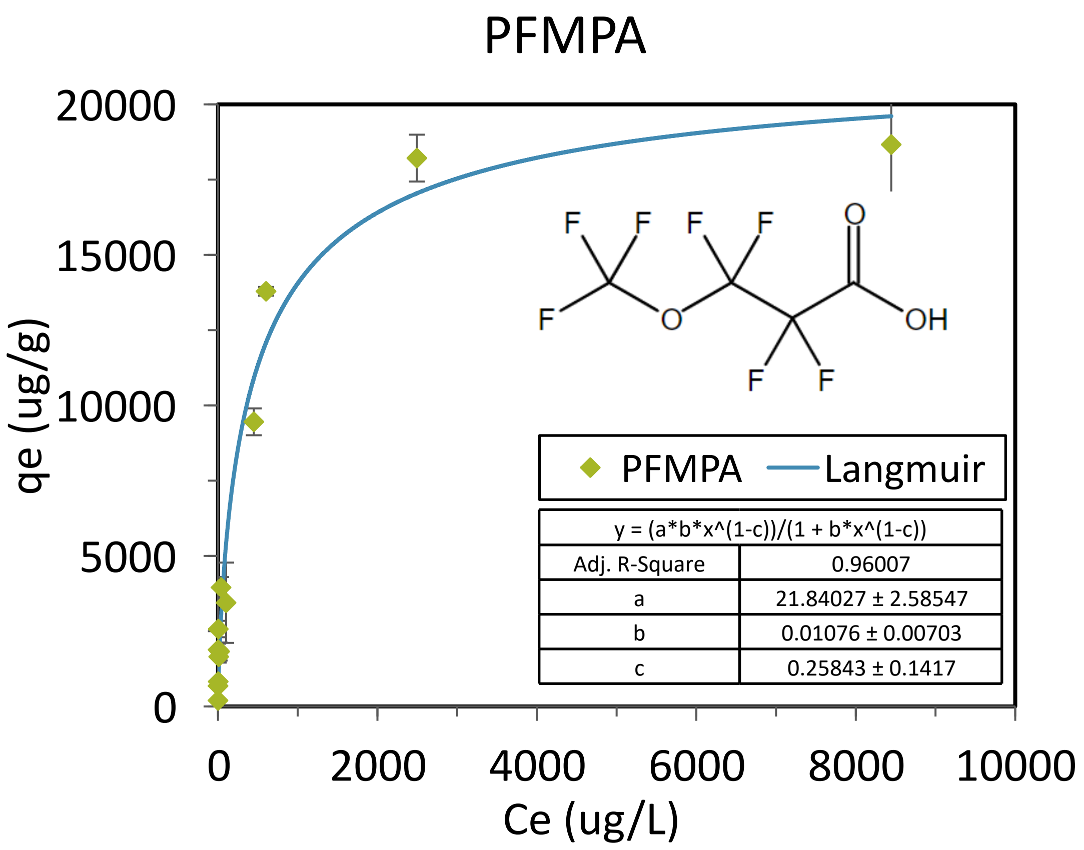

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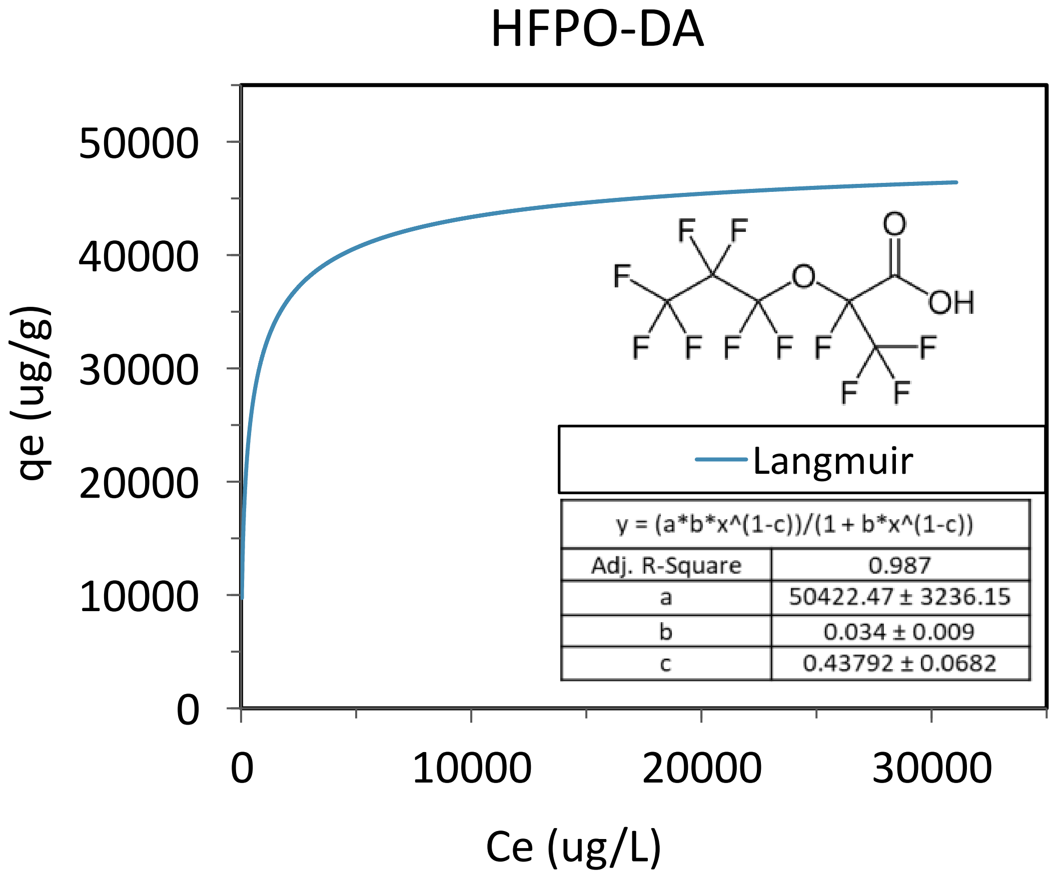

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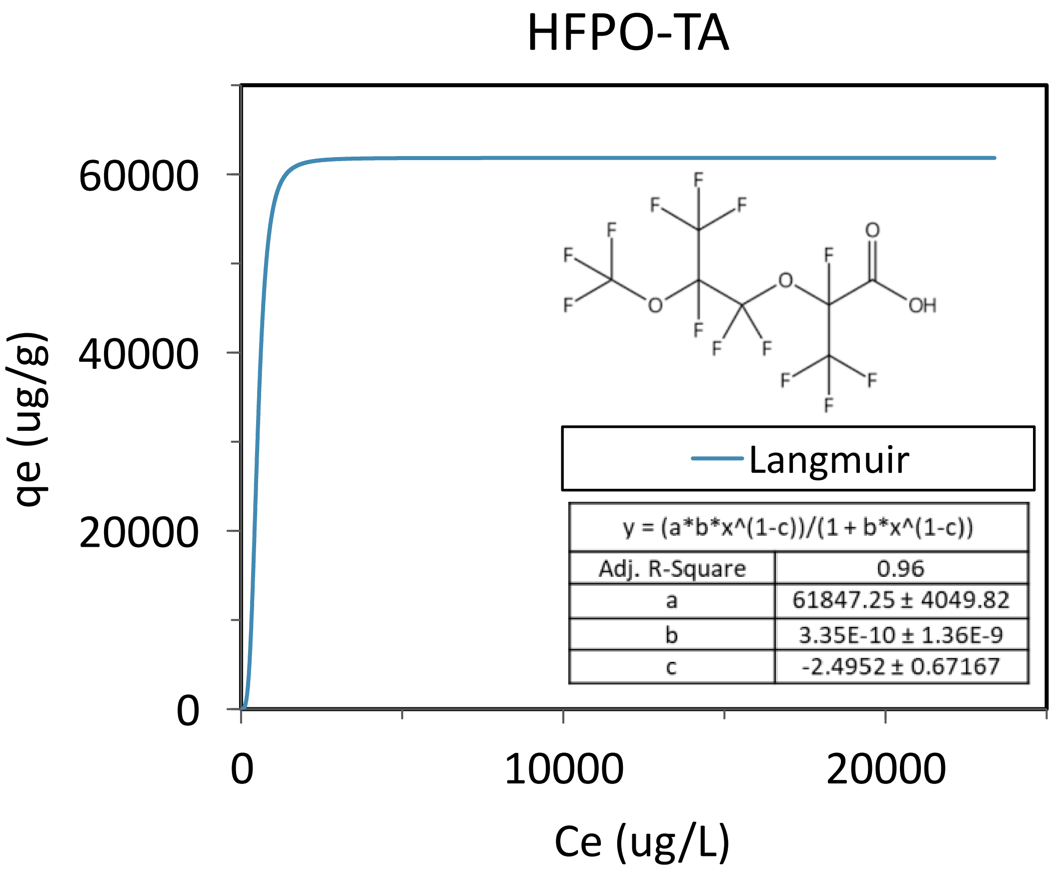

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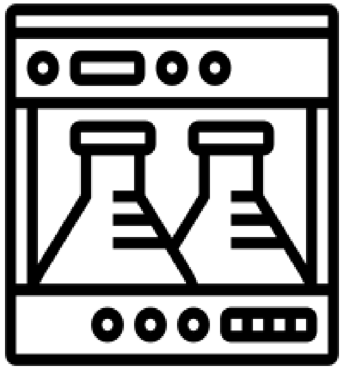
Methods

400 ml GW at
1 PPM PFBS
(Spiked)

Different level of
co-contaminants
spiked

40 mg Flex
(Adsorbent)

Horizontal Shaker
150 rpm, 7d, 298 K



Pipette out
subsample

Microcentrifugation
20,000g 10 min

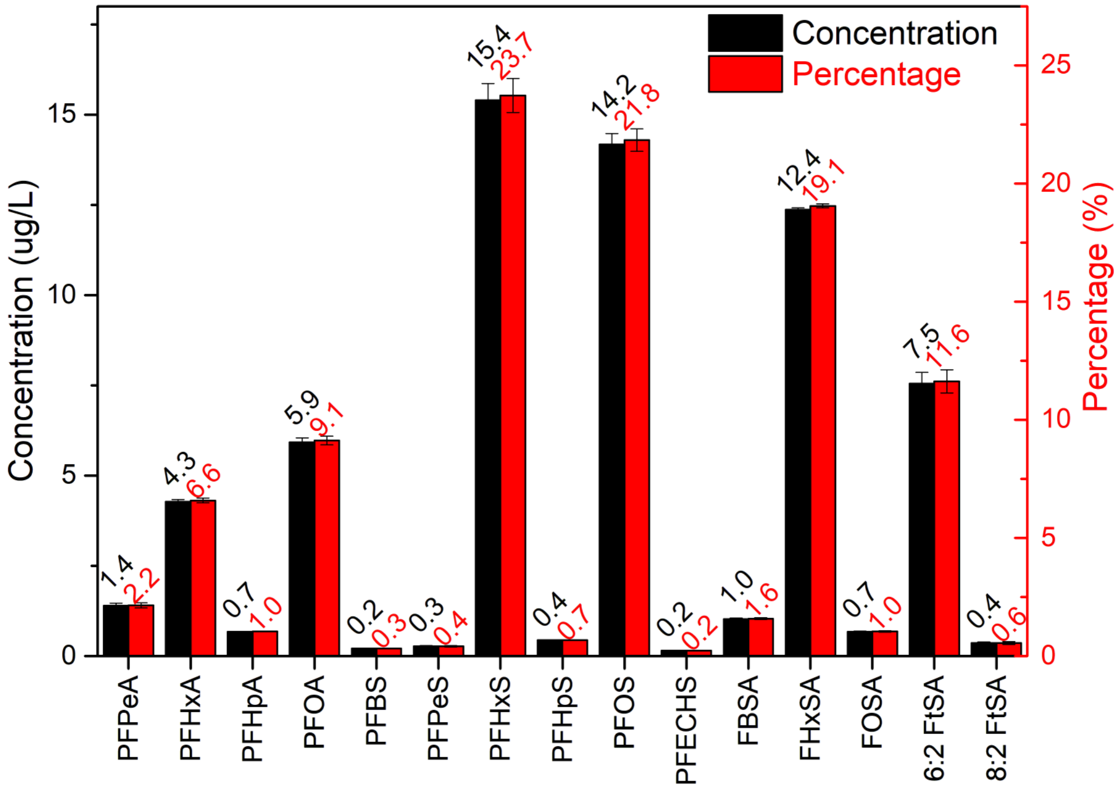
Further preparation
(dilution, addition of
internal standards)

UHPLC-HRMS Analysis

Profile of the Groundwater

Groundwater from Wurtsmith Airforce Base

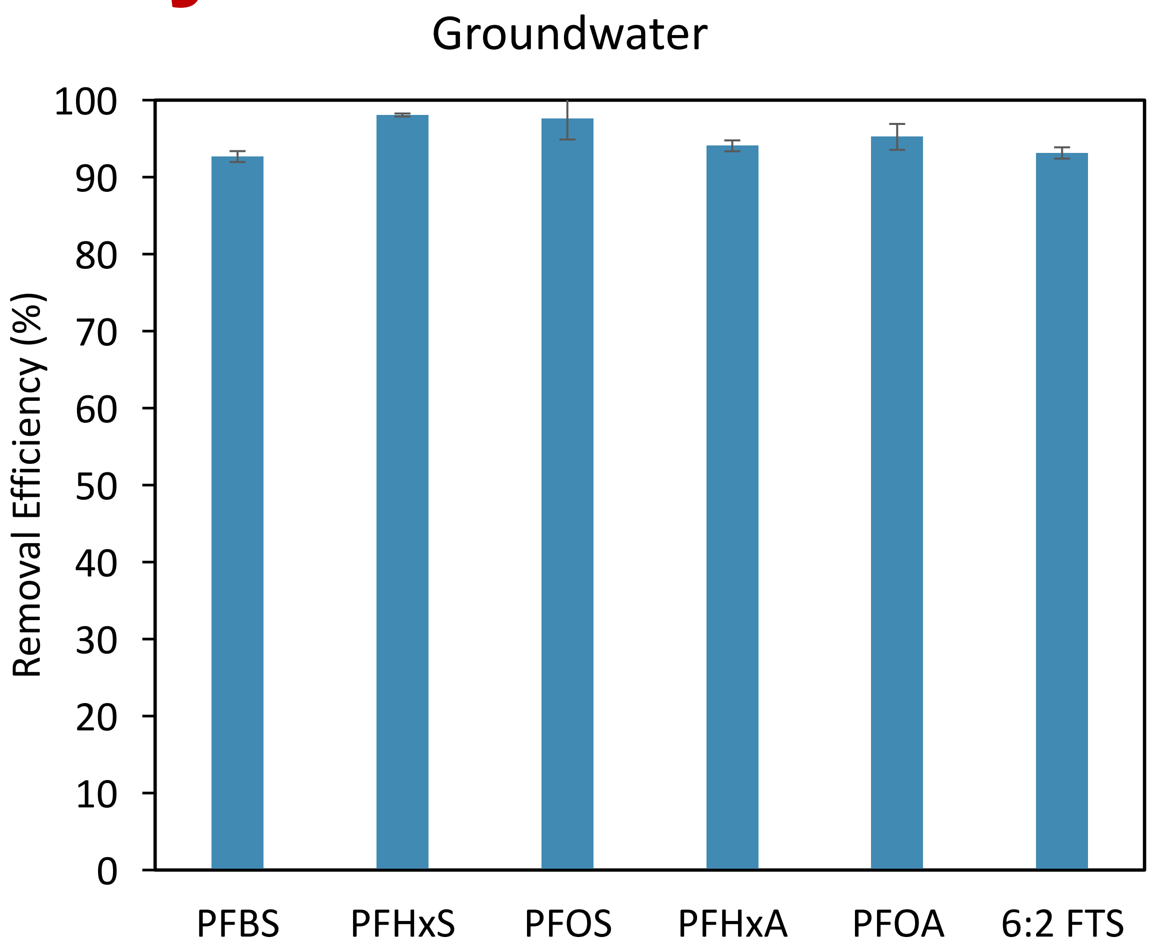
$\sum_{49}$PFASs = 64.9 µg/L.



