Granular Activated Carbon (GAC) Batch Adsorption of Per-and-Polyfluoroalkyl Substances (PFAS) from Drinking Water

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Outline

1 Research Background

- PFAS, occurrence, and importance of treatment
- Effective treatment technologies and challenges

2 Research Approach

- Knowledge gaps
- Objectives
- Materials
- Methods

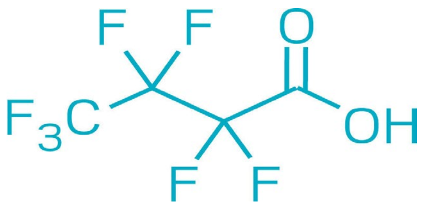
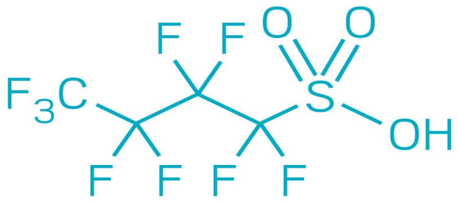
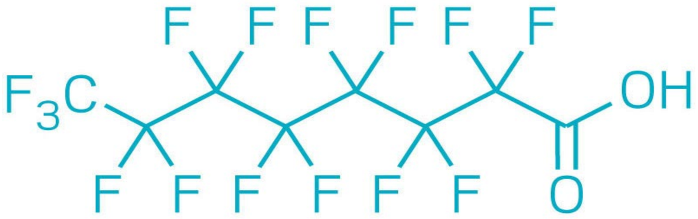
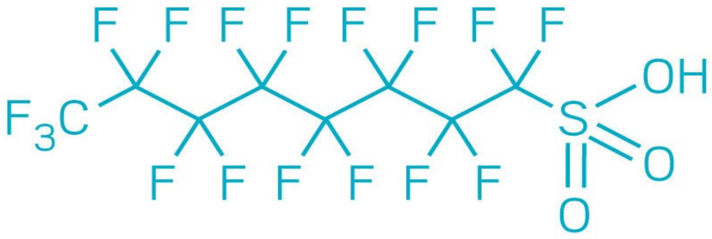
3 Research Findings

- Adsorption kinetics
- Adsorption isotherms

1. Research Background

1.1 PFAS, occurrence, and importance of treatment

Fluorinated aliphatic substances: extremely stable, hydrophobic, lipophobic

PFAS	Perfluoroalkyl carboxylic acids (PFCA)	Perfluoroalkyl sulfonic acids (PFSA)
Carbon chain length: 4 (C4)	PFBA 	PFBS 
Carbon chain length: 8 (C8)	PFOA 	PFOS 

Molecular structure: American Chemical Society (ACS)
https://cen.acs.org/sections/pfas.html

1. Research Background

1.1 PFAS, occurrence, and importance of treatment

Main exposure pathways - <u>Nationally</u>

Ingestion through diet

Indoor dust inhalation

Communities with contaminated drinking water

Drinking Water

- **6 PFAS Monitored for UCMR3:**
  PFBS, PFHxS, PFHpA, PFOA, PFOS, PFNA

- **9 PFAS EPA Toxicity Assessments (completed or planned):**
  PFBA, PFHxA, PFOA, PFNA, PFDA, GenX, PFBS, PFHxS, PFOS

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1.2 Effective treatment technologies and challenges

Effective technologies (conventional technologies not effective)

High pressure membrane filtration

GAC adsorption

Anion exchange

- **Established technology**
- **Established regeneration procedure**

Challenges:

- **Factors affecting adsorption: adsorbent, adsorbate, water matrix**
- **Testing under representative conditions required**
- **Lack of fundamental PFAS adsorption parameters**

2.1 Knowledge gaps

- Need additional batch adsorption studies at drinking water relevant PFAS concentrations
- Need baseline PFAS adsorption parameters — without the effect of background water constituents and/or other PFAS
- Need to investigate batch adsorption kinetics fundamentals — reaction based kinetic models

2.2 Objectives

1. Batch adsorption kinetics (buffered water)
    - Initial estimate of isotherm parameters
    - Time to equilibrium (t_{eq})

2. Batch adsorption isotherms (buffered water)
    - Assessing adsorption isotherms
    - Estimating isotherm parameters
    - Drinking water relevant PFAS concentrations (<1000 ng/L)

3. Investigate the effect of particle size on adsorption kinetics

2.3 Materials

Three bituminous coal based GACs

Filtrasorb 400 (F400) – Calgon

Three particle sizes: 200x325, 100x200, 60x100

Norit 400 – Cabot

Particle sizes: 200x325

UltraCarb 1240 LD (UC1240LD) – Evoqua

Particle sizes: 200x325

Inorganic salts

Buffer: 0.01M Sodium bicarbonate ($NaHCO_3$)

Nine selected PFAS

Five PFCA:

perfluorobutanoic acid (PFBA), C4

perfluorohexanoic acid (PFHxA), C6

perfluorooctanoic acid (PFOA, C8

perfluorononanoic acid (PFNA), C9

perfluorodecanoic acid (PFDA), C10

Three PFSA:

perfluorobutane sulfonic acid (PFBS), C4

perfluorohexane sulfonic acid (PFHxS), C6

perfluorooctane sulfonic acid (PFOS), C8

One ether acid:

perfluoro-2-propoxypropanoic acid (PFPrOPrA, GenX), C6

2.4 Methods

Experimental Design

27 single solute kinetic tests —nine PFAS × three GACs (200x325)

→

Objective1

- $\mathbf{t_{eq}}$
- Diffusion Coeff.
- $\mathbf{k_f}$ initial estimate

27 single solute isotherm tests — nine PFAS × three GACs (200x325)

→

Objective2

27 pairs of baseline isotherm parameters

8 single solute kinetic tests — four PFAS × two sizes (100x200 and 60x100) of F400

→

Objective3

Effect of particle size on adsorption kinetics

2.4 Methods

Measured parameters	Kinetics analysis	Isotherm analysis
❖ PFAS: online solid phase extraction liquid chromatography mass spectrometry(LC-MS-MS) ❖ pH and Temperature	❖ Liquid-layer-diffusion controlled mass transfer model (LL) ❖ Pore- and surface-diffusion controlled mass transfer model (PSDM)	Freundlich equation: $q_e = k_f \times c_e^{1/n}$ where: q_e - solid phase PFAS loading (µg/g GAC) c_e - liquid phase PFAS concentration (ng/L) k_f & $1/n$ - Freundlich parameters

