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It can be done

Assessment of Ionic and Neutral PFAS Using Newly Developed Equilibrium Regimen Passive Sampler

Analytical Services | Health Assessment | Novel Chemistries | Remediation & Treatment | Site Characterization | Toxicology

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The need

- PFAS are hydrophobic and oleophobic and display surfactant properties.
- Uses: fire-fighting foams (AFFF), non-staining carpets, water-resistant paper, and more.
- Growing evidence for adverse PFAS health effects.
- 2016 EPA guidance of 70 ng/L; States are mandating stricter regulations/guidelines of PFAS and PFOS.
- 100s of contaminated sites need characterization and remediation.
- Environmental concentration can fluctuate depending on precipitation.
- Cross-contamination makes sampling a challenge.

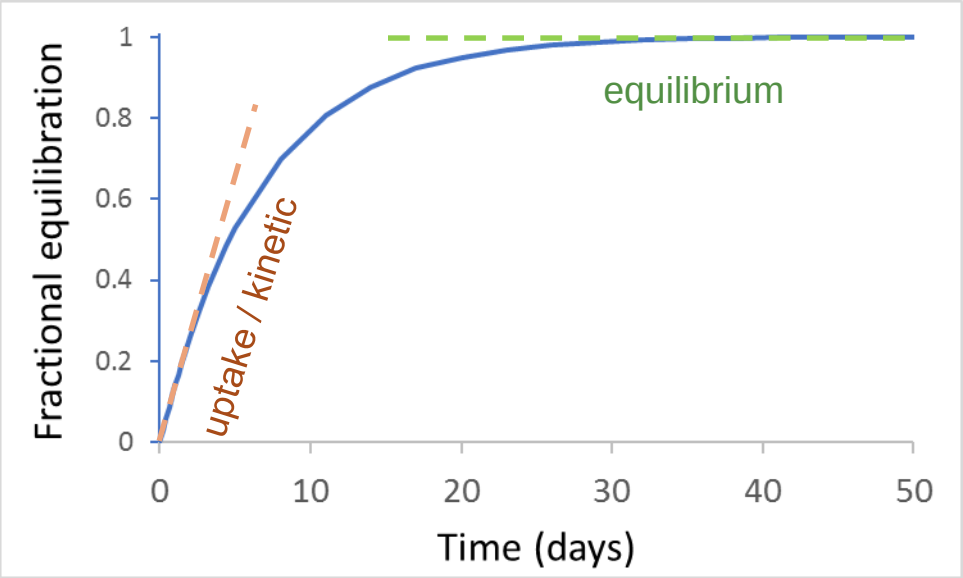
Why passive sampling?

General

- Passive samplers for hydrophobic organic contaminants
  - Improved detection limits
  - Time-integrated results
  - Insights into bioavailability
  - Smaller sample size
  - Less cross-contamination risk

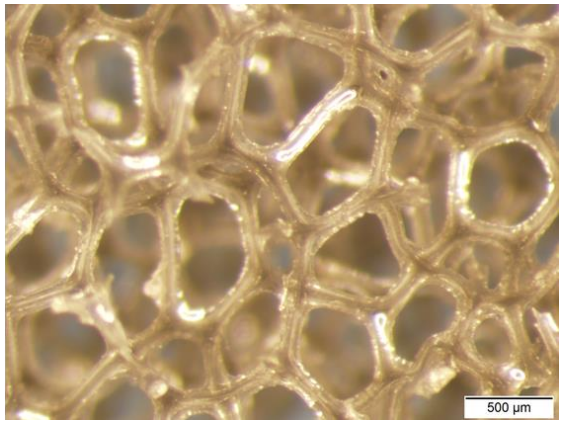
PFAS considerations

- Wide range of properties
- The sorbent is key!
- Kinetic vs. equilibrium regimen



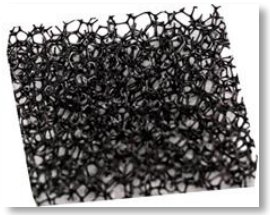
PFAS Insight™

- Equilibrium regimen sampler
- After initial testing, down-selected to 2 types of sorbents for further investigation
  - Both sorbents are open-cell polymers
  - 45 pores per inch; SA ~0.4–0.5 m^2/g
- Tested for 15 analytes
  - non-ionic (precursors) and anionic (sulfonates and carboxylate species)
- Analytical method
  - AB Sciex QTRAP 5500 Triple Quadrupole MS
  - Method compliant with DoD QSM 5.1 Table B-15 requirements