Analyte	**Value**
pH	8.15
Calcium	50 mg/L
Sodium	2.6 mg/L
Nitrate	0.32 mg/L
General Chemistry	
BOD	<2.0 mg/L
COD	7.9 mg/L
TOC	2.4 mg/L
Volatile Organic Compounds	
Acetone	8.3 µg/L
Nonhalogenated Organics	
Diesel	0.43 mg/L

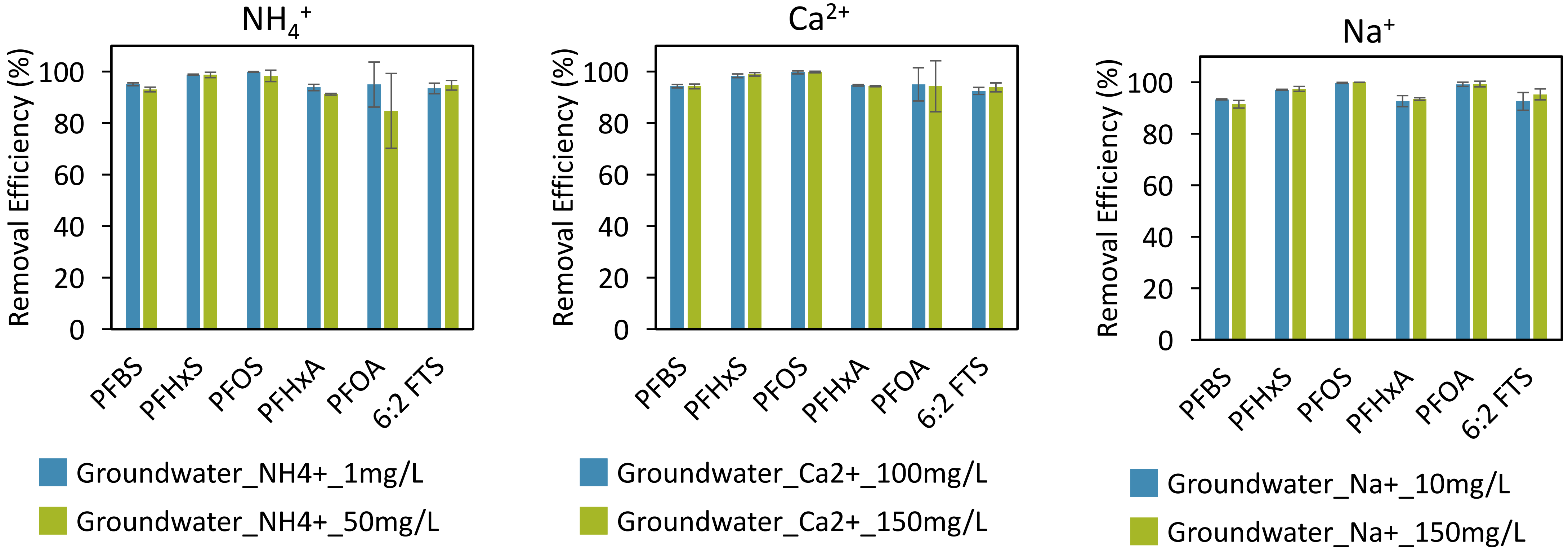
Impact of Water Chemistry

- PFBS was spiked at 1 ppm
- Two levels of ions and co-contaminants were added to model environmentally relevant concentrations as well as extreme conditions



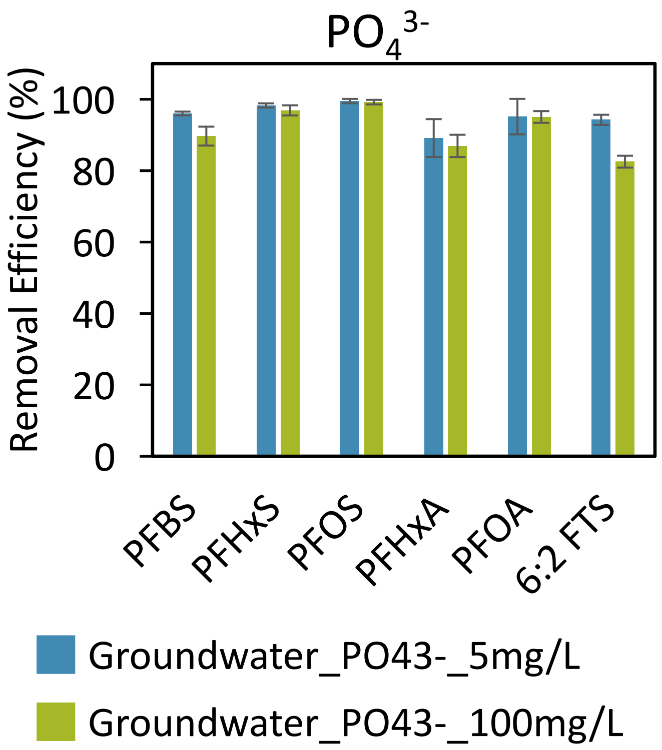
Impact of Cations

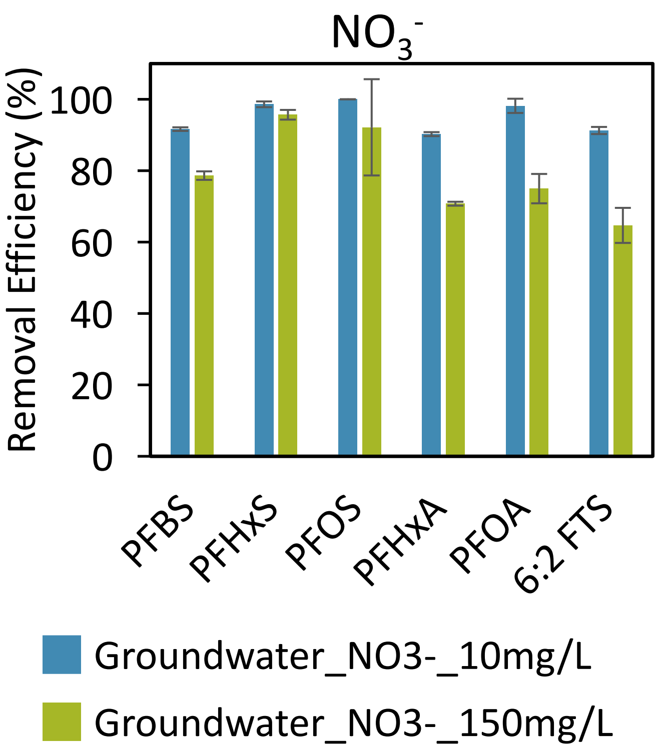
- No levels of any of the cations tested had any significant effect of the removal efficiency of FLEX.

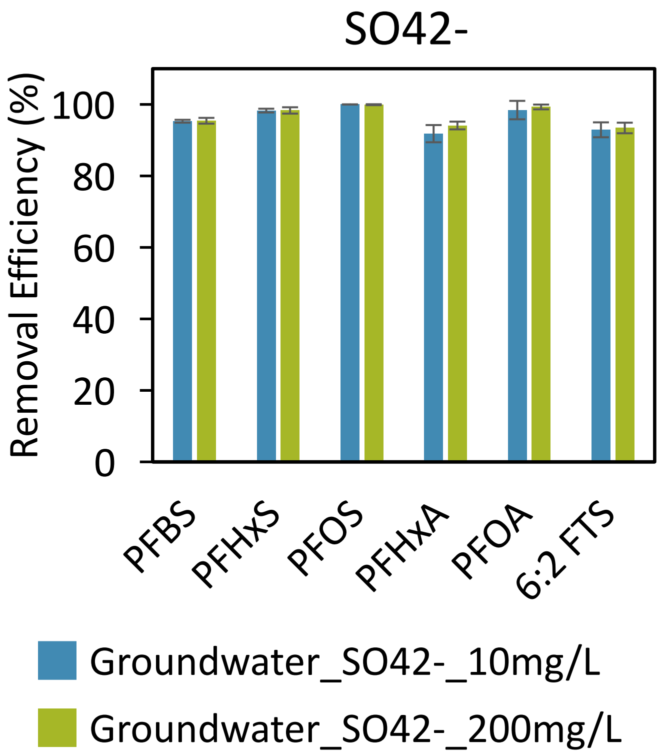


Impact of Anions

- Except for higher concentration of nitrate (150 mg/L), no levels of any of the anions tested had any significant effect of the removal efficiency of FLEX.

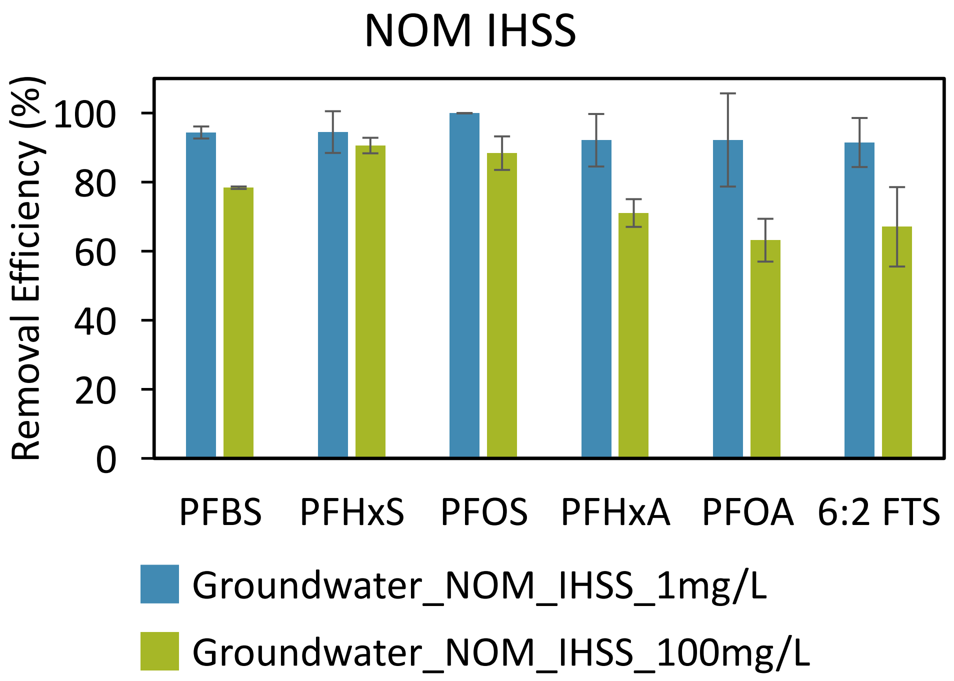


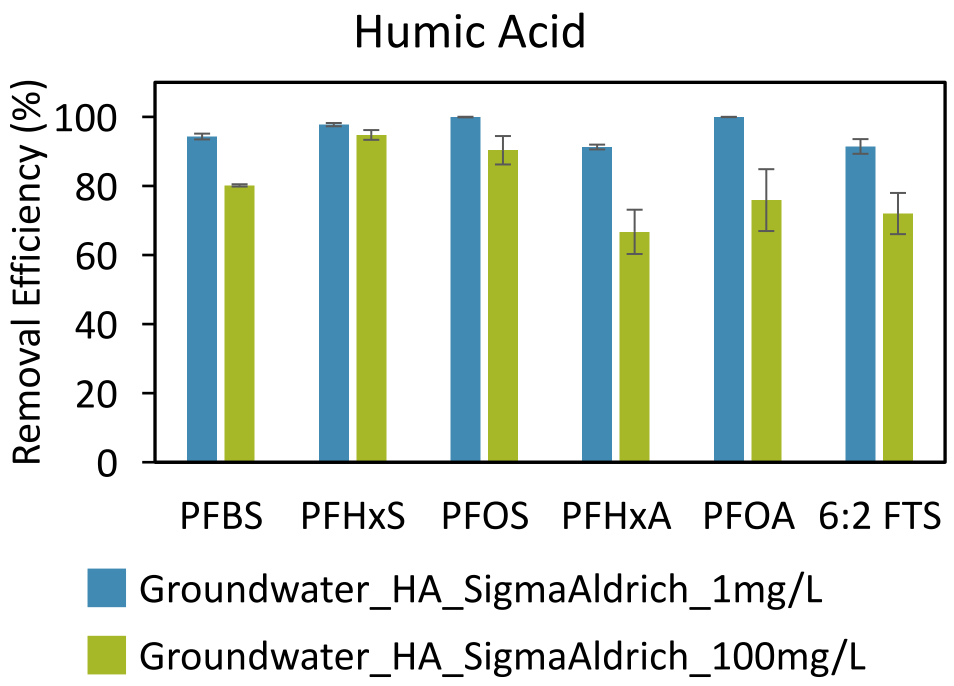




Impact of Organic Matter

- Environmentally relevant concentrations of organic matter (1mg/L) did not have any significant effect on sorption of PFAS on modified clay.
- High concentration of both types of organic matter tested (100 mg/L) reduced the removal efficiency by 20 to 40% for some compounds.





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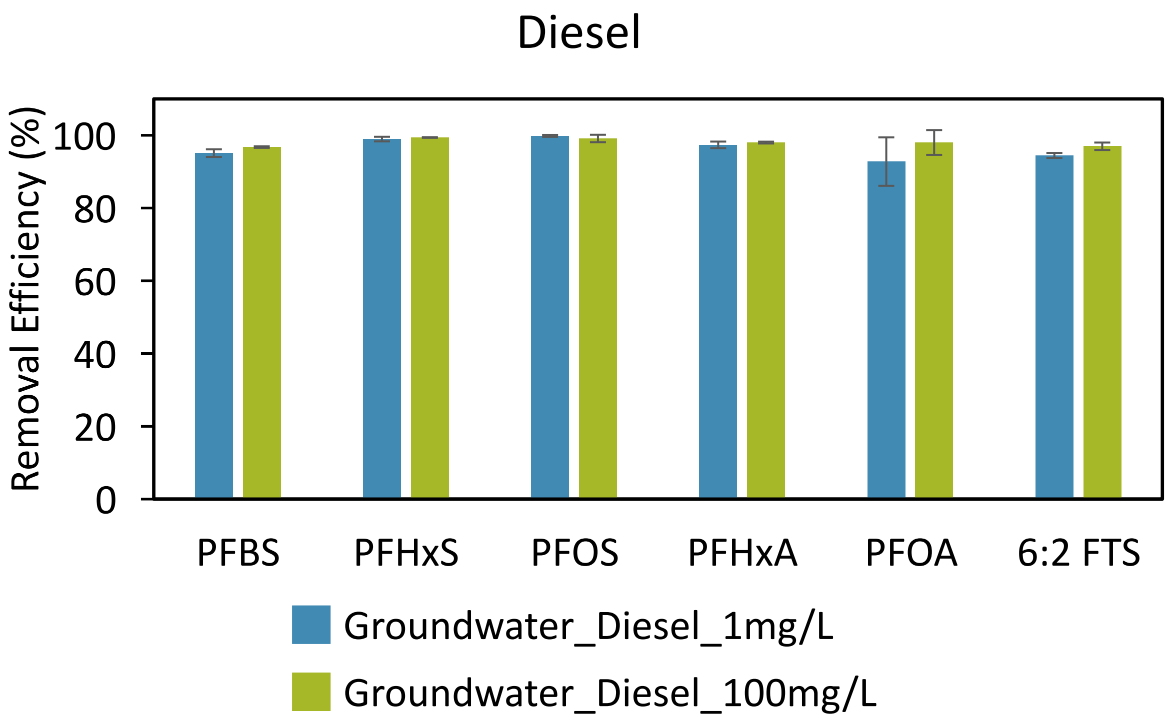
Impact of Co-contaminant

- No levels of any of the diesel had any significant effect of the removal efficiency of FLEX.