3.1 Adsorption kinetics

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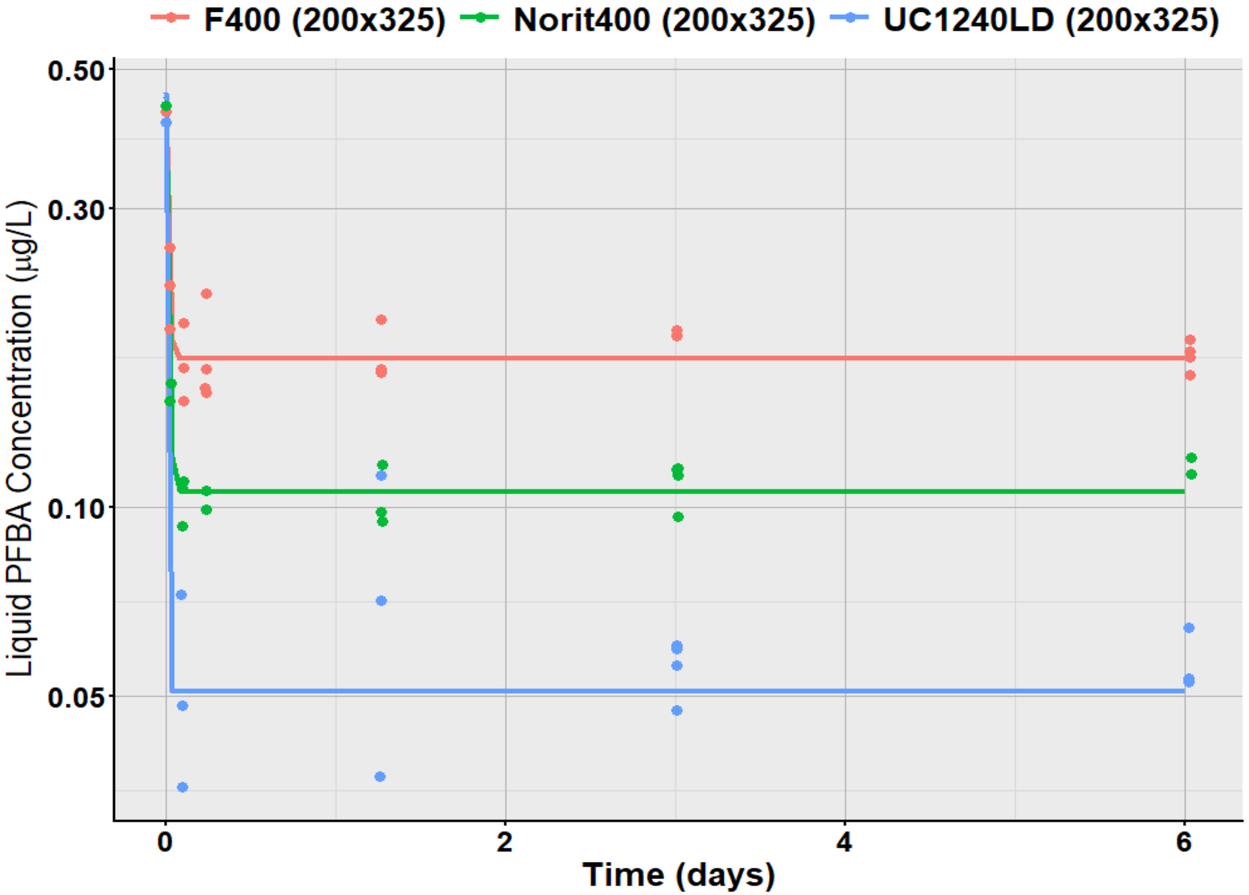
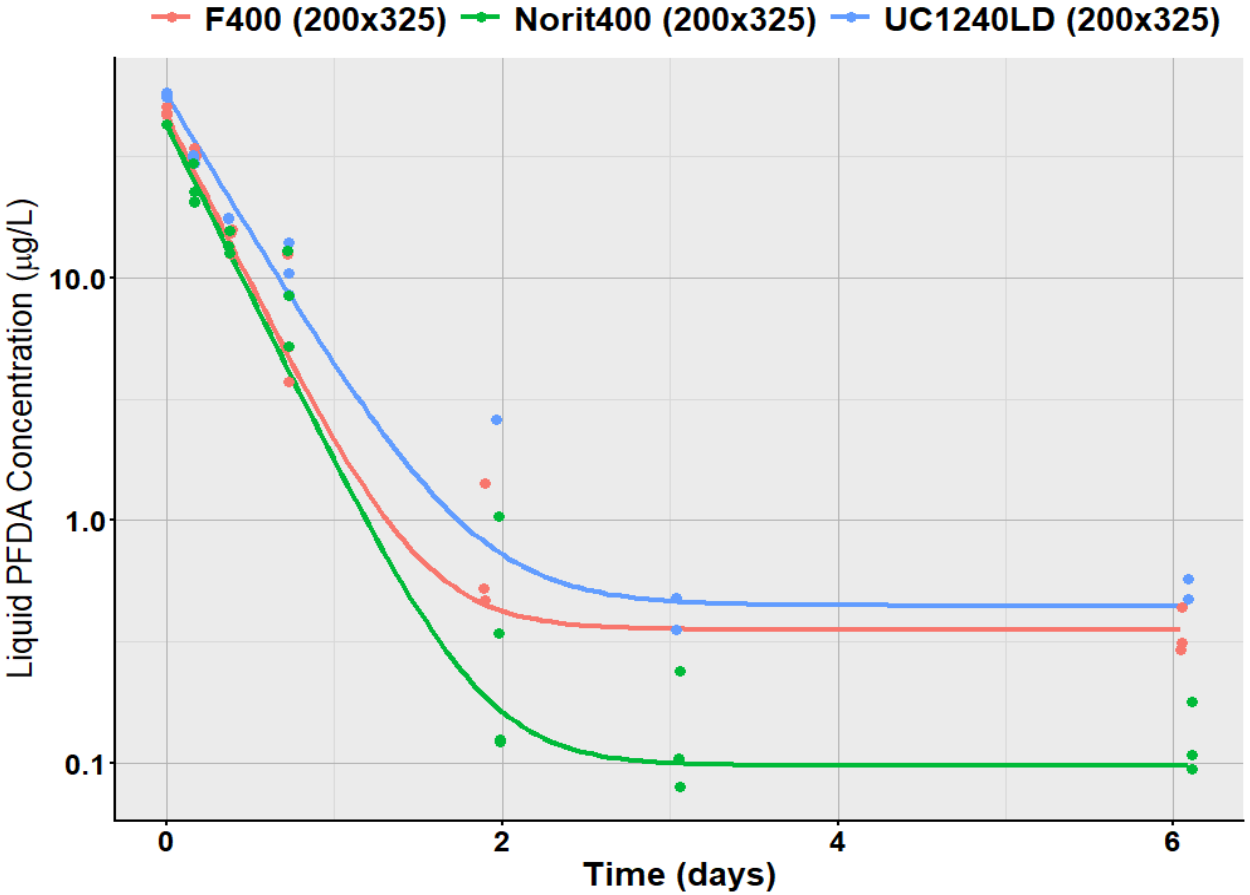
PFBA