Analyte	# of C
Precursors	
6:2 FTS	6
8:2 FTS	8
NMeFOSAA	8
NEtFOSAA	8
Sulfonates	
PFBS	4
PFHxS	6
PFOS	8
PFDS	10
Carboxylates	
PFHxA	6
PFHpA	7
PFOA	8
PFNA	9
PFDA	10
PFUnA	11
PFDoA	12

PFAS uptake kinetics



1 x 1 cm piece of sorbents

0.01 M NaCl background electrolyte

Spike PFAS target analytes
Initial conc. 10 - 100 µg L^{-1}

Triplicates for all treatments plus duplicated blanks and controls

Shaken at 130 rpm, 23±1ºC and sampled over 0-22 d

Sample dilution
Surrogates & Internal standard spiked

Analysis on LC-MS/MS

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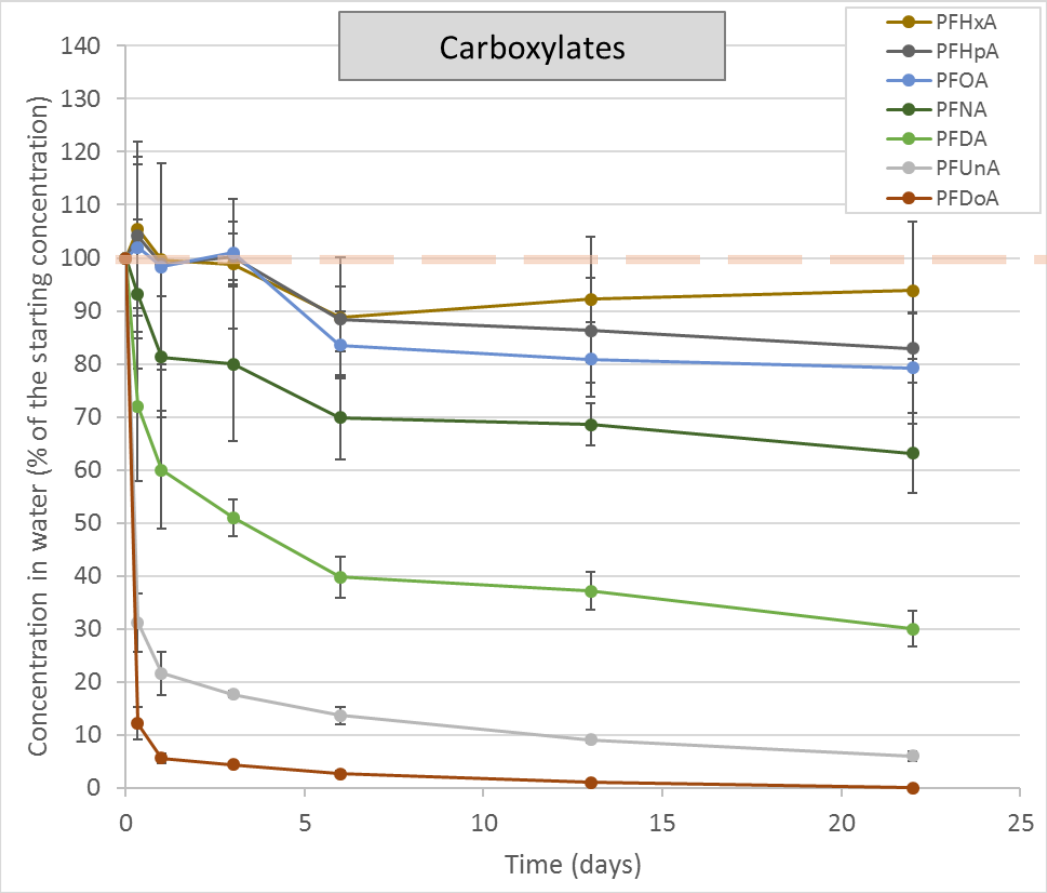
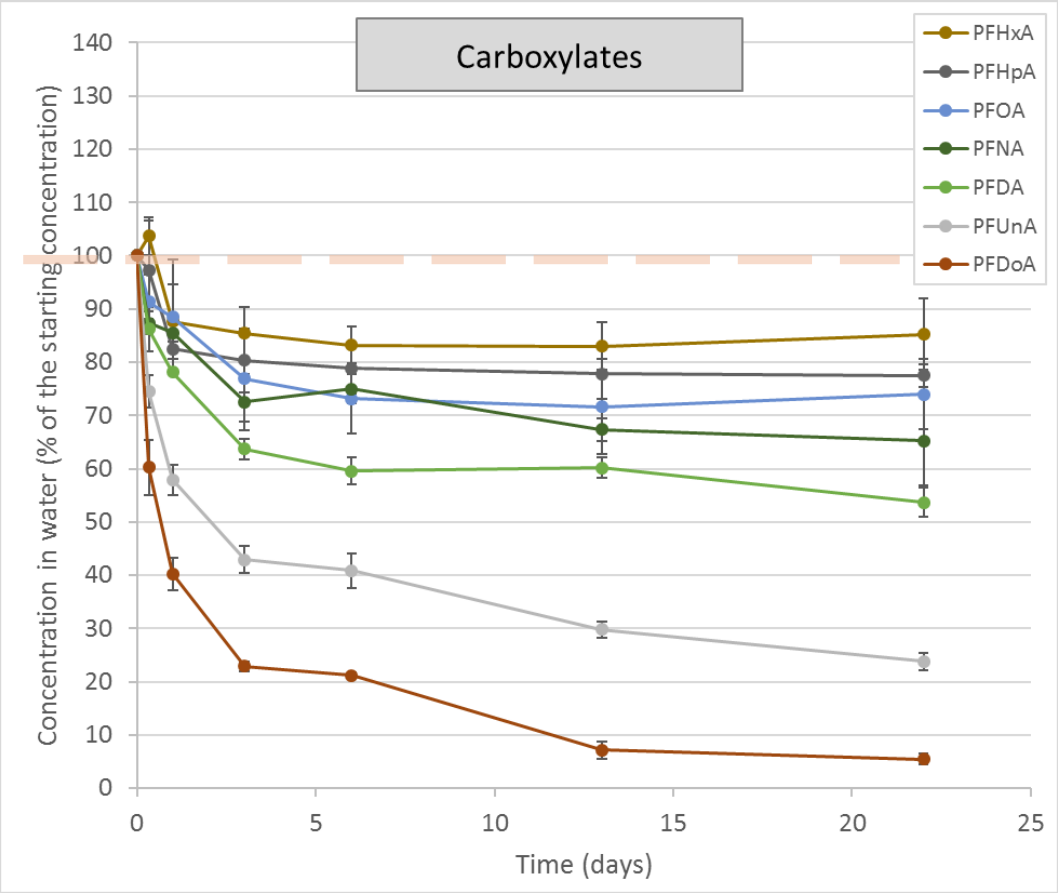
PFAS uptake – water concentration vs. time