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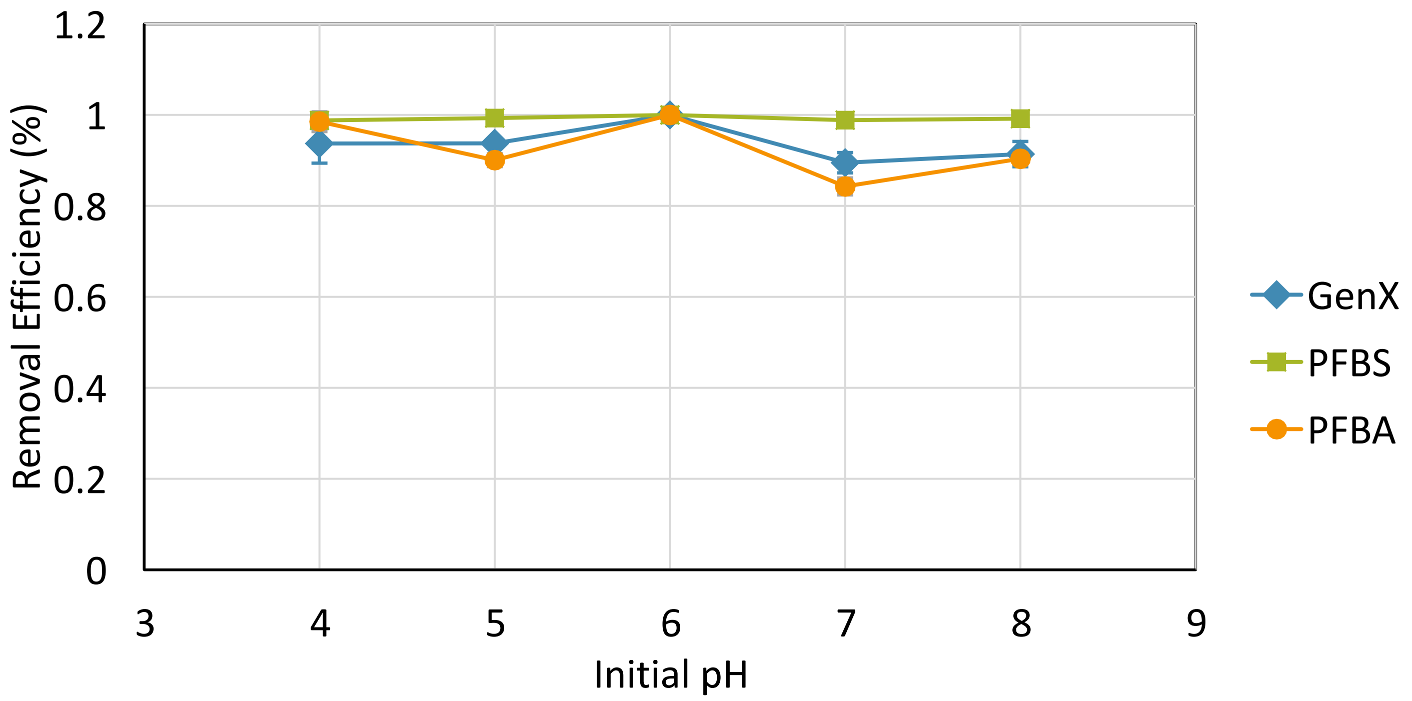
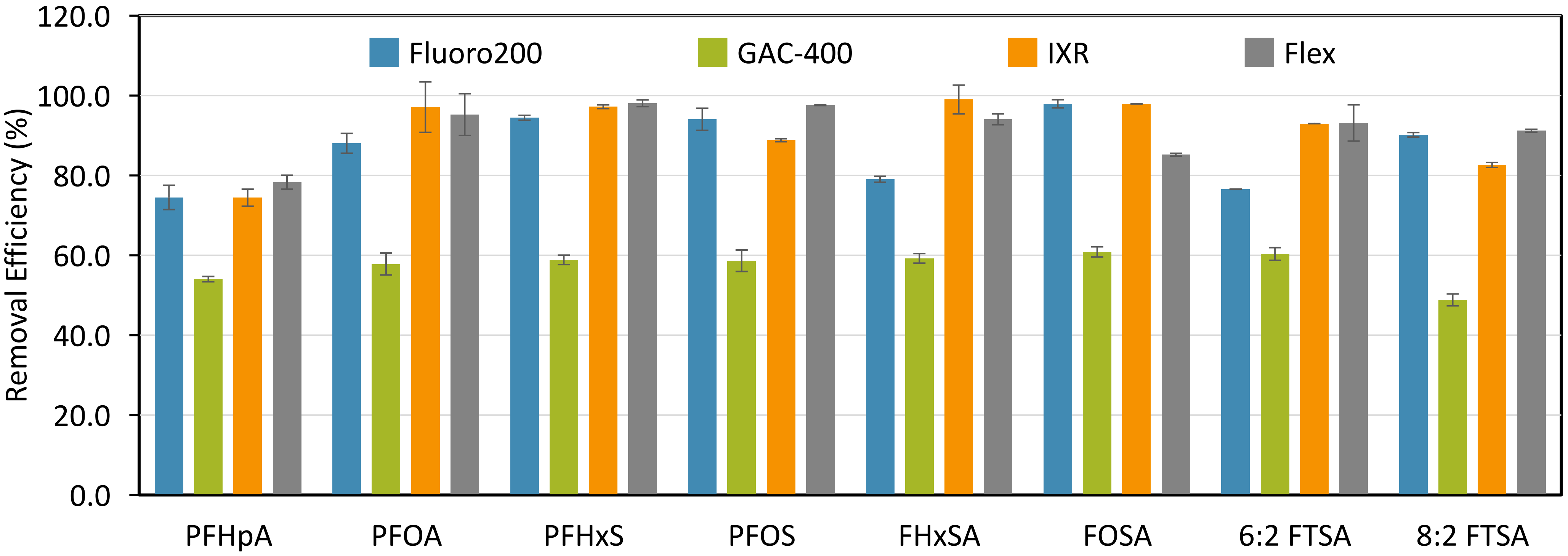
Impact of pH

- Different levels of pH tested had no significant effect on removal efficiency of FLEX for PFBS, PFBA and GenX (HFPO-DA).



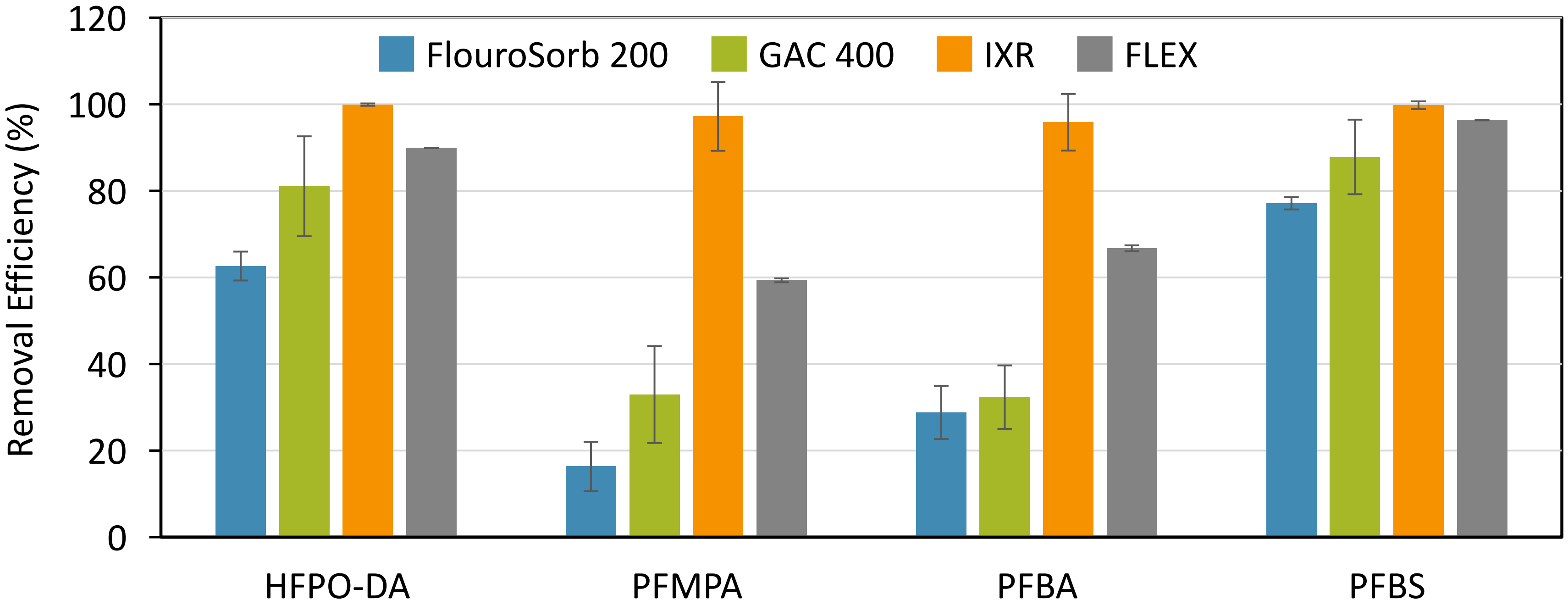
Performance Comparison

- Four sorbents namely, FLUORO-SORB, GAC 400, Ion exchange resin and FLEX were tested in AFFF impacted groundwater matric



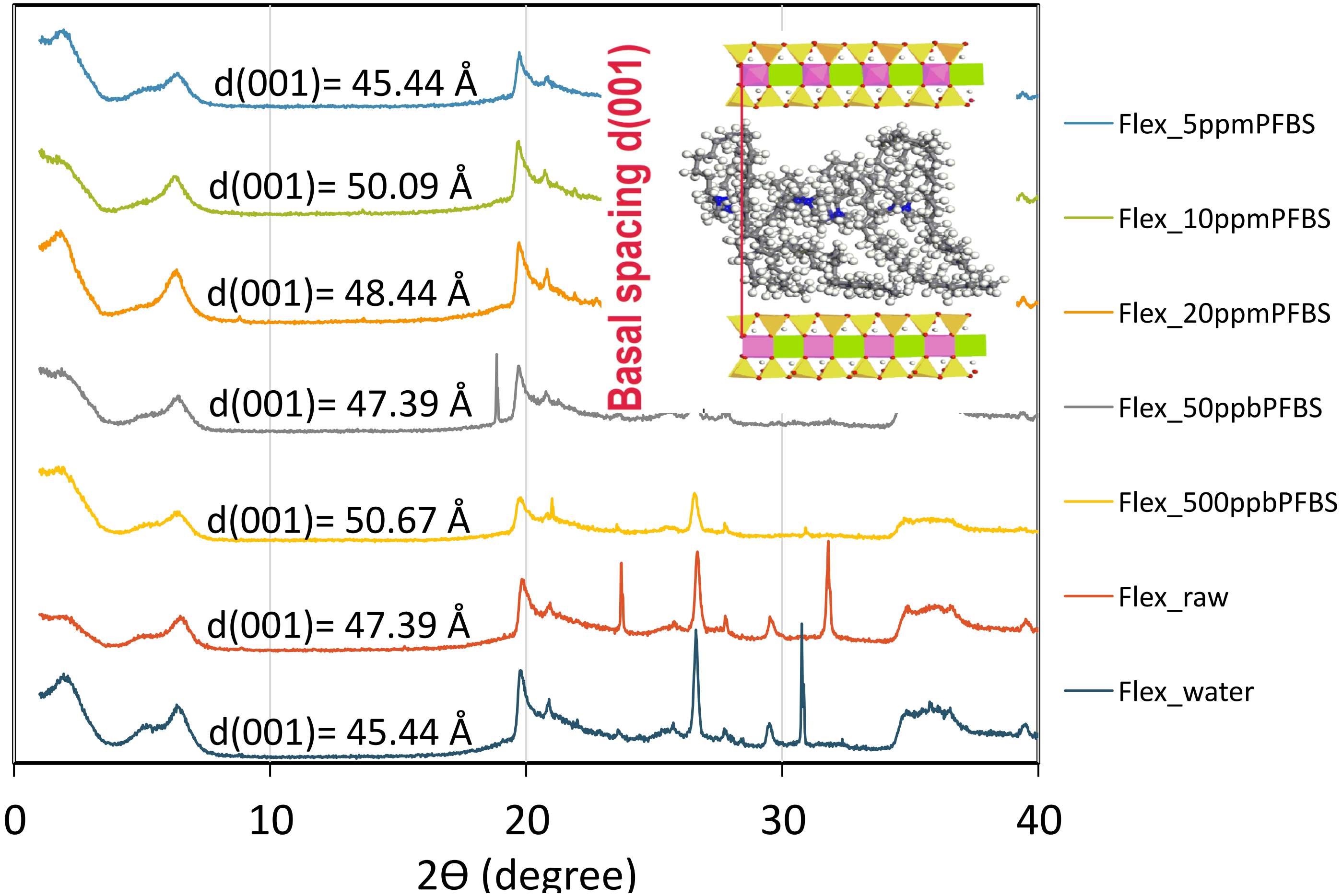
Performance Comparison

- Comparative assessment of removal efficiency of different sorbents including, FLUORO-SORB, GAC 400, Ion exchange resin and FLEX, in groundwater matric
- Spiked concentration of 1 ppm for ether-PFAS and short-chain PFAAs.
- FLEX outperforms GAC and FLUORO-SORB® for and short-chain perfluoroalkyl acids and ether-PFAS.

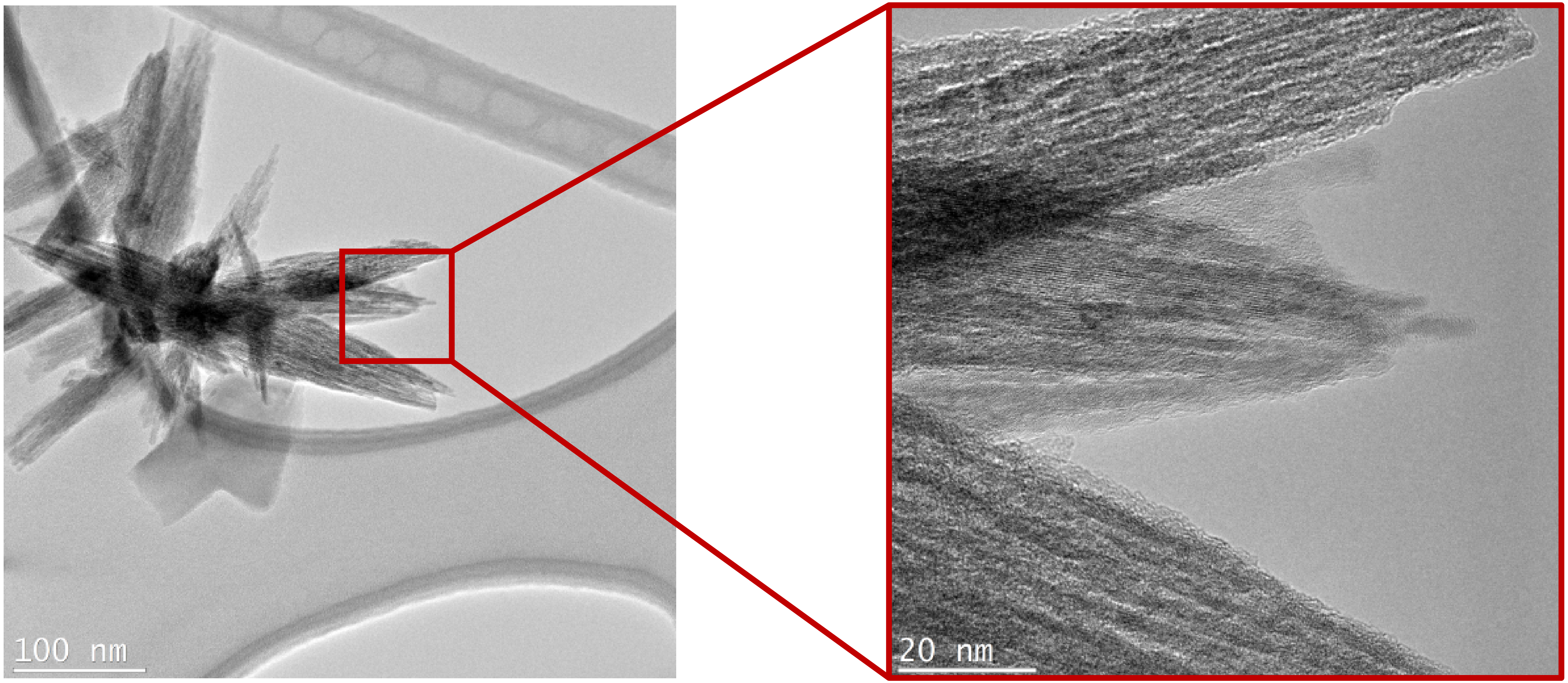


XRD of raw and loaded FLEX

- **Increased Basal Spacing in FLEX:**
    - Significantly larger than non-modified Na-Bentonite (D(100) of raw Na-Bentonite: **13.6 Å**)
    - Indicates the presence of intercalants
- **Enhanced Sorption Capacity:**
    - Larger basal spacing allows the clay sorbent to retain PFAS molecules within the layers