PFDA



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3.1 Adsorption kinetics

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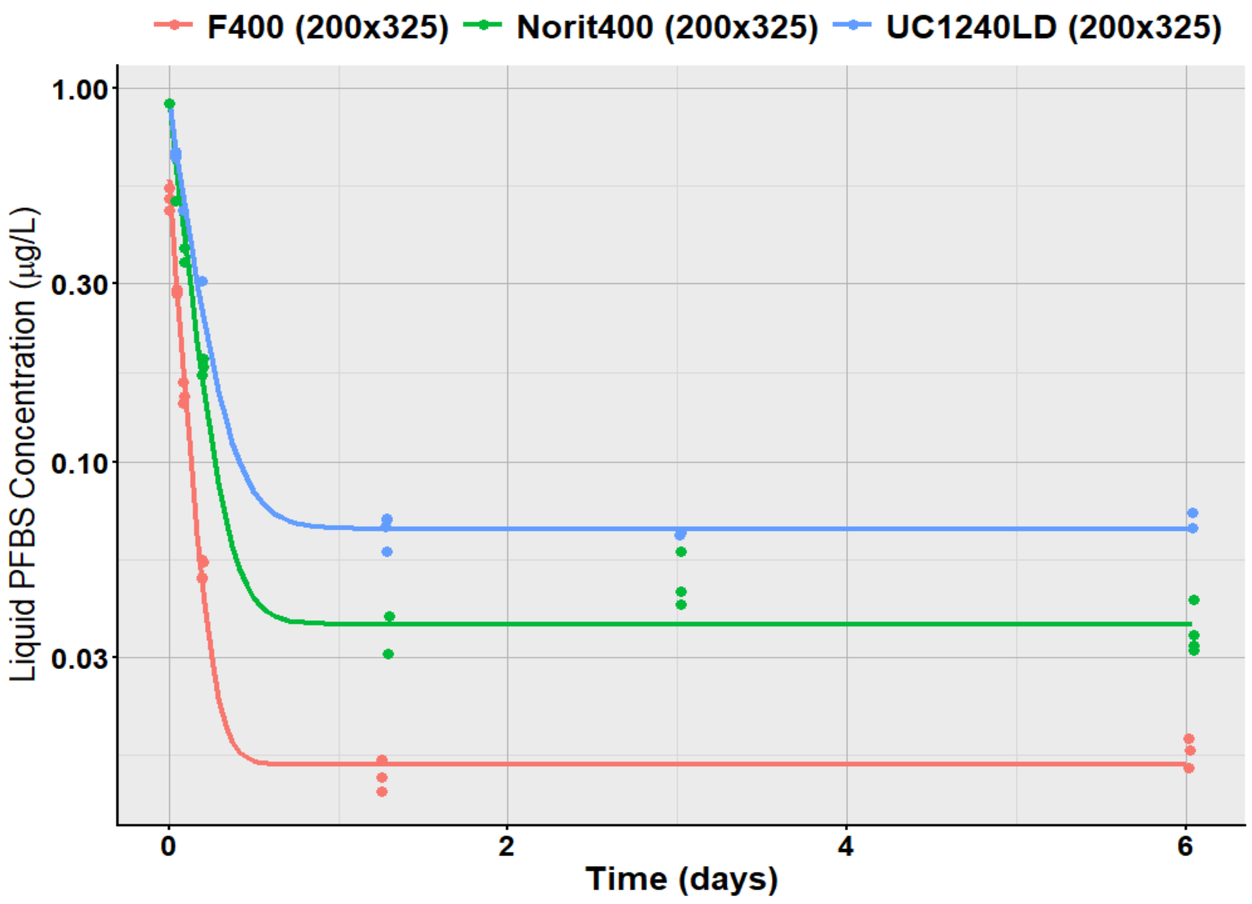
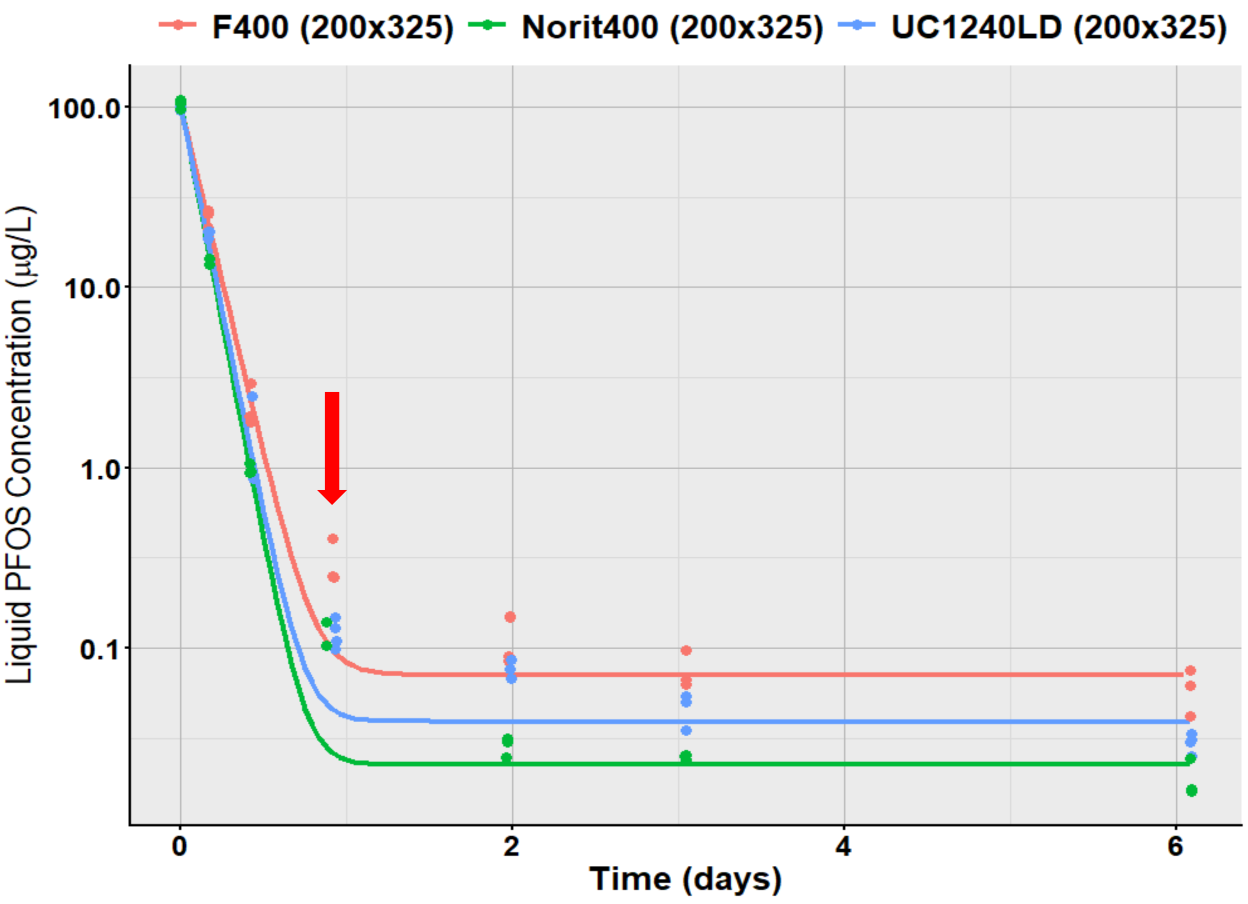
PFBS