Sorbent 1



Sorbent 2



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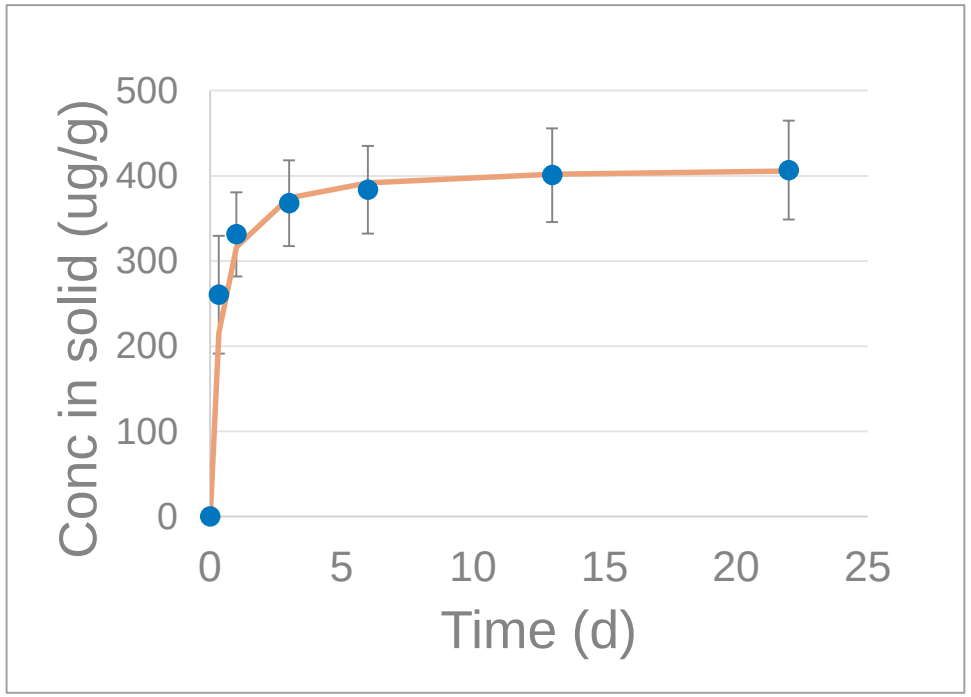
PFAS uptake – pseudo-second order kinetics