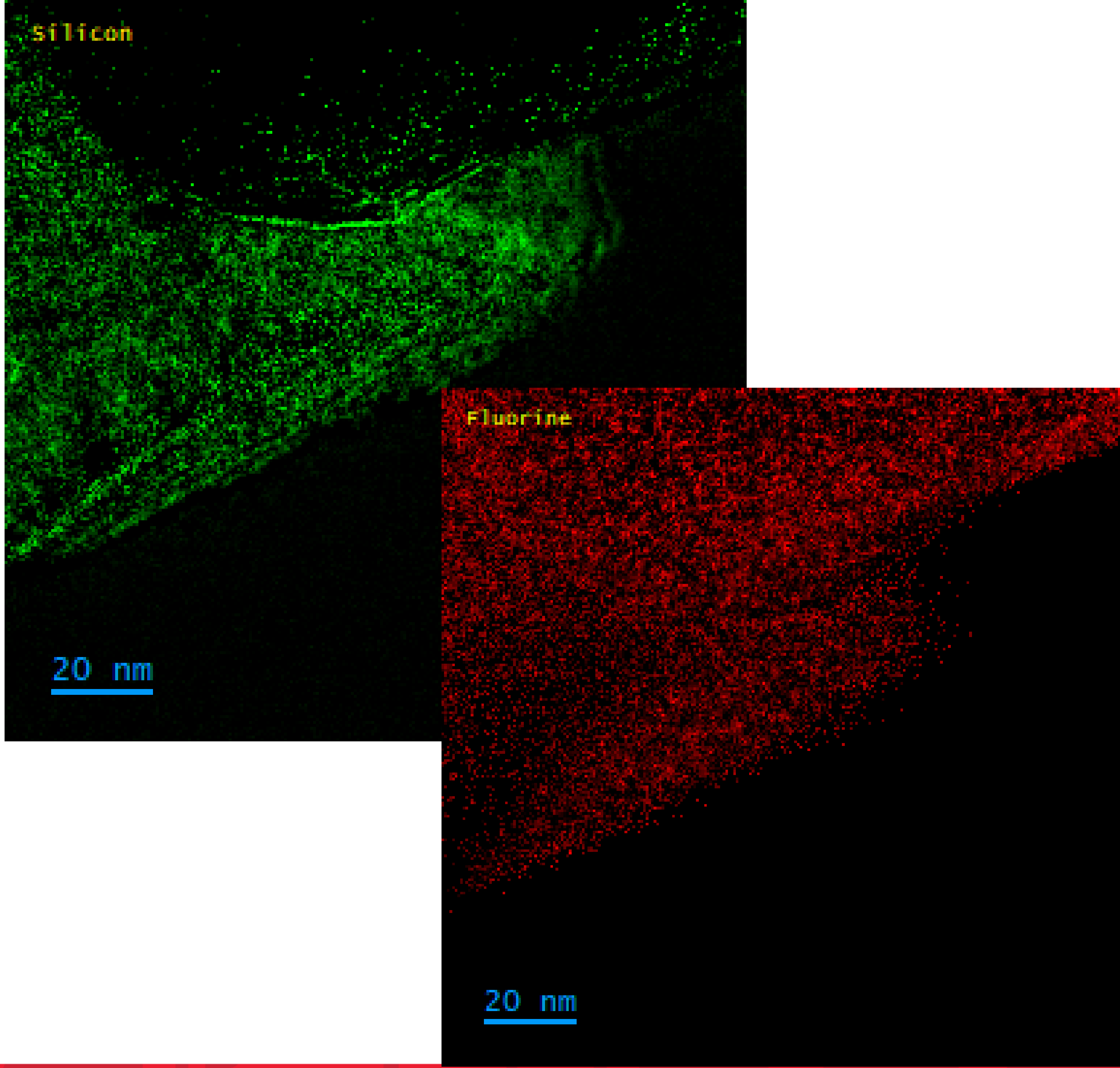


TEM Images of FLEX particles



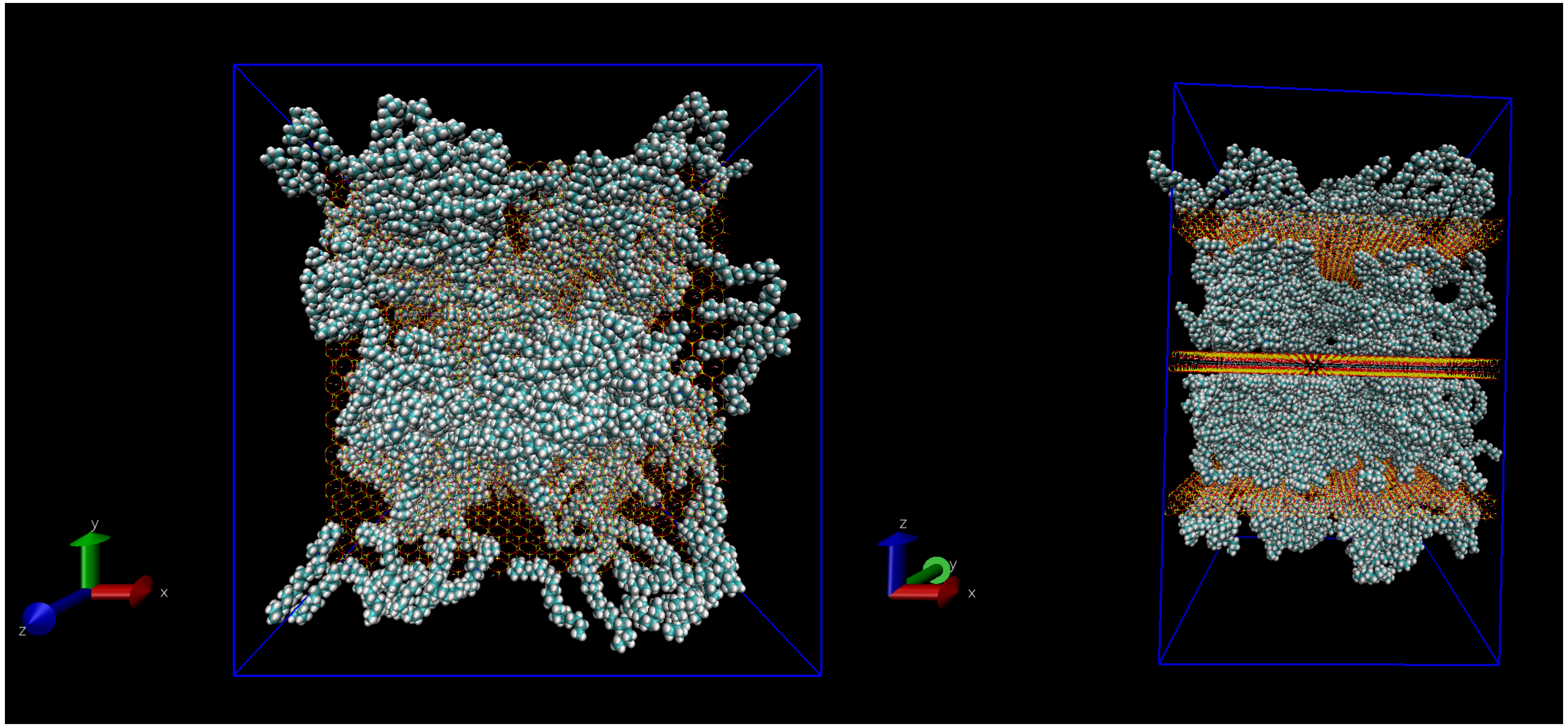
TEM-EDS

- TEM-EDS results show the uniform distribution of fluorine on FLEX;
- PFAS molecules are adsorbed on surface as well as the interlayers of the modified clay



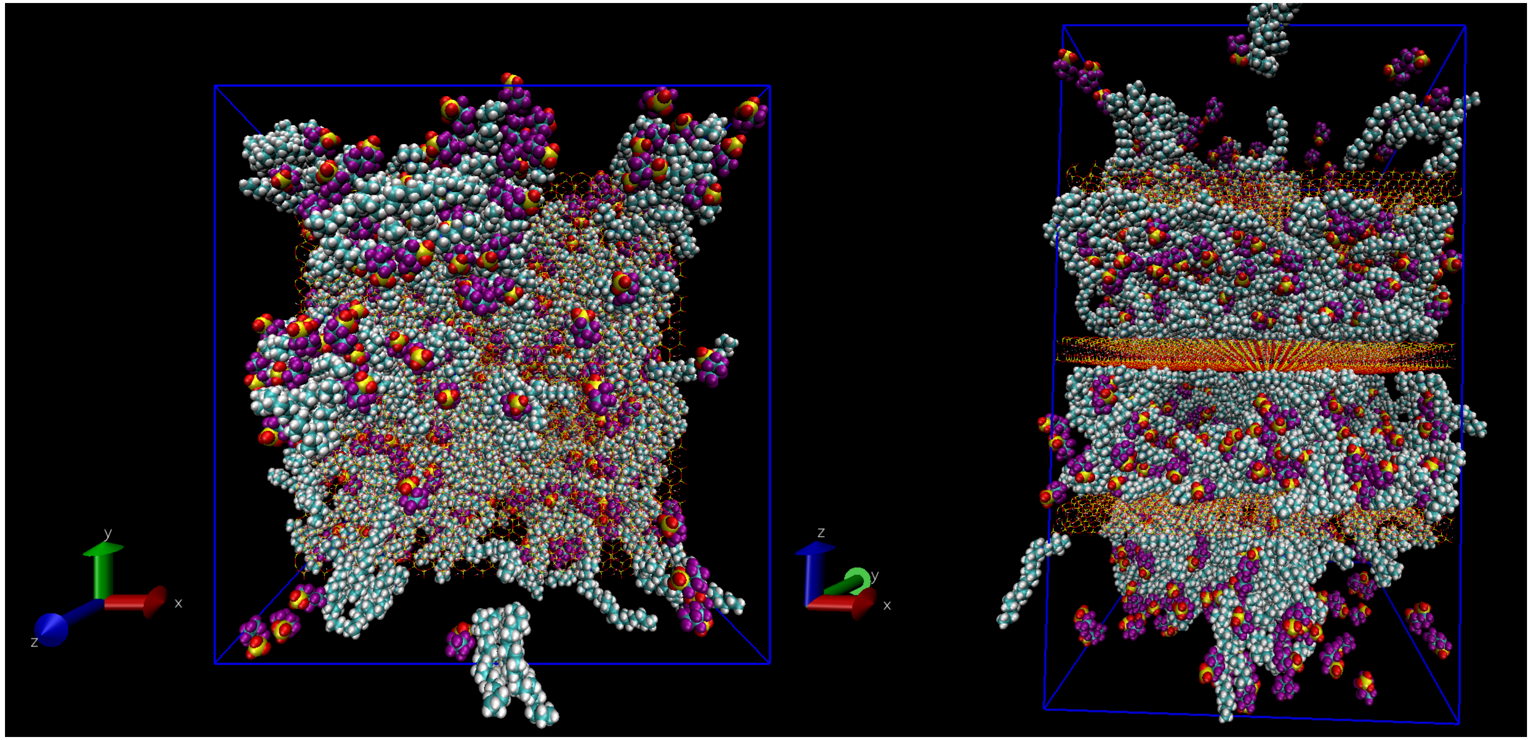
Molecular Dynamics (MD) Simulation

- MD simulation of the surfactant-modified bentonite clay
- CEC value: Charge of surfactant = 1:1
- Most of the surfactants enter the interlayer, while ~20% on the top and bottom surface.



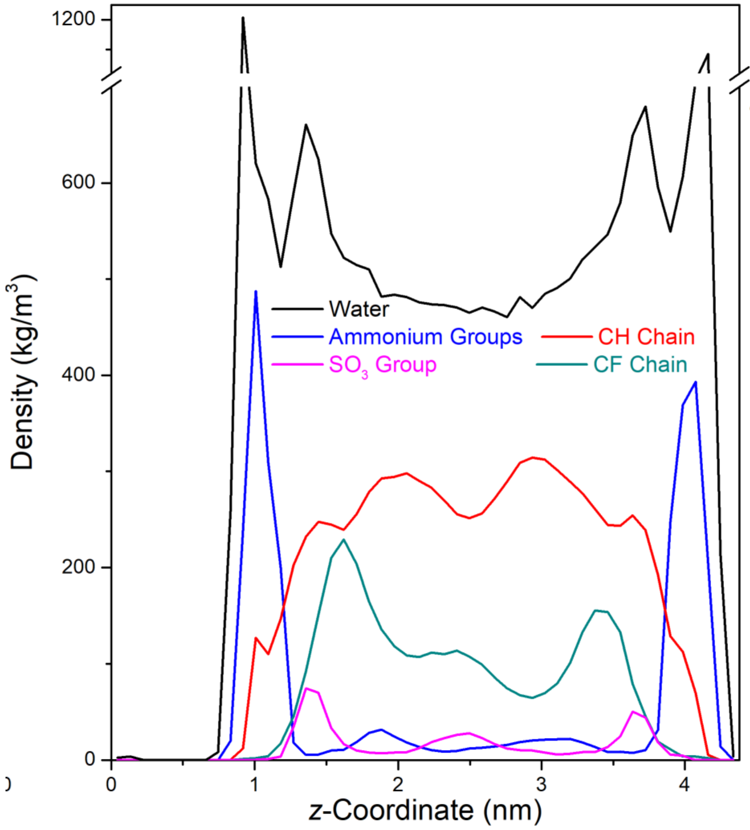
Molecular Dynamics (MD) Simulation

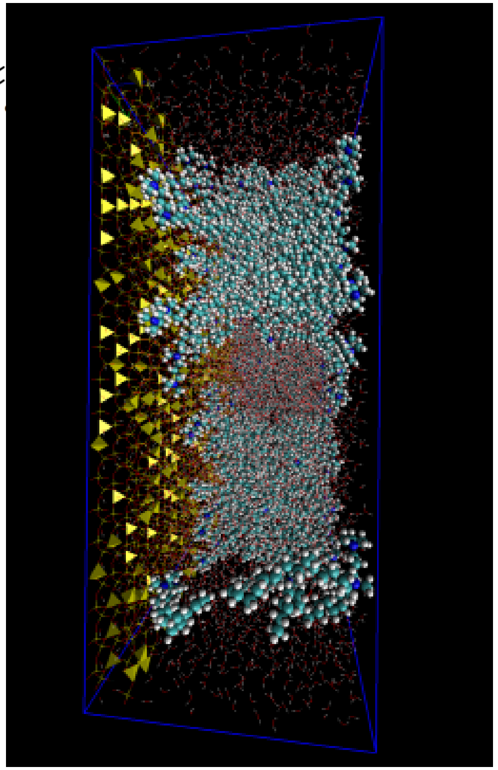
- MD simulation of the surfactant modified bentonite clay in the presence of PFBS
- PFBS adsorbs on the surface and inside the interlayers of the modified clay
- PFBS molecules are closely associated with intercalants, suggesting strong interactions



MD Simulation of FLEX

- Surfactant-modified bentonite clay was simulated to better understand the distribution of the intercalant and PFAS
- Most PFAS molecules are sorbed near the ammonium group on the intercalant
- Sorption is likely driven by ion exchange mechanisms.