PFOS



3.1 Adsorption kinetics

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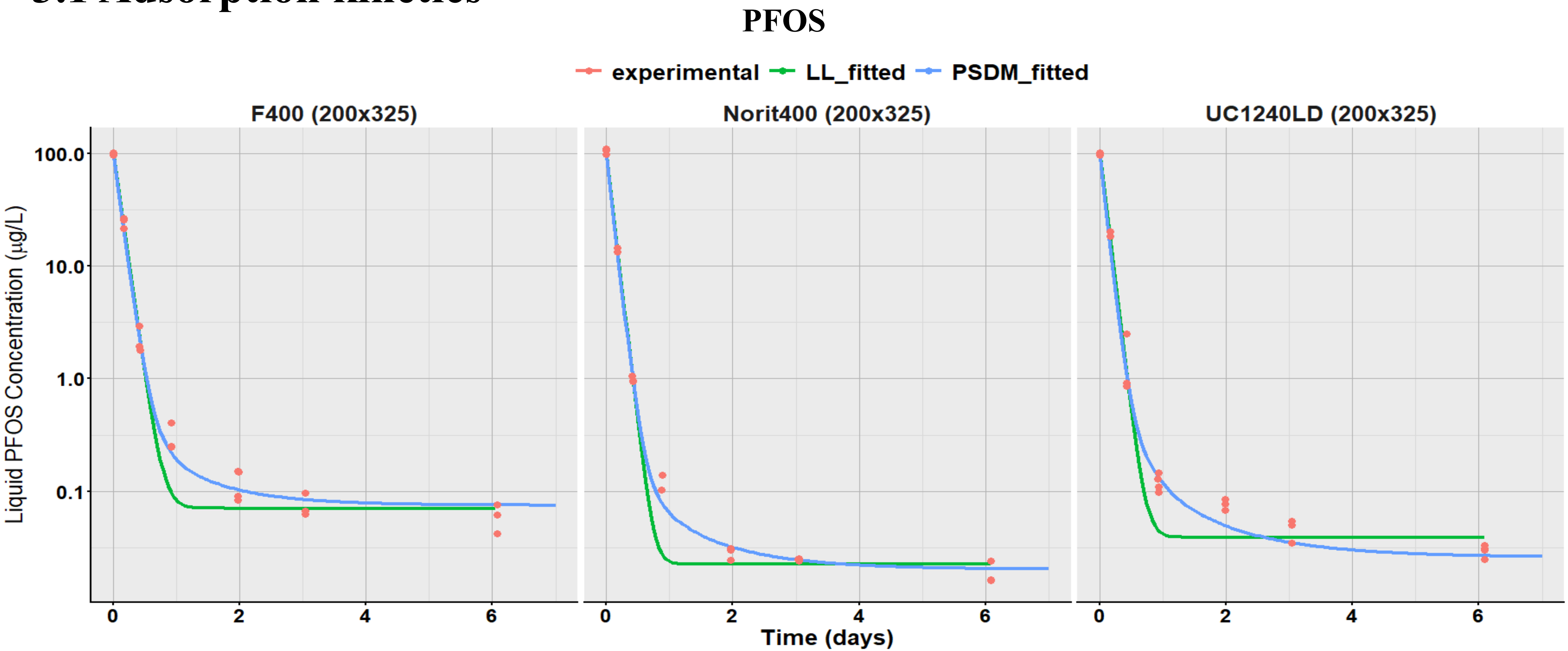
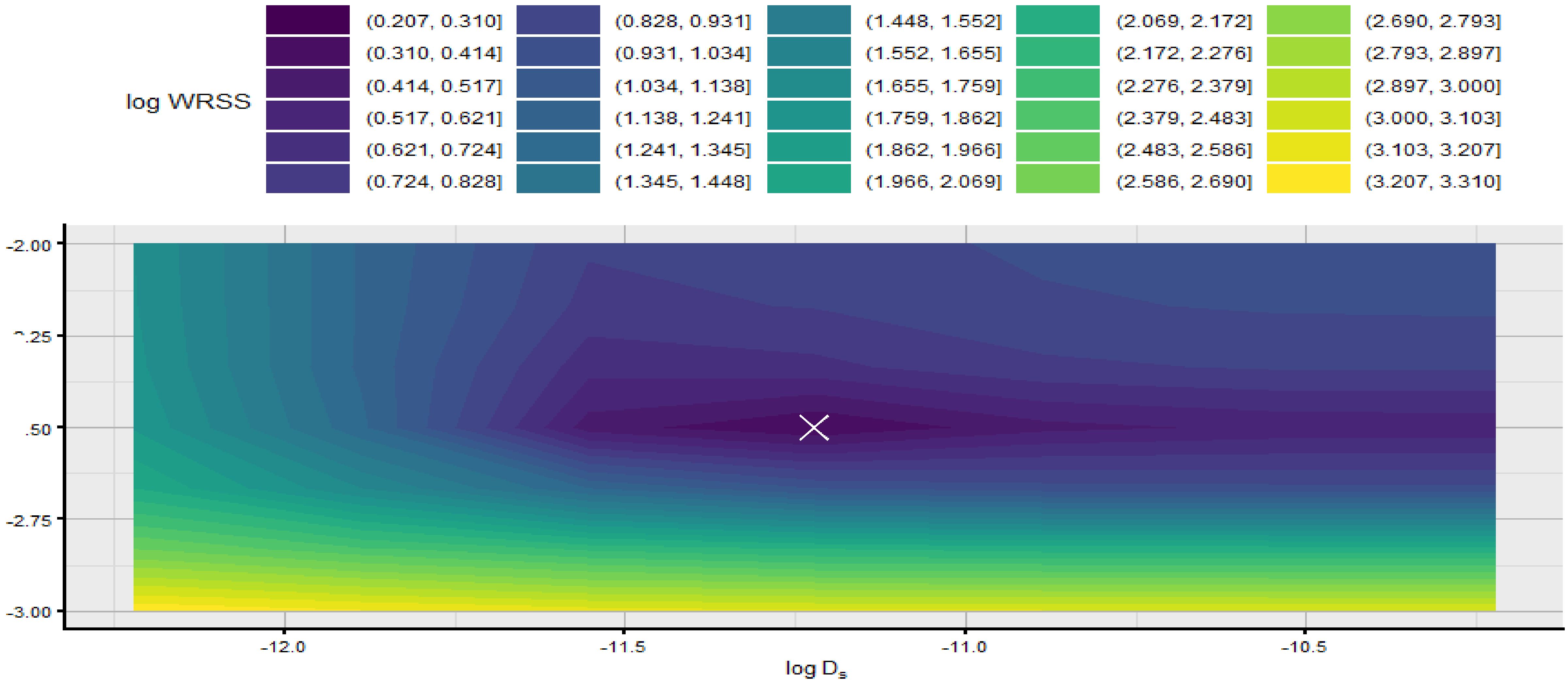