Non-linear: $C_s = \frac{{C_e}^2\, k\, t}{1 + C_e\, t}$

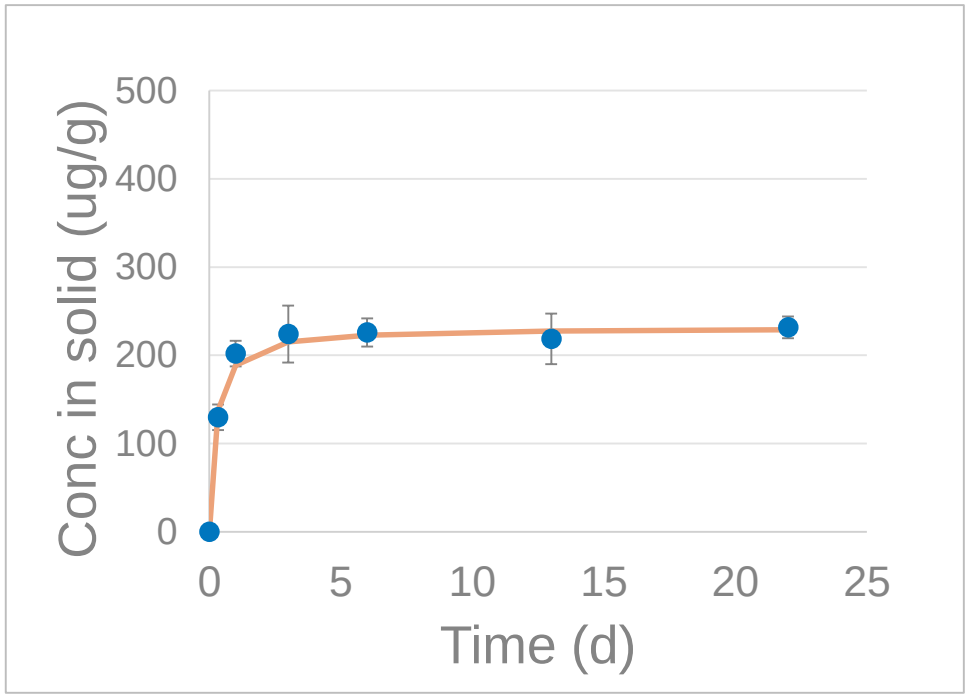
Linear: $\frac{t}{C_S} = \frac{1}{kC_e^2} + \frac{t}{C_e} = \frac{1}{v_0} + \frac{t}{C_e}$