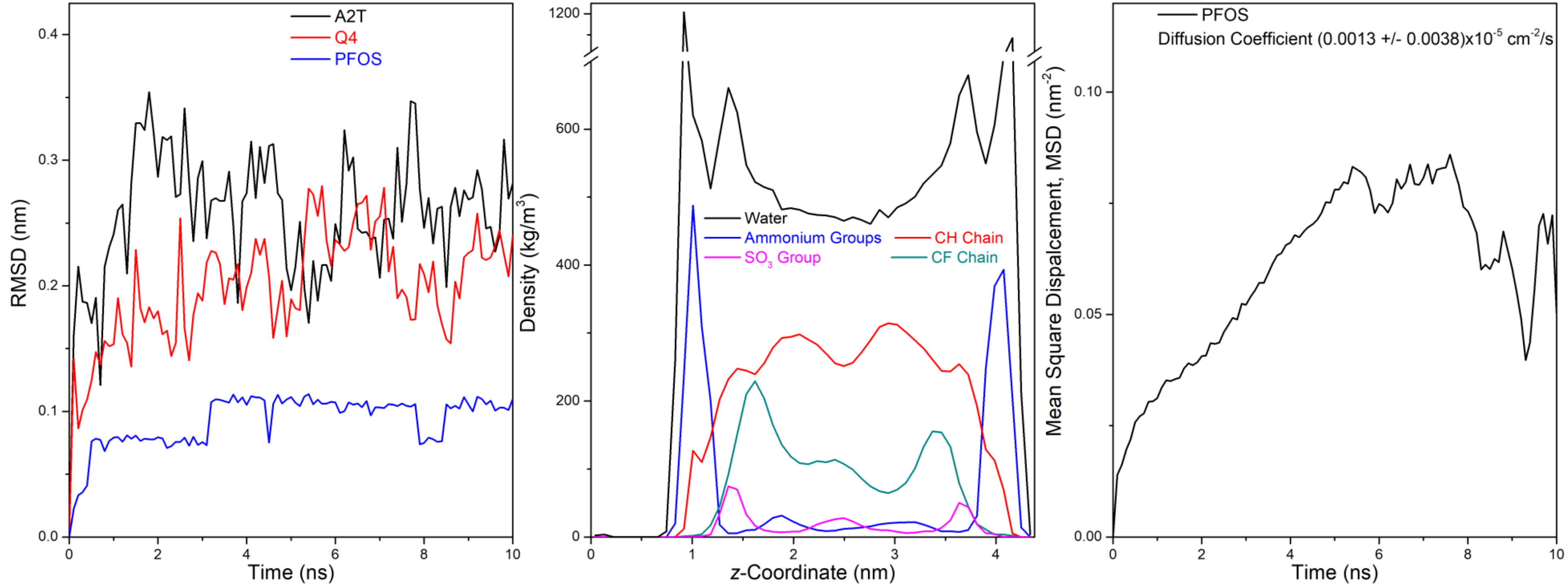


MD Simulation of FLEX

Diffusion coefficient of PFOS sorbed by FLEX is about 200 times smaller than PFOS in water

PFOS sorbed by FLEX: $(0.0013\ {}^{238}_{93}\ 0.0038){}^{3}_{2}10^{-5}$ cm^2/s

PFOS in water: 0.508×10^{-5} cm^2/s (Water Res. 144, 162-171)

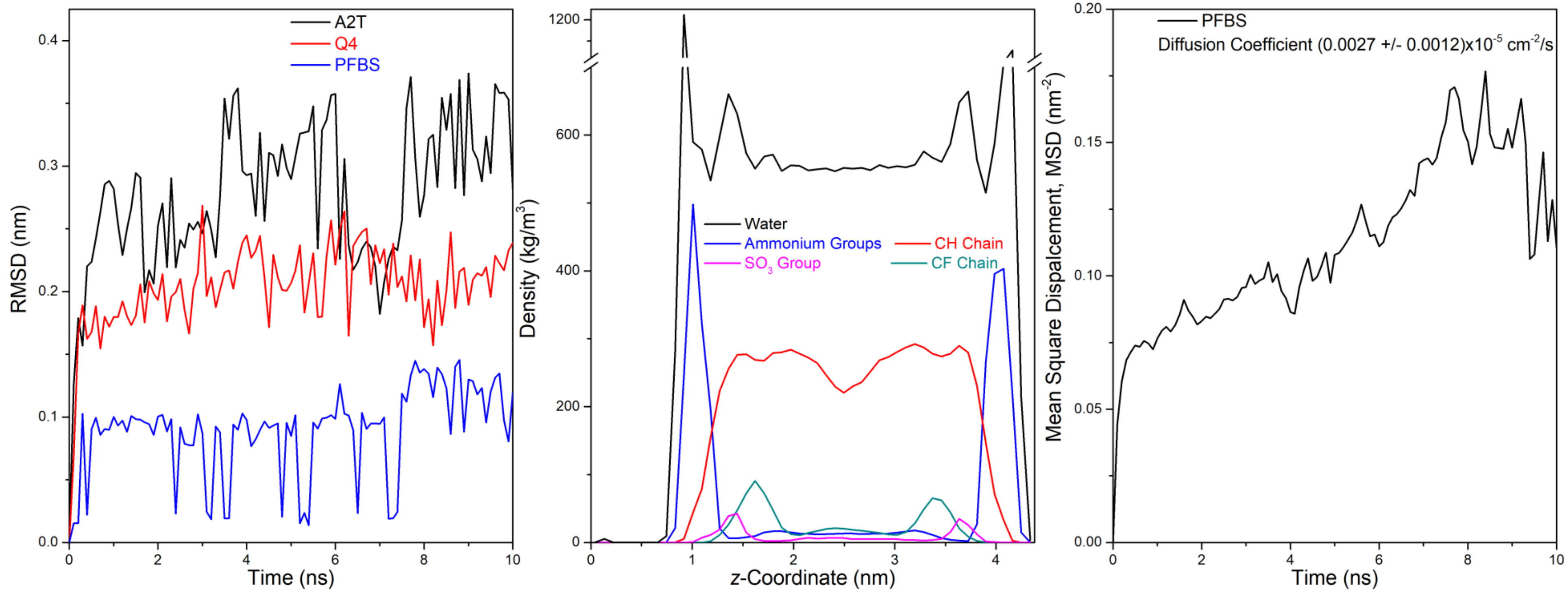


MD Simulation of FLEX-PFBS

Diffusion coefficient:

FLEX-PFBS: (0.0027 $^{238}_{93}$ 0.0012)$^{3}_{2}$10^-5 cm^2/s

PFOS: 0.508 ×10^-5 cm^2/s (Water Res. 144, 162-171)

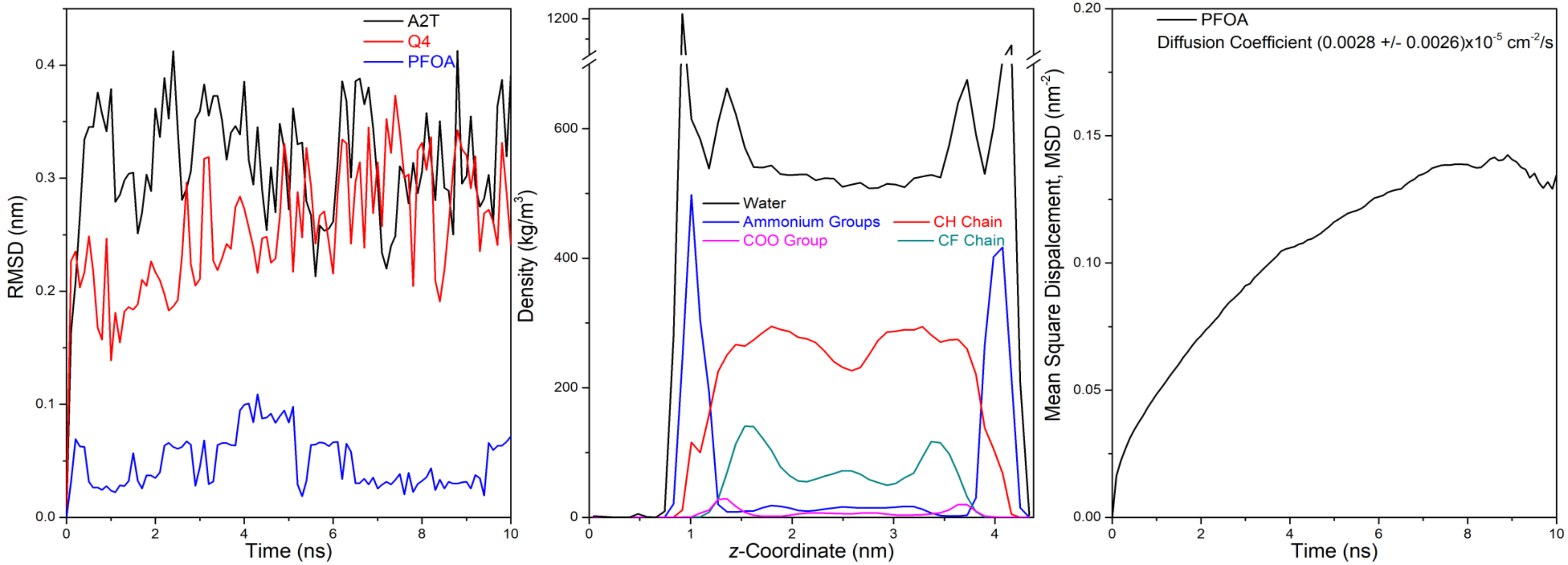


MD Simulation of FLEX-PFOA

Diffusion coefficient:

FLEX-PFOA: (0.0029 $^{238}_{93}$ 0.0008)$^{3}_{2}$10^-5 cm^2/s

PFOA: 0.437 ×10^-5 cm^2/s (Water Res. 144, 162-171)



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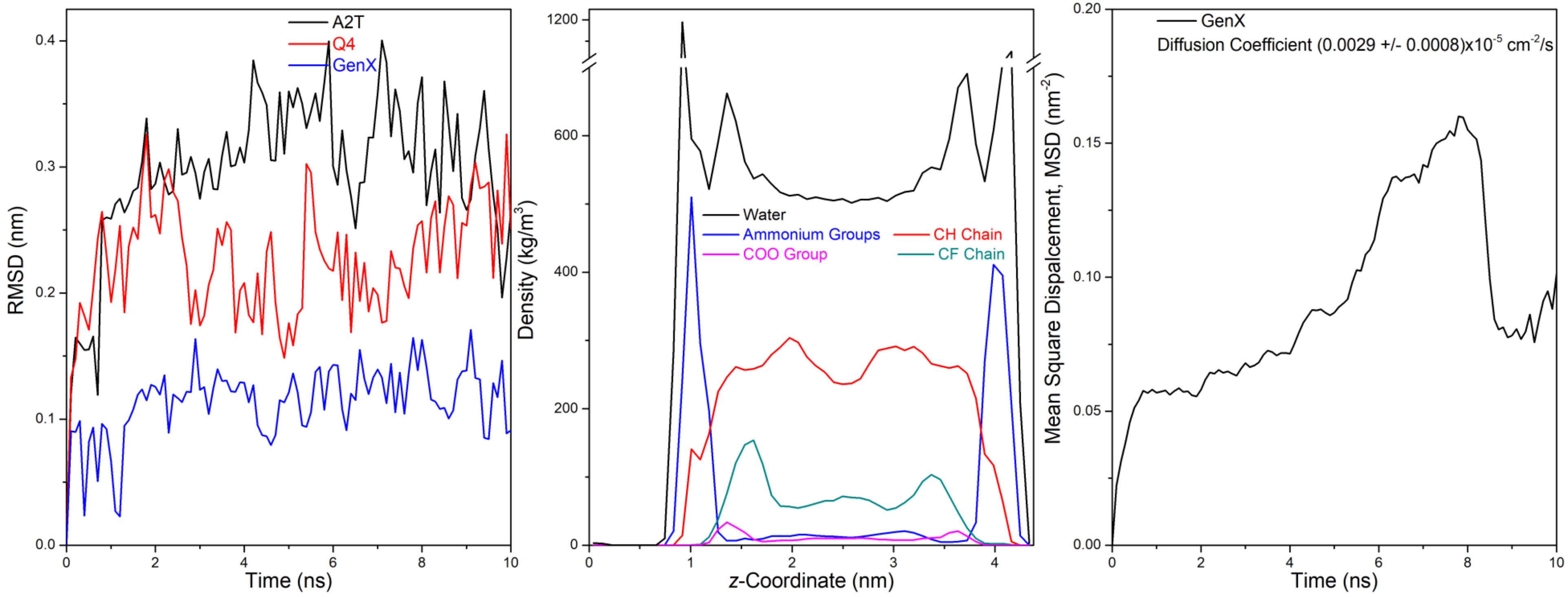

Conclusions

- FLUORO-SORB® FLEX is effective for sorbing short-chain, long-chain, and ether PFAS.
- It is more effective for short-chain PFAS compared to granular activated carbon (GAC).
- The new generation product performs well across diverse water chemistries.
- High d-spacing allows PFAS to adsorb into the interlayers.
- Sorption is likely controlled by hydrophobic effects and ion exchange processes.
- PFAS sorbed by Flex has a significantly low diffusion coefficient, which could imply resistance to leaching.

Acknowledgments

Contact information

Prof. Jinxia Liu (jinxia.liu@mcgill.ca)

Faezeh Pazoki (faezeh.pazoki@mail.mcgill.ca)

Financial Support:

NSERC CRSNG

MINERALS TECHNOLOGIES

CETCO

Thank you.