3. Research Findings



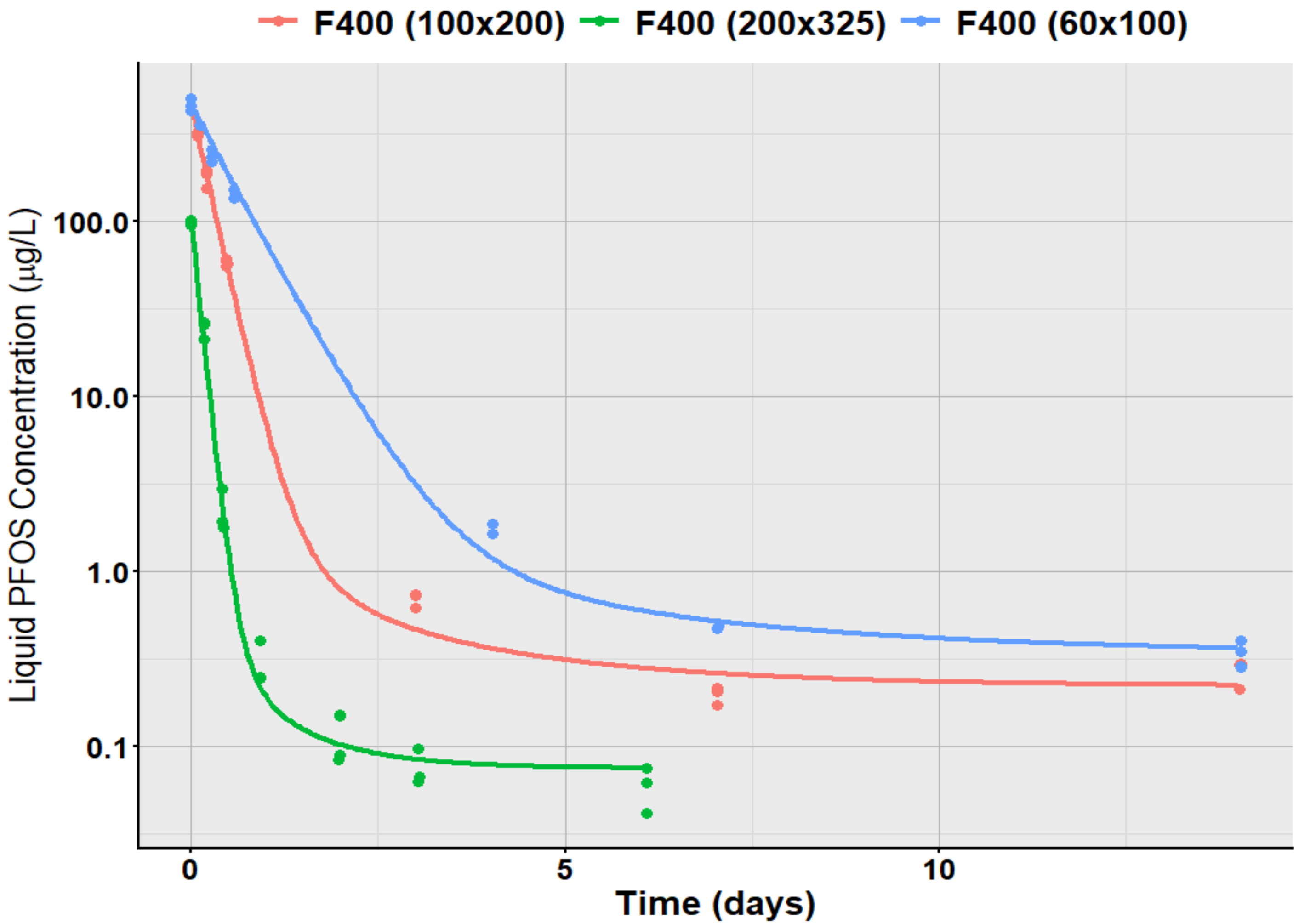
3.1 Adsorption kinetics

Larger particle size = Longer t_{eq}

- **t_{eq} (200x325) at least 3 days**
- **t_{eq} (100x200) at least 10 days**
- **t_{eq} (60x100) at least 14 days**

Particle size	D_S (cm^2/s)
200x325	$1 \times 10^{(-11.33)}$
100x200	$1 \times 10^{(-11.21)}$
60x100	$1 \times 10^{(-10.86)}$

PFOS – F400 kinetics, PSDM fitted **



3.1 Adsorption kinetics

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Two rapid small-scale column test (RSSCT) design approaches:

$$\frac{D_{s,Small\ column}}{D_{s,Large\ column}} = \left[\frac{d_{p,Small\ column}}{d_{p,Large\ column}}\right]^X$$

Where:

d_p = mean particle diameter

X = 1, for proportional diffusivity assumption (PD-RSSCT)

X = 0, for constant diffusivity assumption (CD-RSSCT)

GAC	d_p (µm)	d_{pL}/d_{pS}	D_S - % difference	
			PD - RSSCT	CD - RSSCT
A: F400 (200x325)	59.0	$d_{pB}/d_{pA} = 1.89$	-44.58%	23.50%
B: F400 (100x200)	111.5	$d_{pC}/d_{pB} = 1.79$	20.50%	55.57%
C: F400 (60x100)	199.5	$d_{pC}/d_{pA} = 3.38$	-14.95%	66.01%

3.2 Adsorption isotherms

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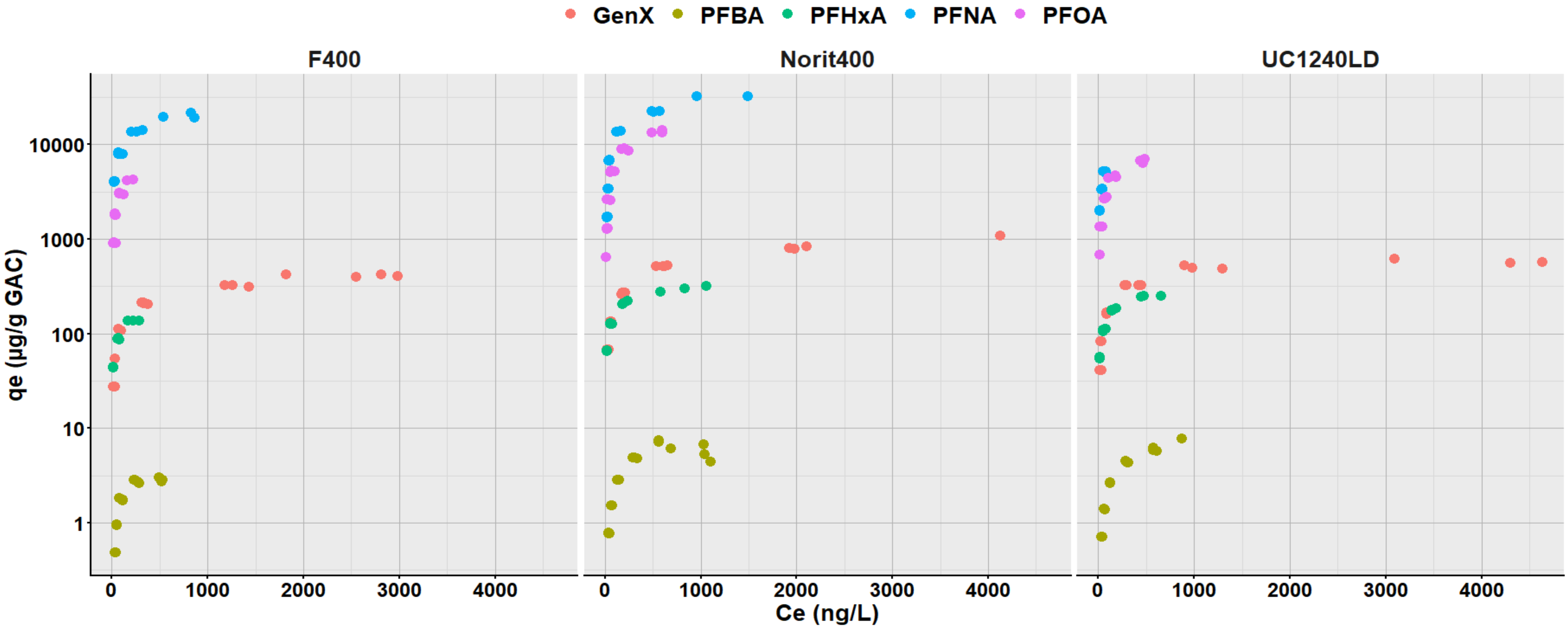