Sorbent 1



PFOS

Sorbent 2



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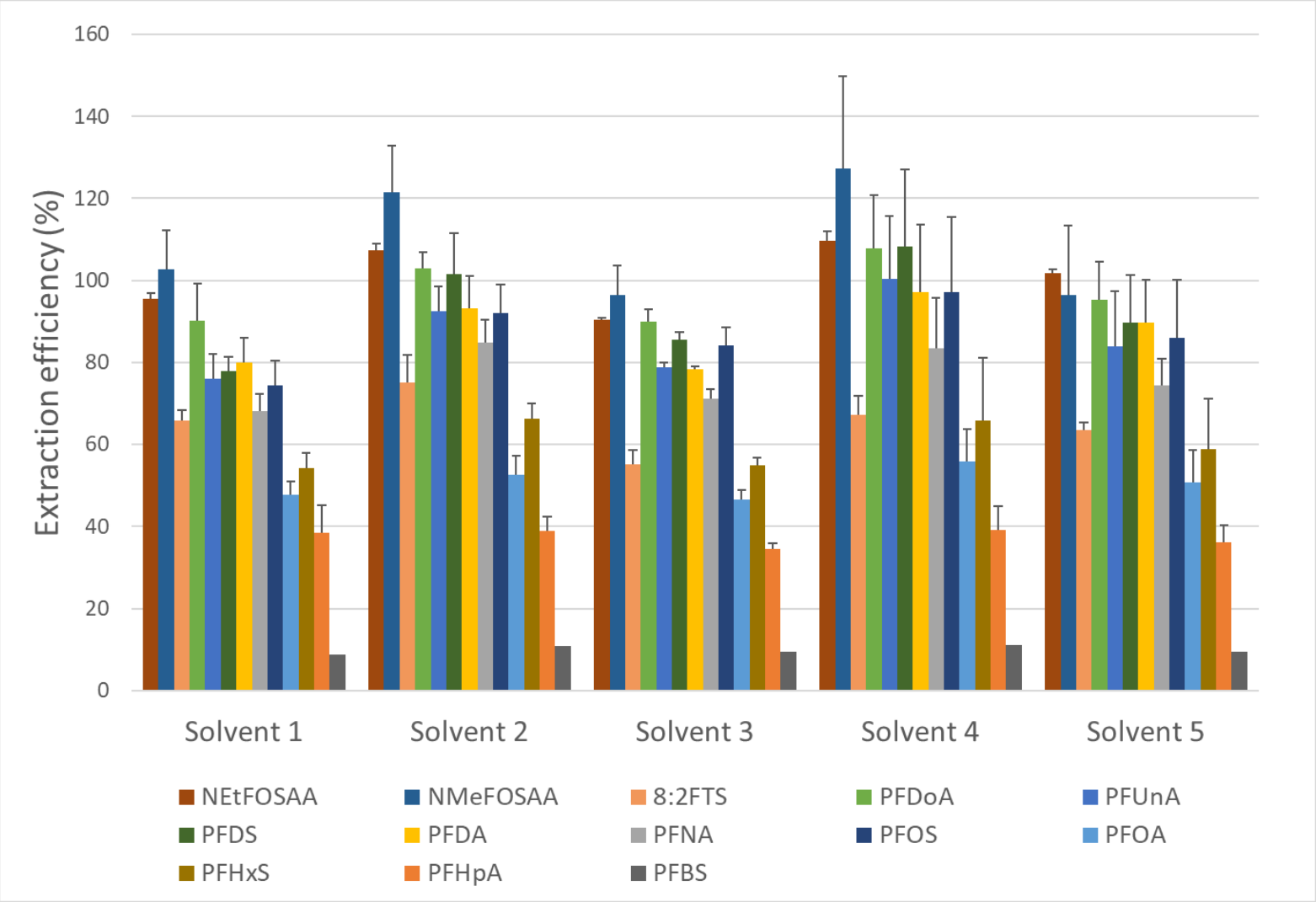
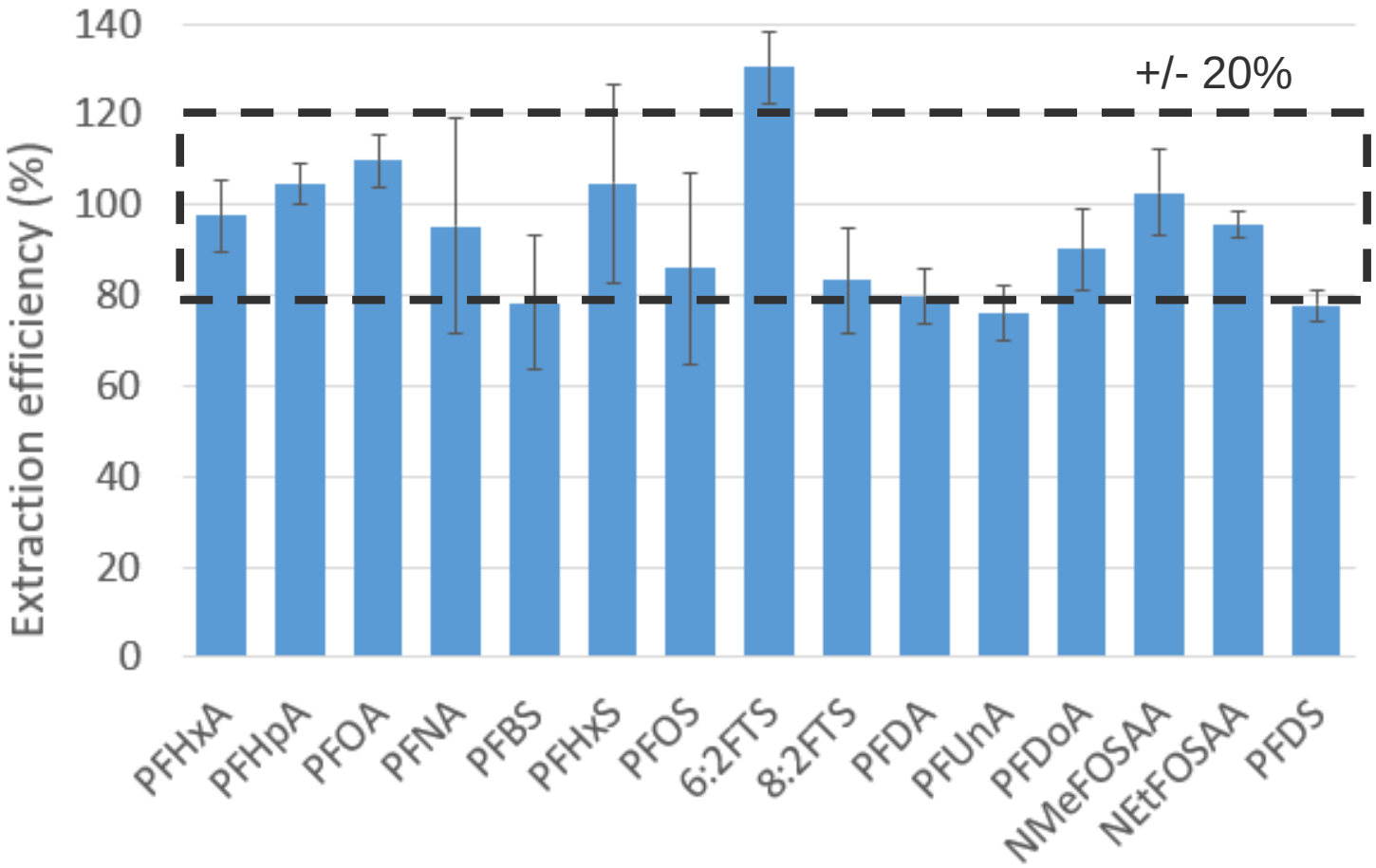
Extraction of spent sorbent