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Adsorption Capacity

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Langmuir-Freundlich model: $q_e = \frac{q_m * b * C_e^{1-c}}{1 + b * C_e^{1-c}}$

q_m= Maximum sorption capacity
q_e= Equilibrium sorption capacity
C_e= Equilibrium concentration

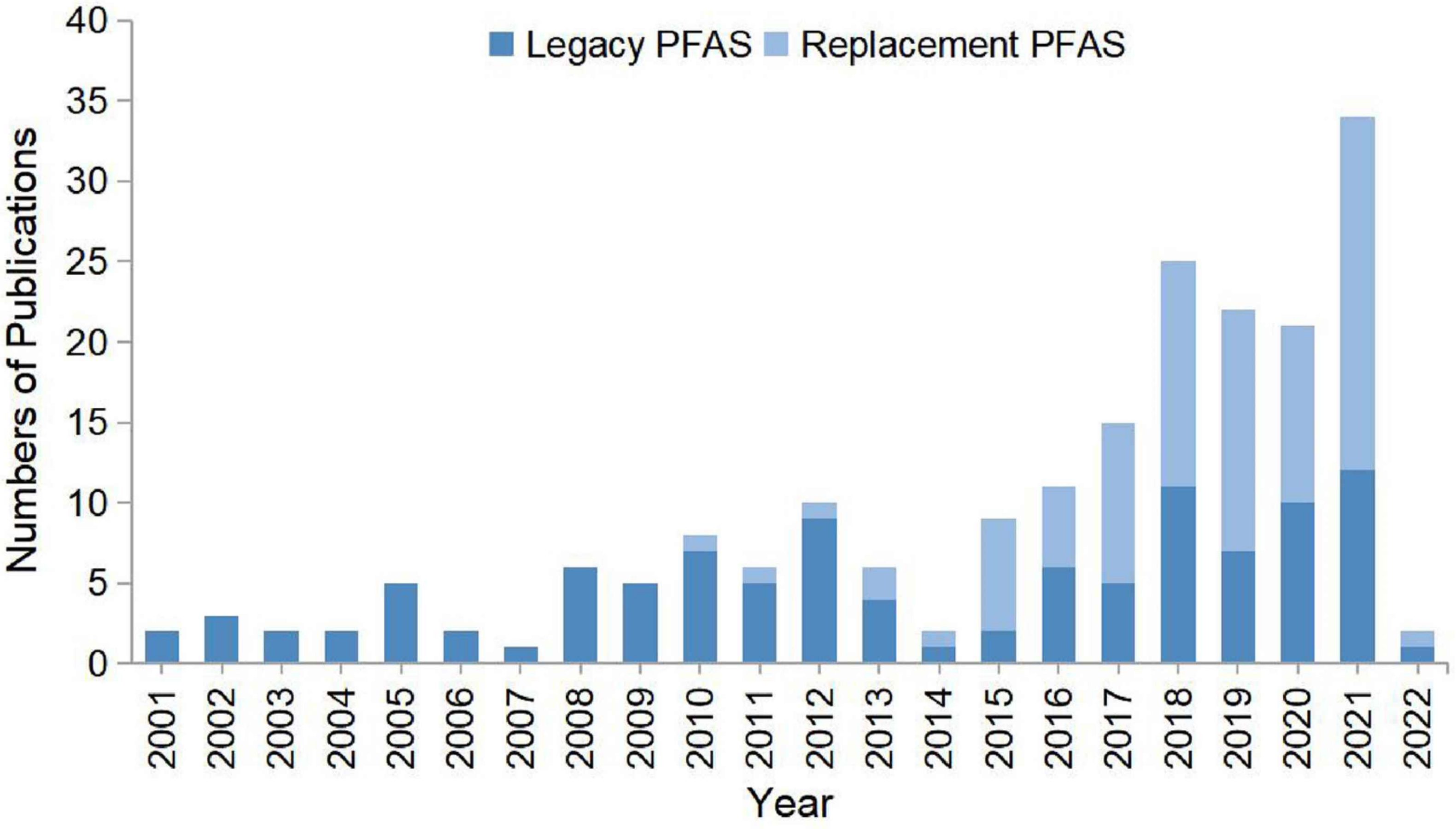
	PFBS	PFOS	PFBA	PFOA	PFMPA	HFPO-DA	HFPO-TA
q_m (mg/g)	20	71	13	40	21.8	50	62
q_m (umol/g)	66.6	142	60.7	96.6	50.2	142.8	123

Background

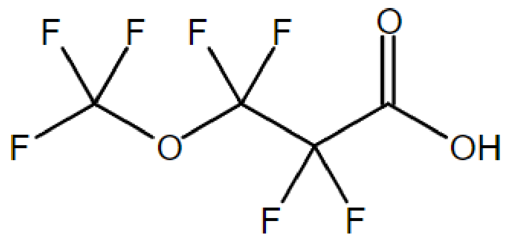
GenX Toxicity:

- 28-day oral exposure in male mice led to liver necrosis
- Potentially more toxic to liver than PFOA

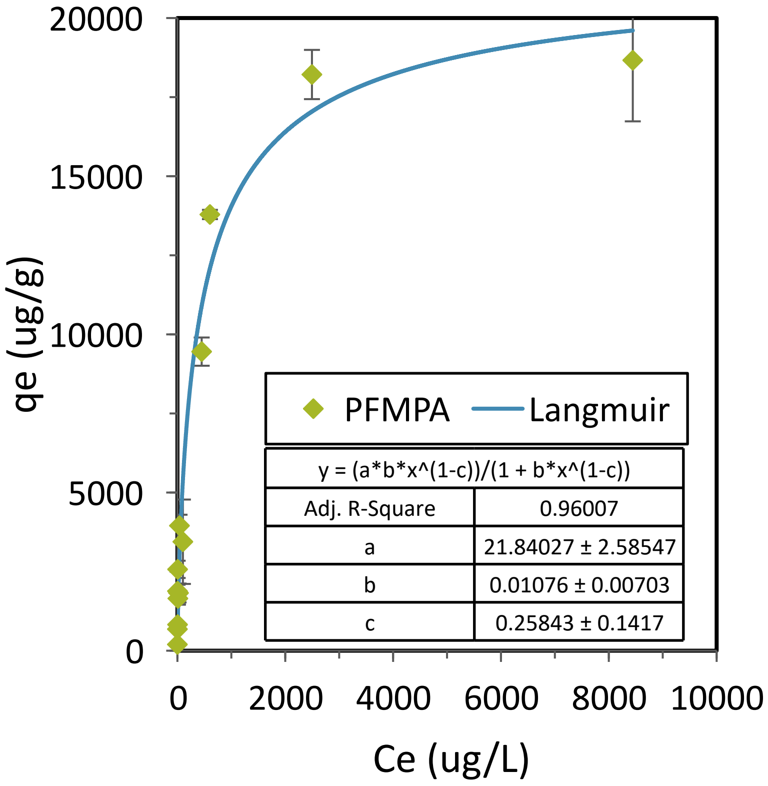
Insufficient research on the removal of emerging PFAS

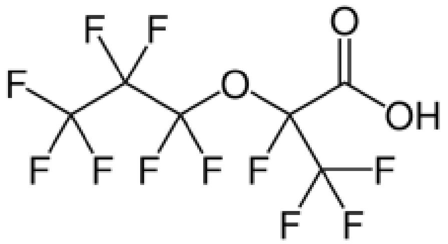


Distribution of the numbers of references cited in this paper is organized by year.
Eco-Environ. & Health. 2022 *1*(2), pp.117-131