3.2 Adsorption isotherms

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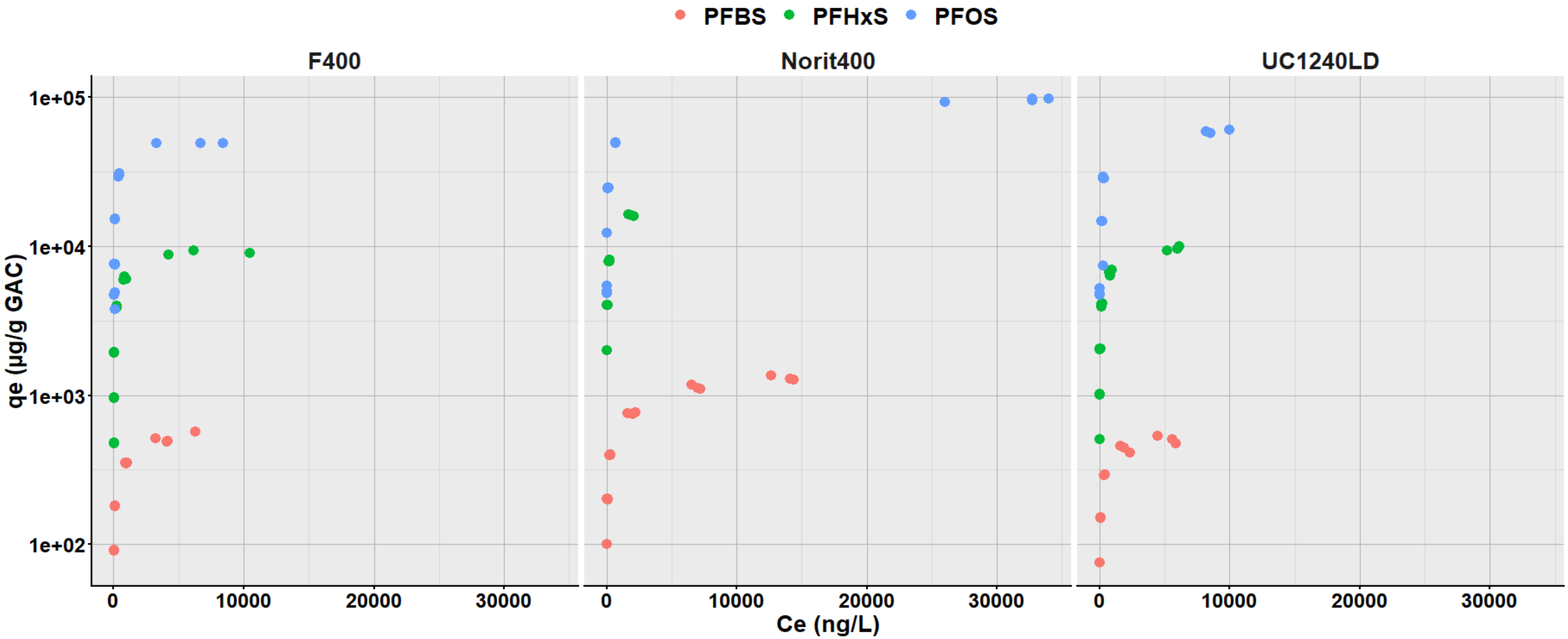