- <u>Experimental design</u>
  - Five pH-modified organic solvents.
  - Three consecutive extractions with varying extraction time and combination of agitation and or/ sonication.
  - Extracts were combined and sampled; no preconcentration.



Extraction of spent sorbent

- Conclusions
  - Some solvents degraded Sorbent 2.
  - Sonication did not cause significant improvement of analyte recovery.
  - Overnight + two short extractions achieve great recoveries, with the minimum of 76% of the initial amount (average of 94%).



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Adsorption isotherm experiments

- 1 x 1 cm of sorbent (~0.025 g) added to 125 mL of PFAS solution with background electrolyte (0.01M NaCl).
- Analytes concentrations range from 0.05 to 500 µg/L except PFDS, NMeFoSAA and NEtFOSAA which were present at ~0.1 x the concentration of other analytes.
- Agitated at room temperature for 21 days.
- Duplicates or triplicates plus positive and negative controls.
- Amount adsorbed determined from water sampling at initiation and termination.
- Results modeled using Langmuir and Freundlich equations.

$$q = q_{max} \frac{K_L\ C}{1 + K_L\ C}$$

$$q = K_F C^n$$

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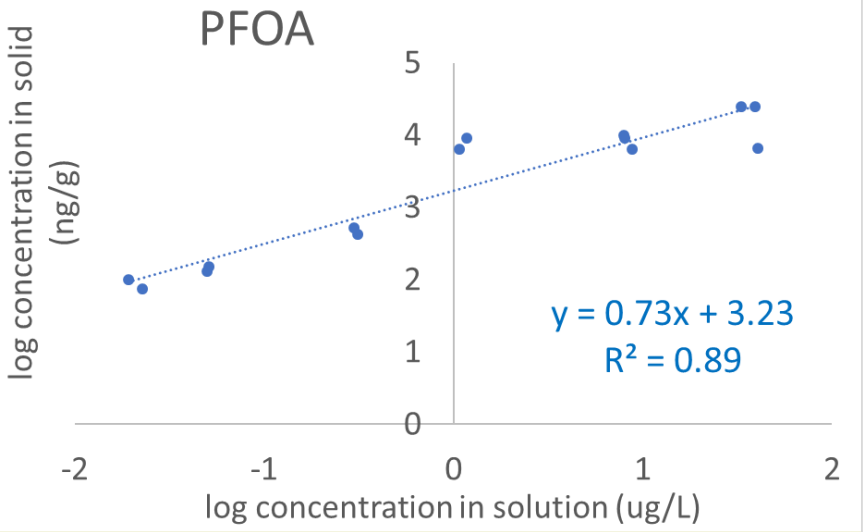
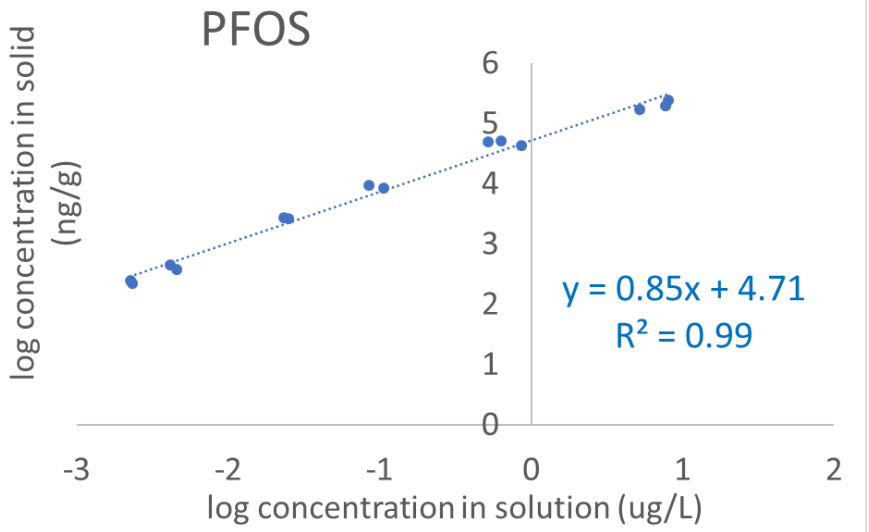
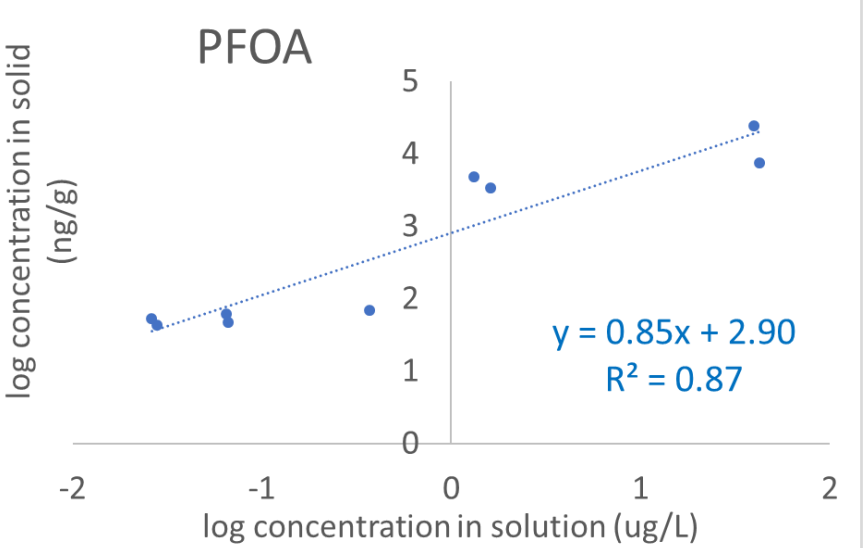
Adsorption isotherms