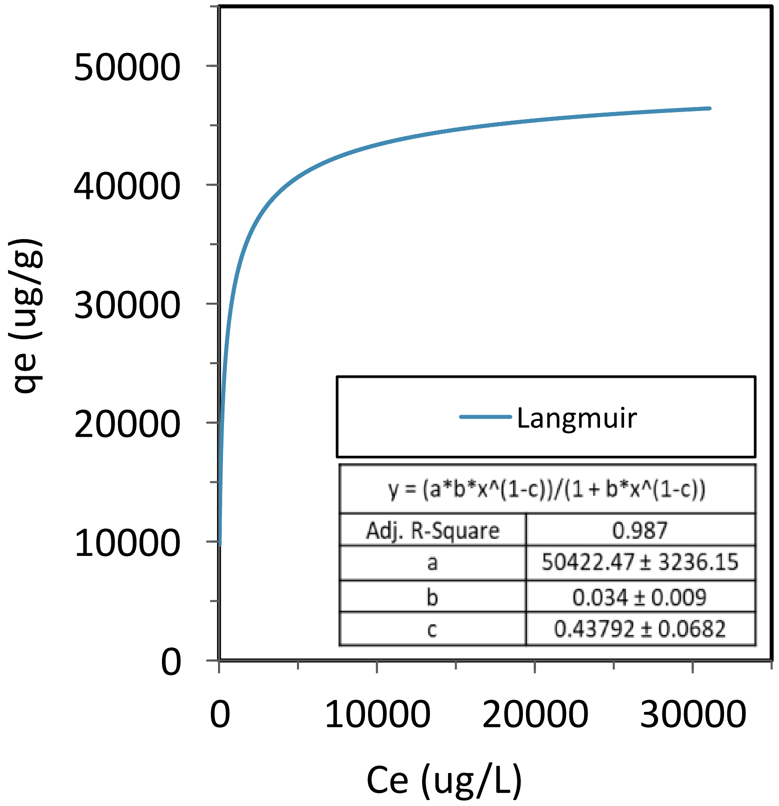


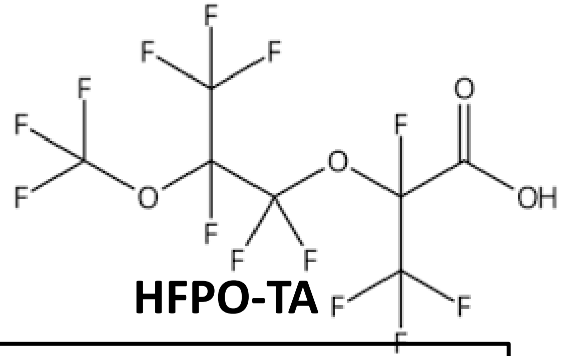
PFMPA



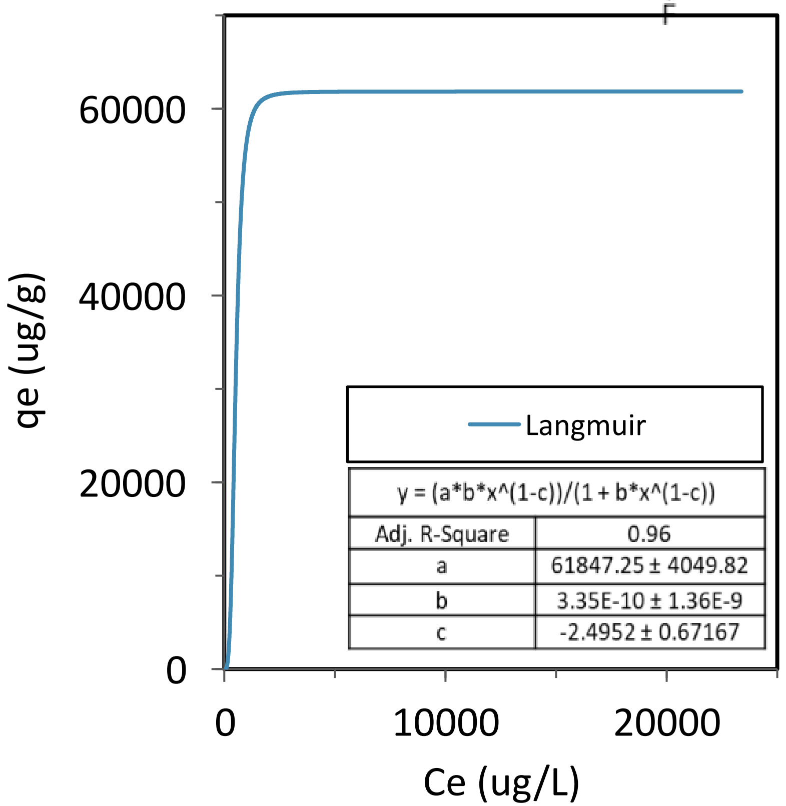


HFPO-DA

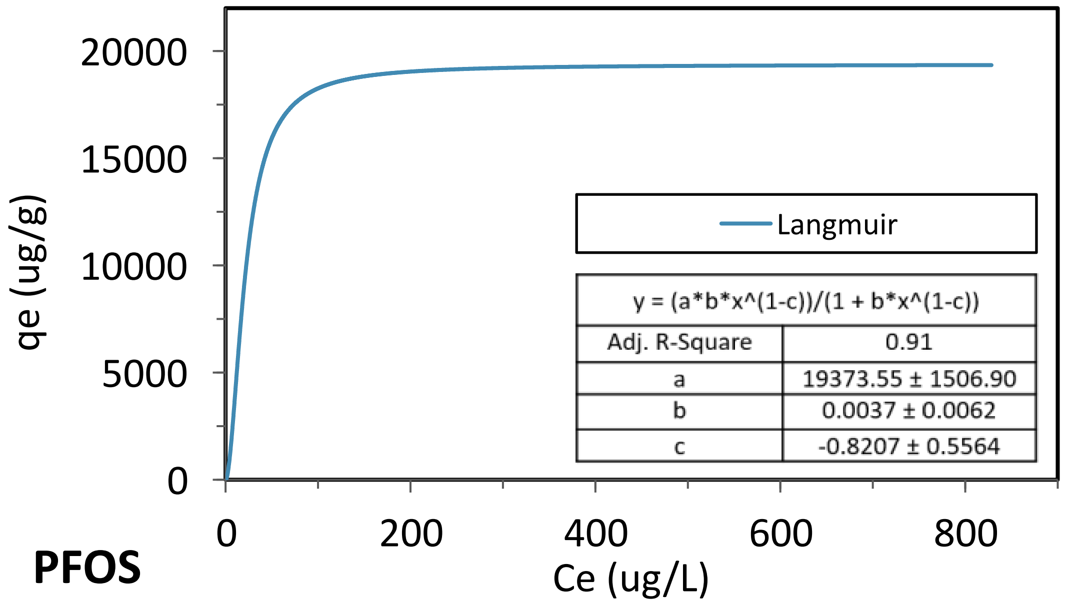




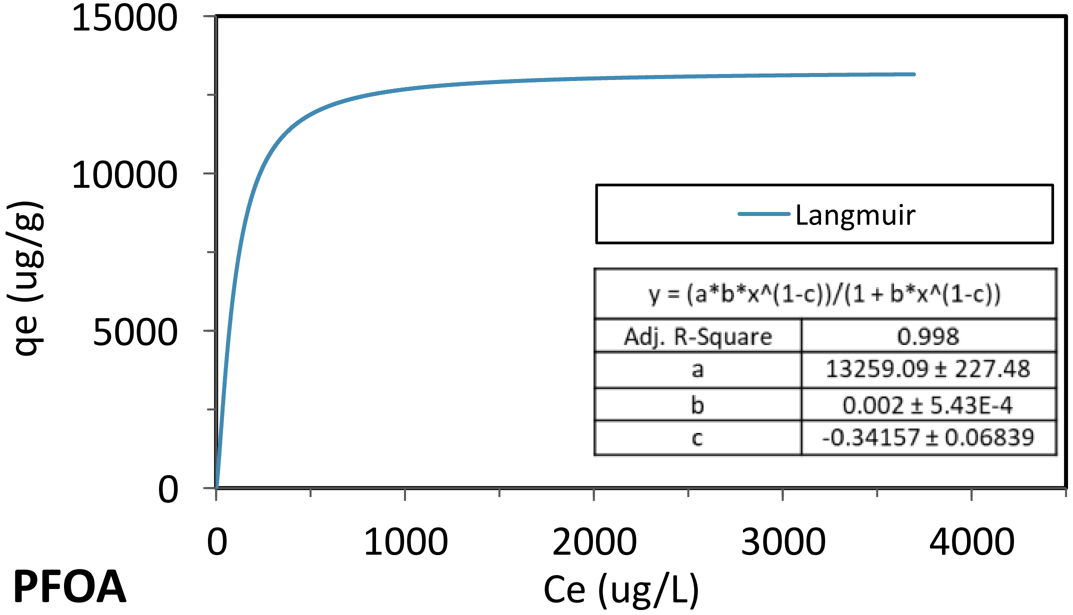
HFPO-TA



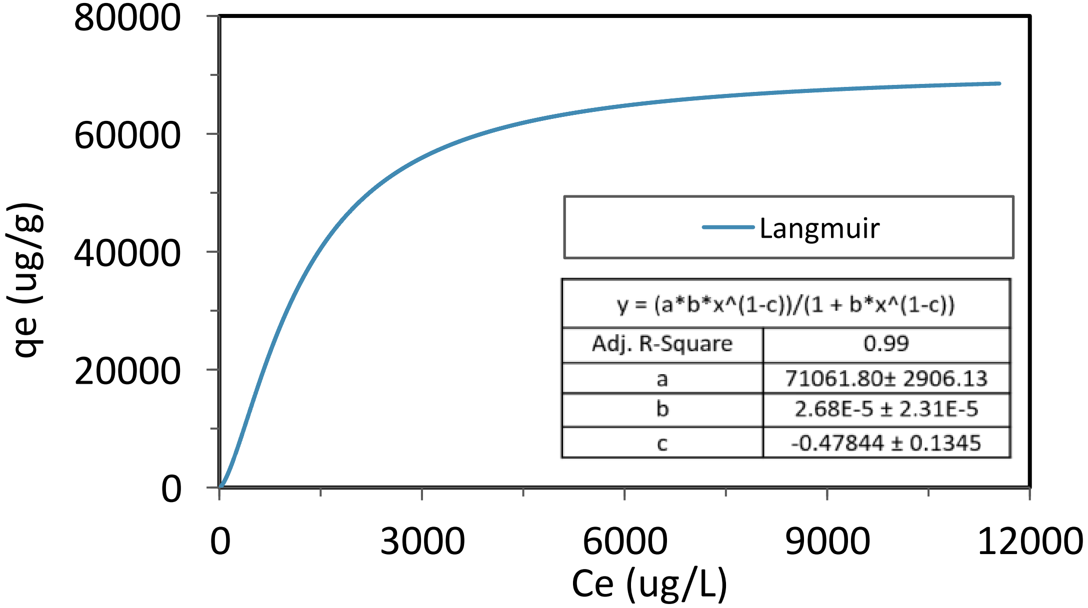
PFBS



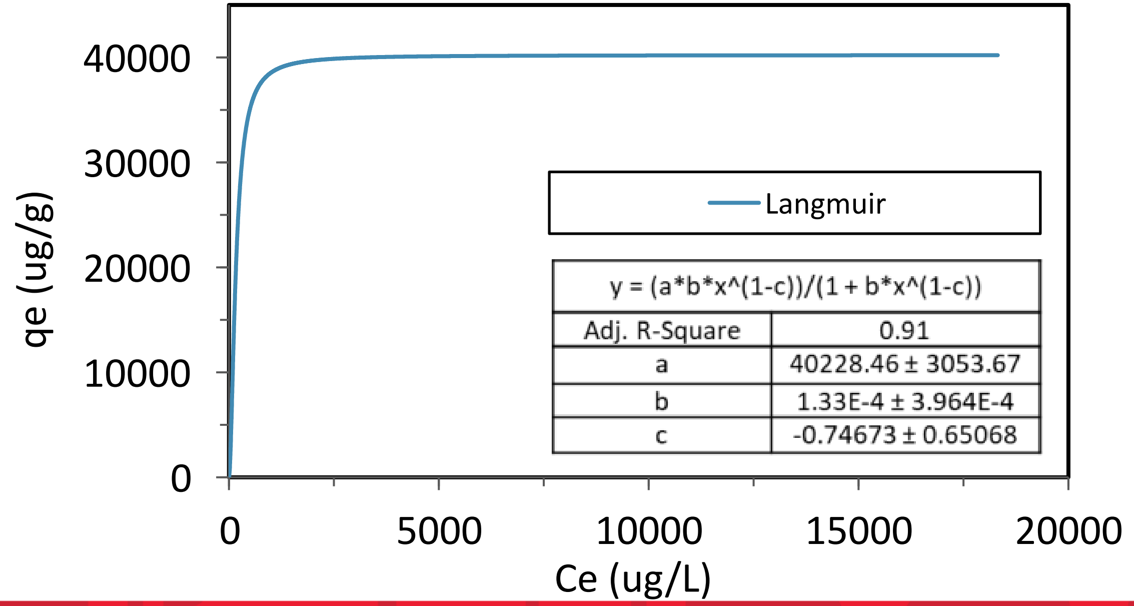
PFBA



PFOS

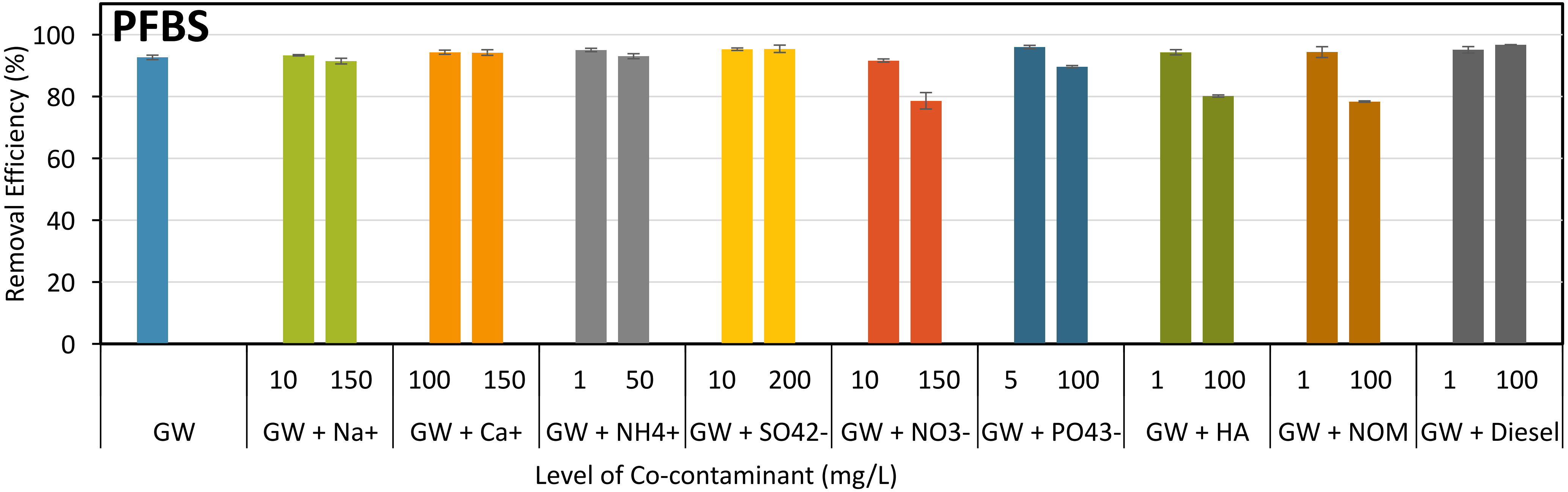


PFOA



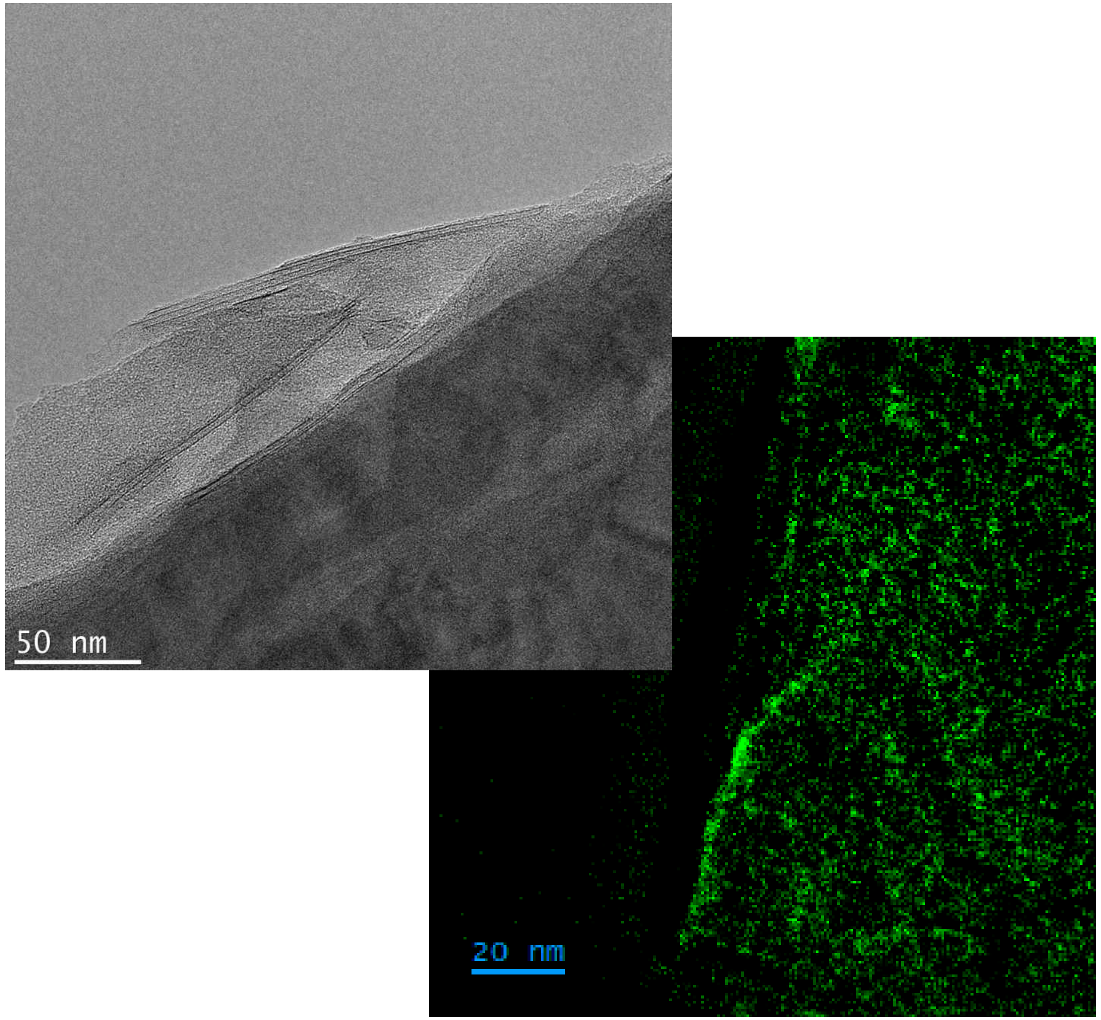
Impact of Water Chemistry

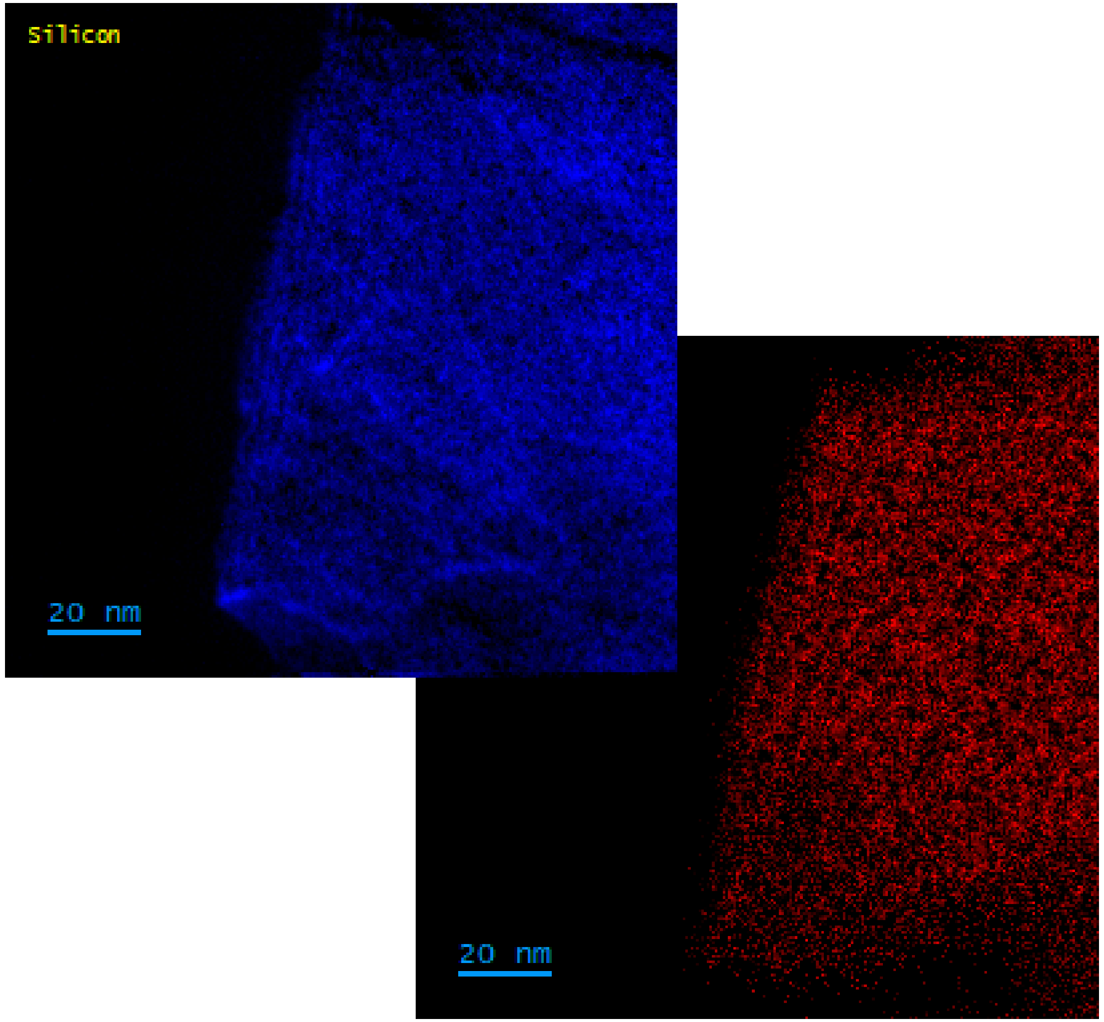
- PFBS was spiked at 1 ppm
- Two levels of ions and co-contaminants were added to model environmentally relevant concentrations as well as extreme conditions



McGill

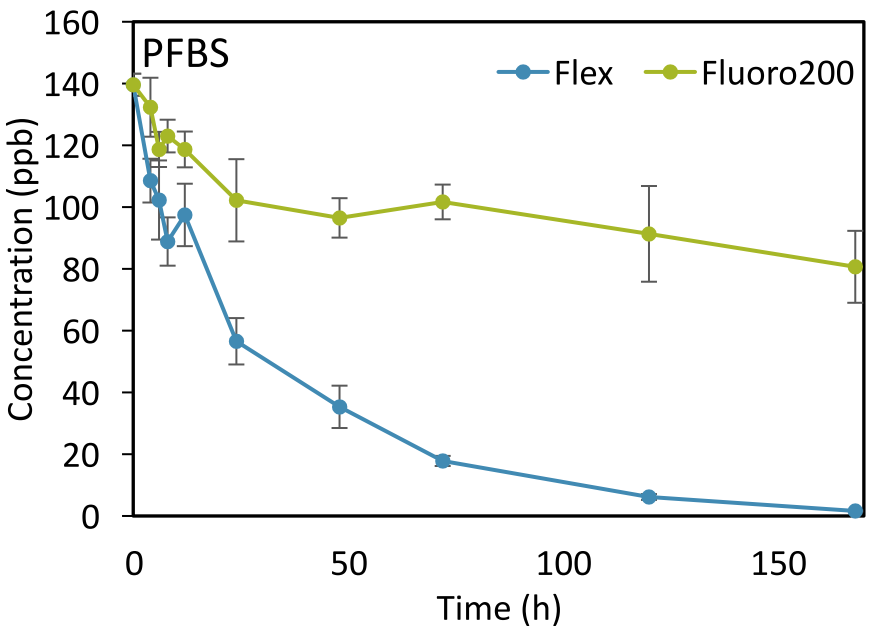
PFBS Distribution on Flex_TEM-EDS

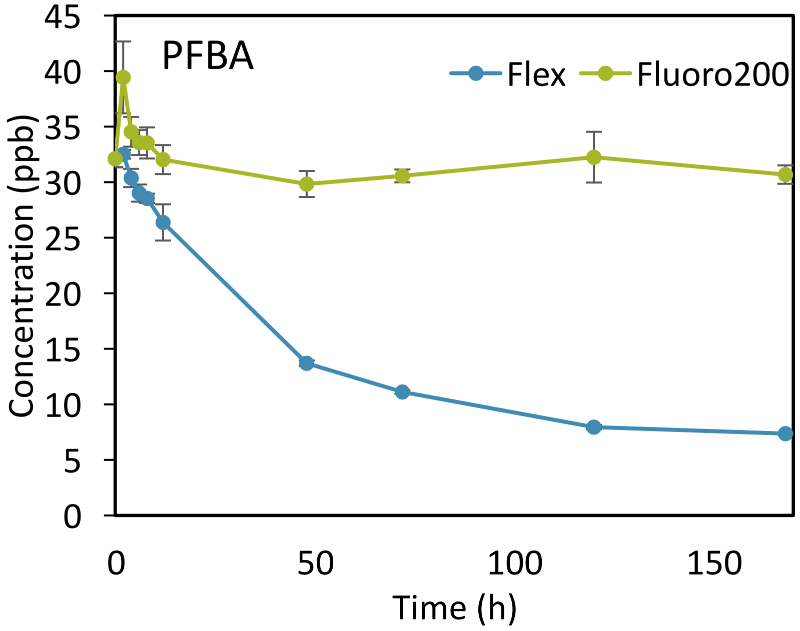




Sorption kinetics

- Sorption kinetic for PFBS (Left) and PFBA (right) on FLEX and FLUORO-SORB.