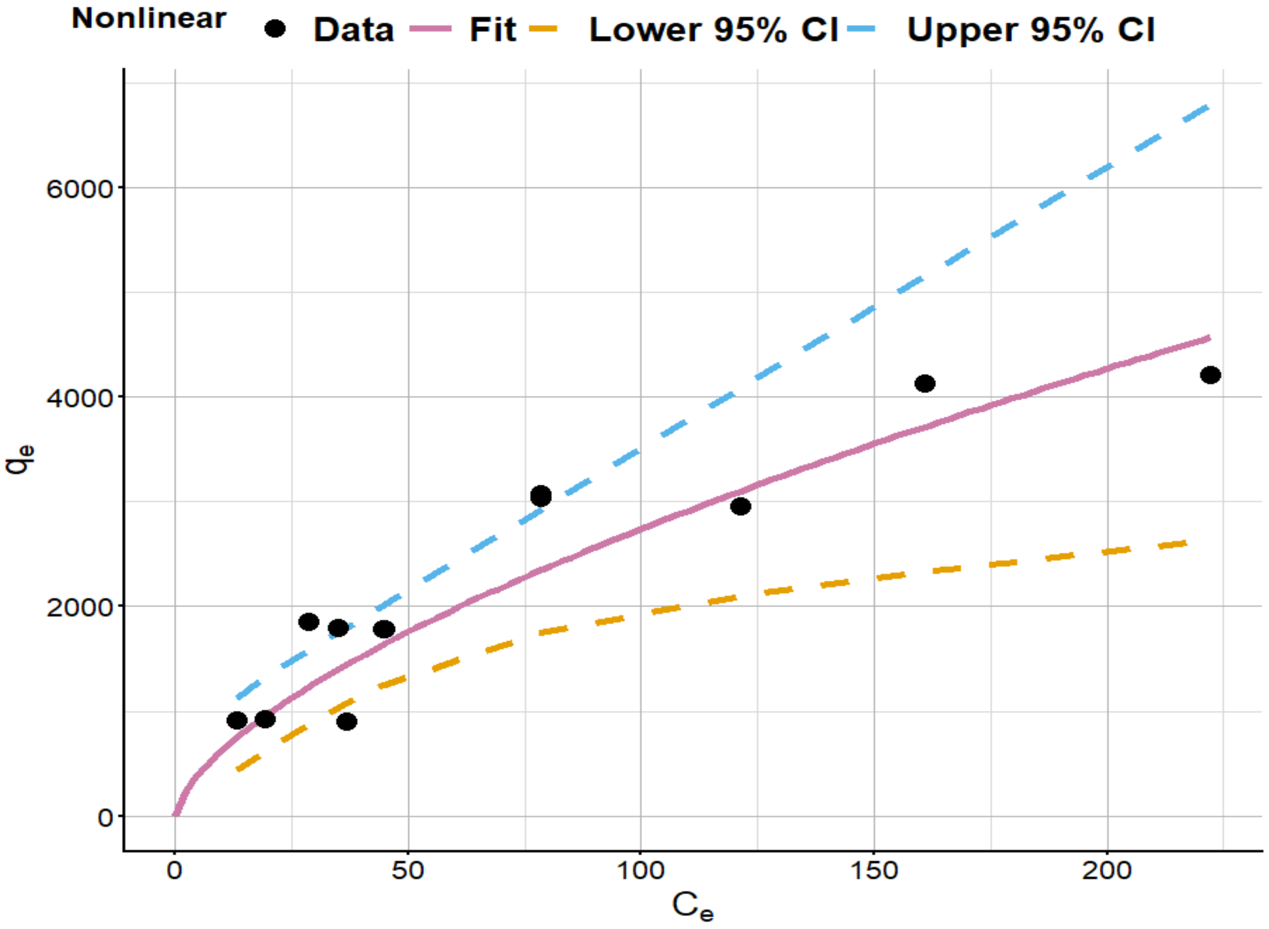
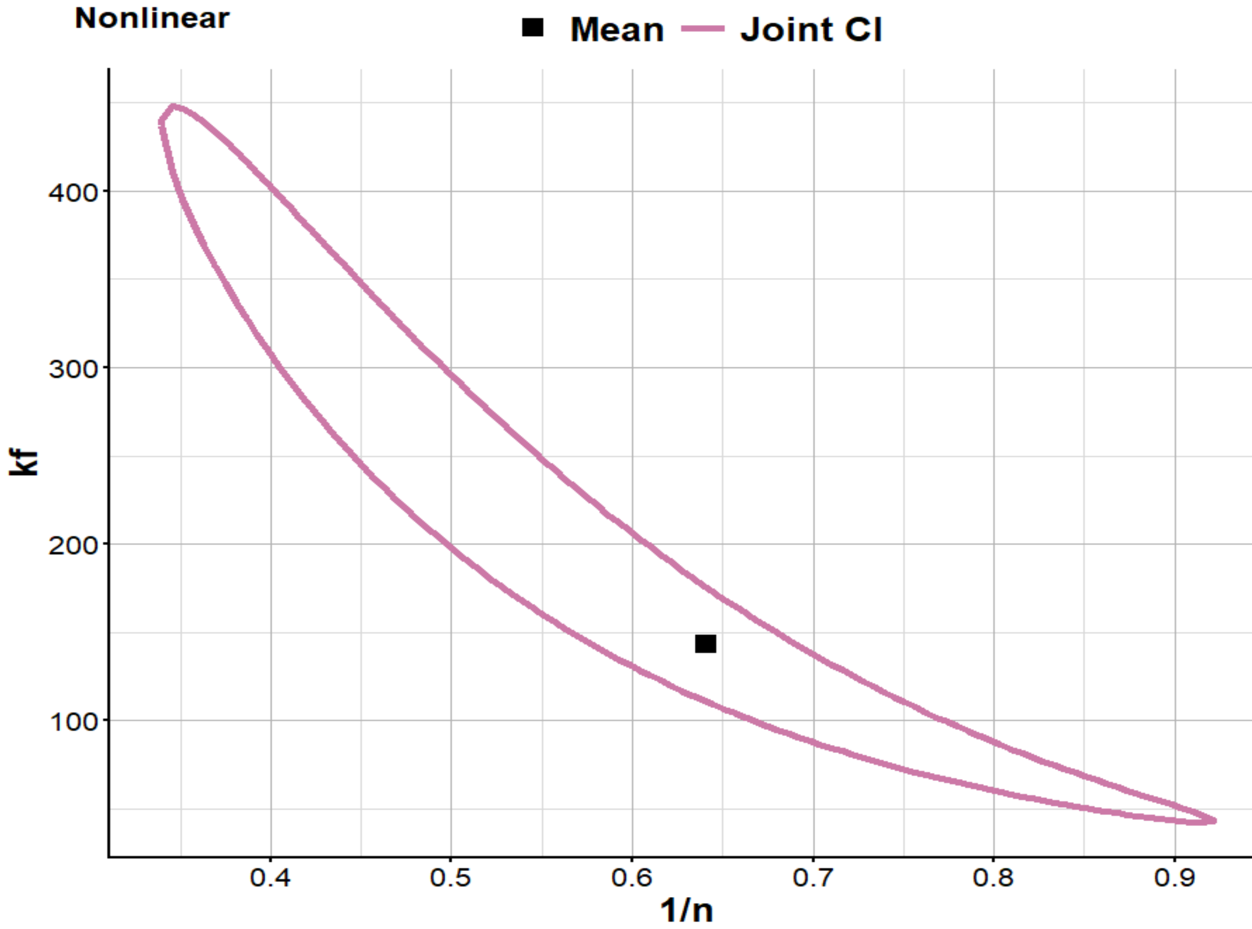


3.2 Adsorption isotherms

PFOA –F400 adsorption isotherm fitted with **Freundlich equation** **





3. Research Findings

Freundlich parameters

PFCA & GenX

PFAS	GAC	kf [(µg/g)(L/ng)$^{(1/n)}$]	1/n
PFBA	F400	0.055	0.66
	Norit400	0.111	0.59
	UC1240LD	0.050	0.76
GenX	F400	6.49	0.54
	Norit400	11.8	0.57
	UC1240LD	13.3	0.48
PFHxA	F400	13.0	0.44
	Norit400	22.9	0.40
	UC1240LD	18.5	0.43
PFOA	F400	143	0.64
	Norit400	133	0.76
	UC1240LD	211	0.58
PFNA	F400	954	0.47
	Norit400	250	0.71
	UC1240LD	567	0.49

PFSA

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PFAS	GAC	kf [(µg/g)(L/ng)$^{(1/n)}$]	1/n
PFBS	F400	30.2	0.35
	Norit400	34.7	0.39
	UC1240LD	34.0	0.33
PFHxS	F400	200	0.45
	Norit400	488	0.47
	UC1240LD	297	0.43
PFOS	F400	810	0.48
	Norit400	3592	0.32
	UC1240LD	1174	0.43

Conclusion

Adsorption Kinetics	Adsorption isotherms
• Similar for 3 GACs & 9 PFAS • Adequately described by the LL model (except for PFOS) • Impacted by GAC particle size: ❑ Increased particle size = increased equilibrium time ❑ PFOS: ▪ D_S changes with particle size ▪ Potential implications for RSSCT scaling approach	• Single solute isotherms — c_e covering drinking water relevant PFAS concentration • Freundlich equation well described • At similar c_e, ❑ q_e among GACs: F400 ≅ UC1240LD < Norit400 ❑ q_e among PFAS: PFBA < PFHxA ≤ GenX < PFBS < PFOA < PFHxS < PFNA < PFOS

Future Research

Continue batch studies to investigate:

27 pairs of baseline isotherm parameters

Multi-solute adsorption isotherm (competition among PFAS)

Effect of particle size on adsorption isotherm

Effect of background water constituents: organic and inorganic

Disclaimer

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****** This presentation contains preliminary findings and conclusions subject to revision following EPA's quality assurance review.

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Thank you!

Questions?

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