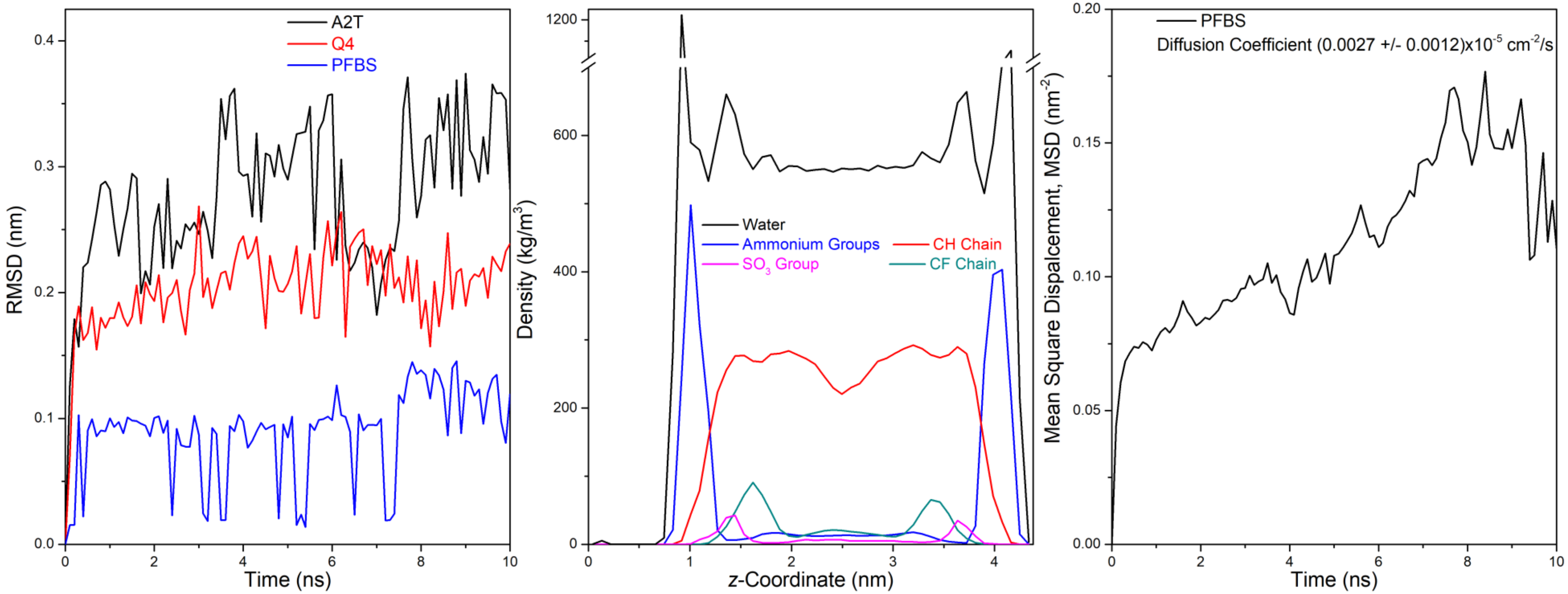


MD Simulation of FLEX-PFBS

Diffusion coefficient:

FLEX-PFBS: (0.0027 $^{238}_{93}$ 0.0012)$^{3}_{2}$10^-5 cm^2/s

PFOS: 0.508 $\times$10^-5 cm^2/s (Water Res. 144, 162-171)

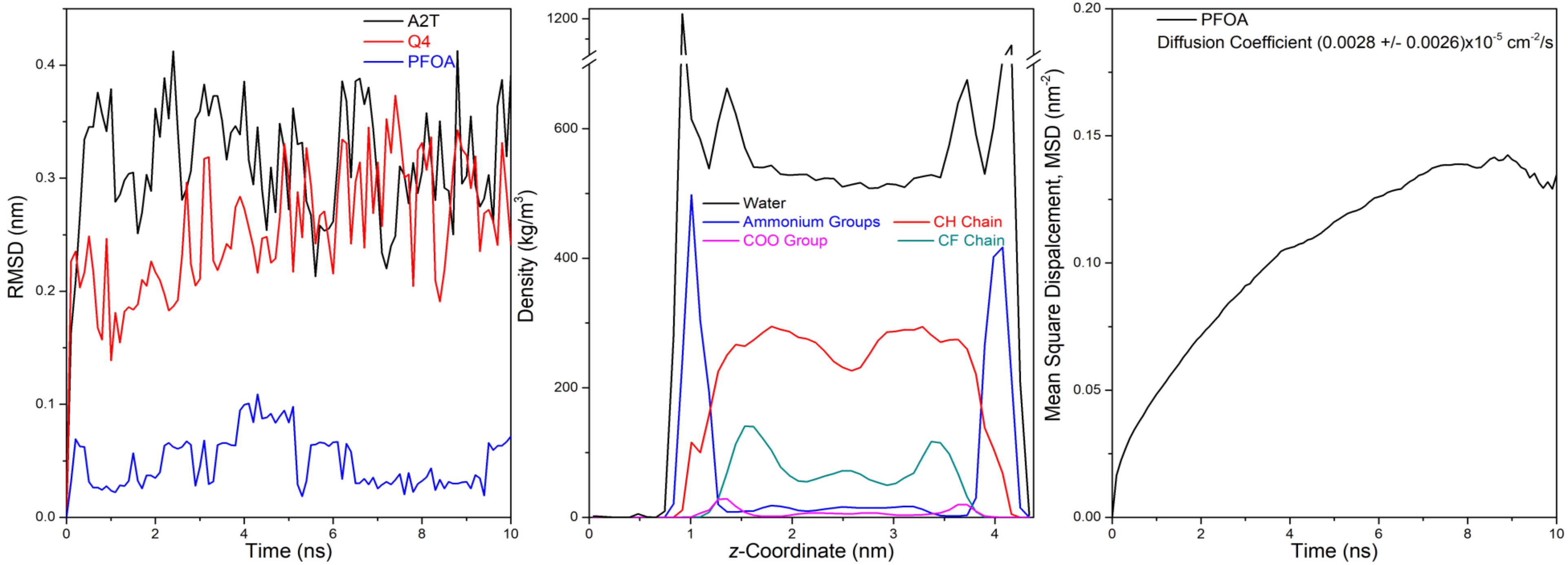


MD Simulation of FLEX-PFOA

Diffusion coefficient:

FLEX-PFOA: (0.0029 $^{238}_{93}$ 0.0008)$^{3}_{2}$10^-5 cm^2/s

PFOA: 0.437 ×10^-5 cm^2/s (Water Res. 144, 162-171)

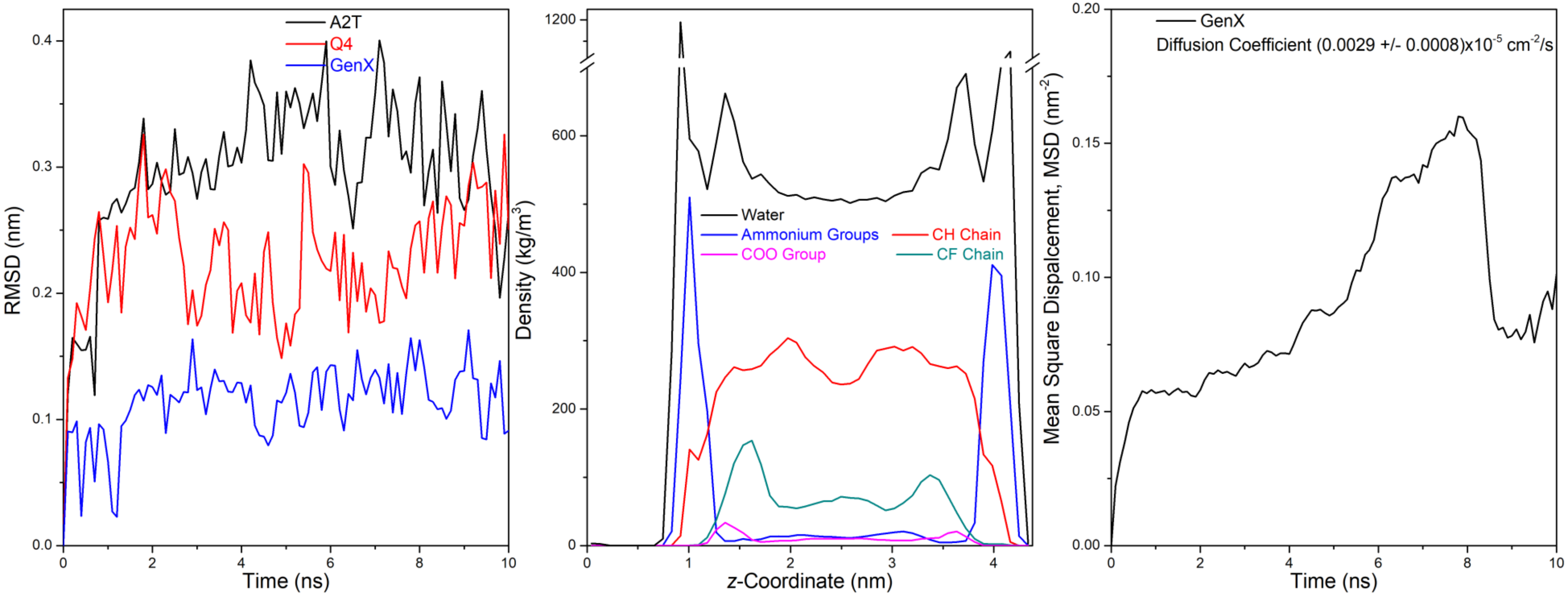


MD Simulation of FLEX-GenX

Diffusion coefficient:

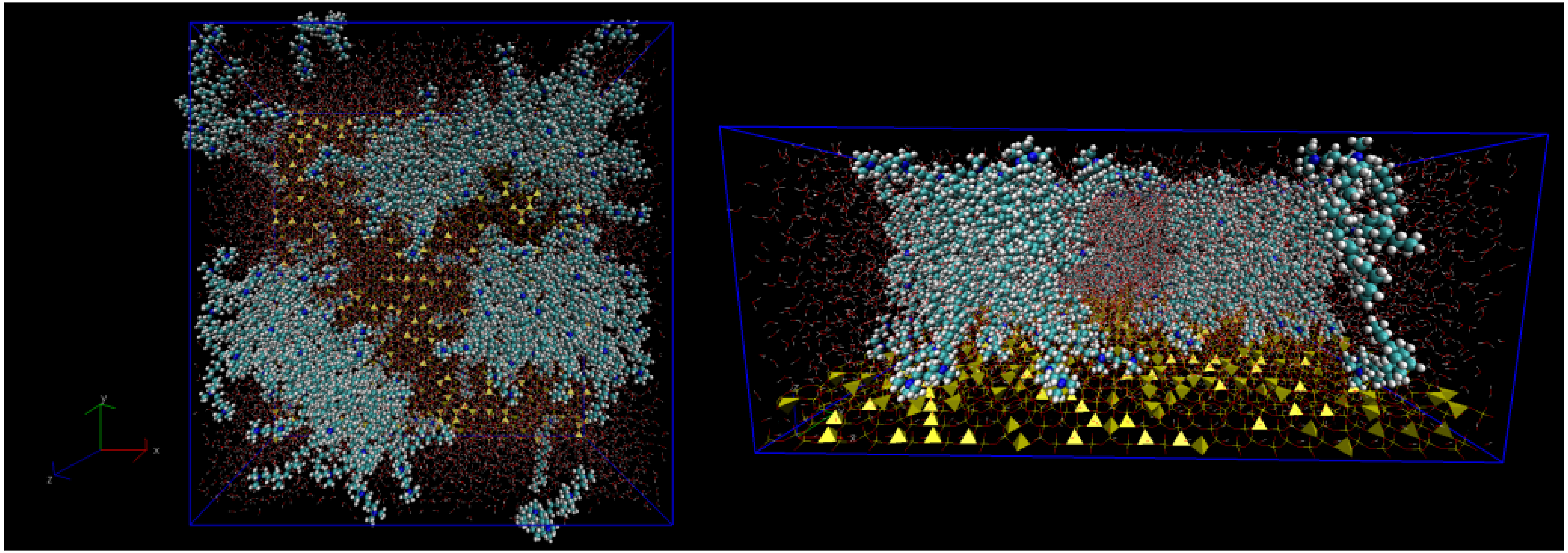
FLEX-GenX: (0.0029 $^{238}_{93}$ 0.0008)$^{3}_{2}$10^-5 cm^2/s

PFOA: 0.437 $\times$10^-5 cm^2/s (Water Res. 144, 162-171)



MD Simulation of FLEX

- Surfactant-modified bentonite clay was simulated to measure the diffusion coefficient of PFAS molecules sorbed by FLEX



DFT-based thermochemistry

- Thermochemistry results show that hydrophobic effect is the main mechanism behind the sorption of PFAS on surfactant modified clay

Water Cage: ΔG= -162.3 kcal/mol, ΔH= -40.3 kcal/mol

Without Water: ΔG= 37.0 kcal/mol

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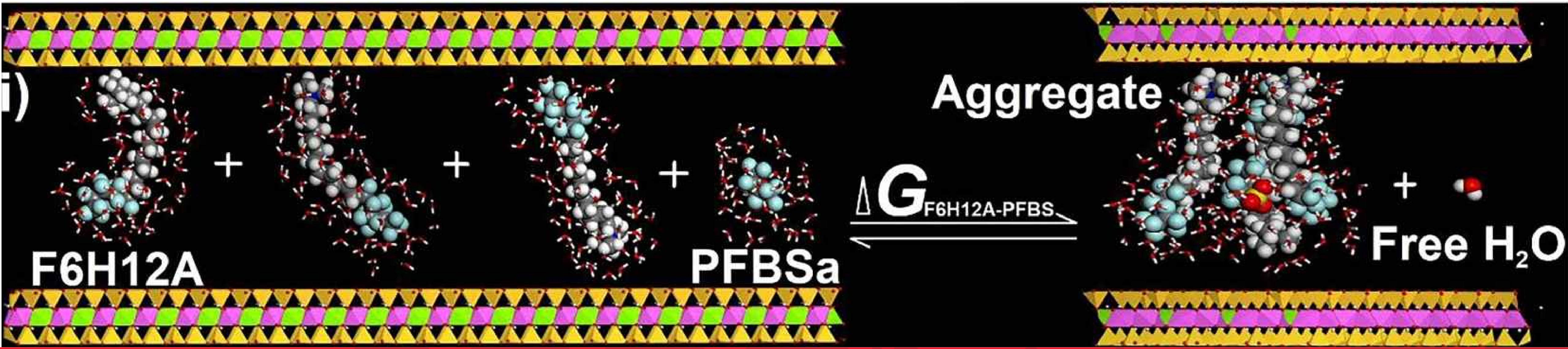

XRD of raw and loaded FLEX

- **Increased Basal Spacing in FLEX:**
  - Significantly larger than non-modified Na-Bentonite (D(100) of raw Na-Bentonite: **13.6 Å**)
  - Indicates the presence of intercalants
- **Enhanced Sorption Capacity:**
  - Larger basal spacing allows the clay sorbent to retain PFAS molecules within the layers

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