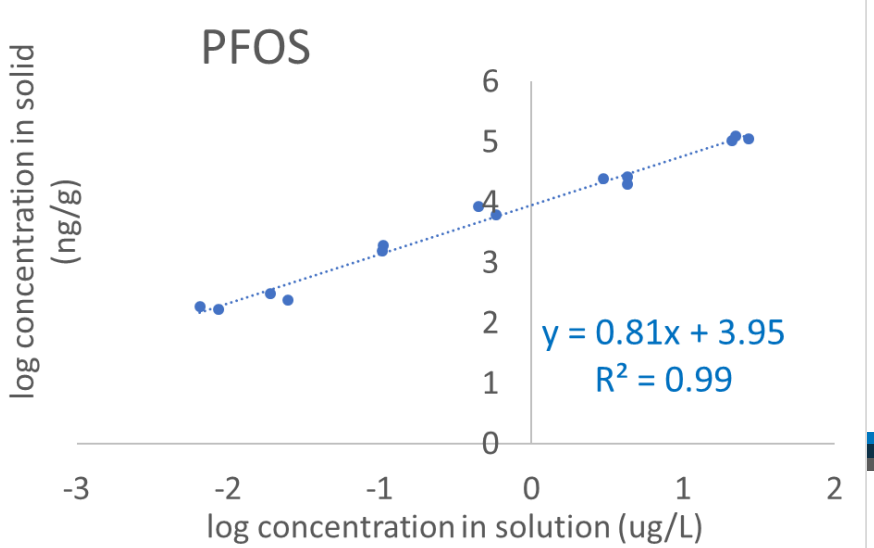
Sorbent 1





Sorbent 2





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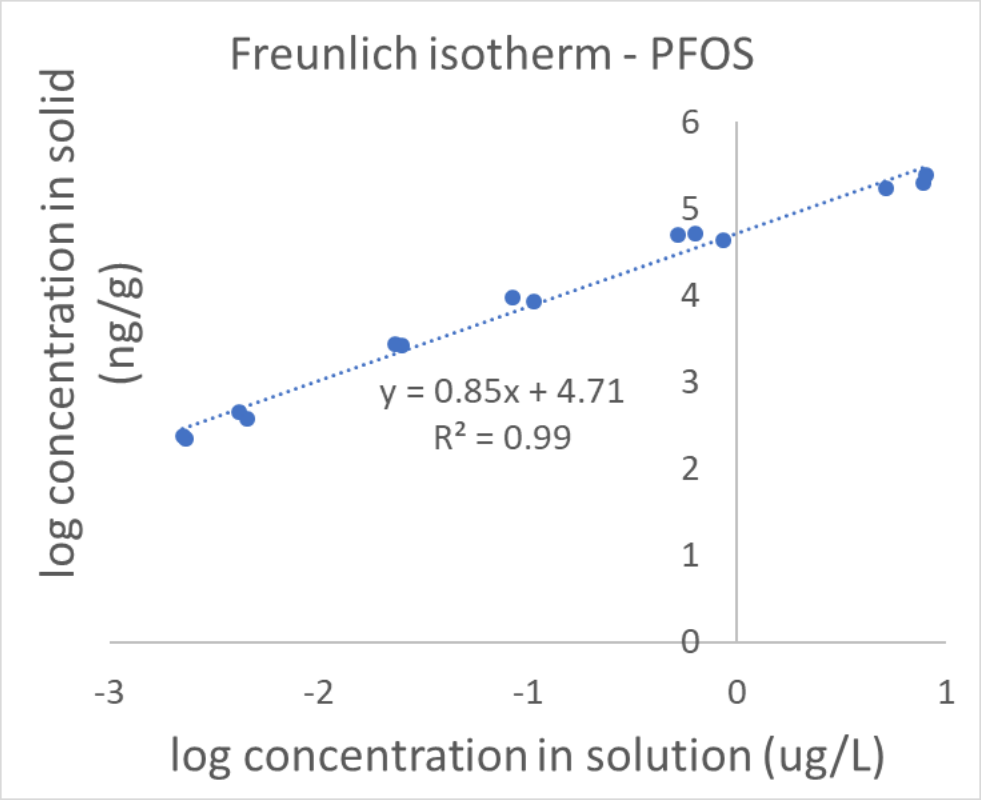
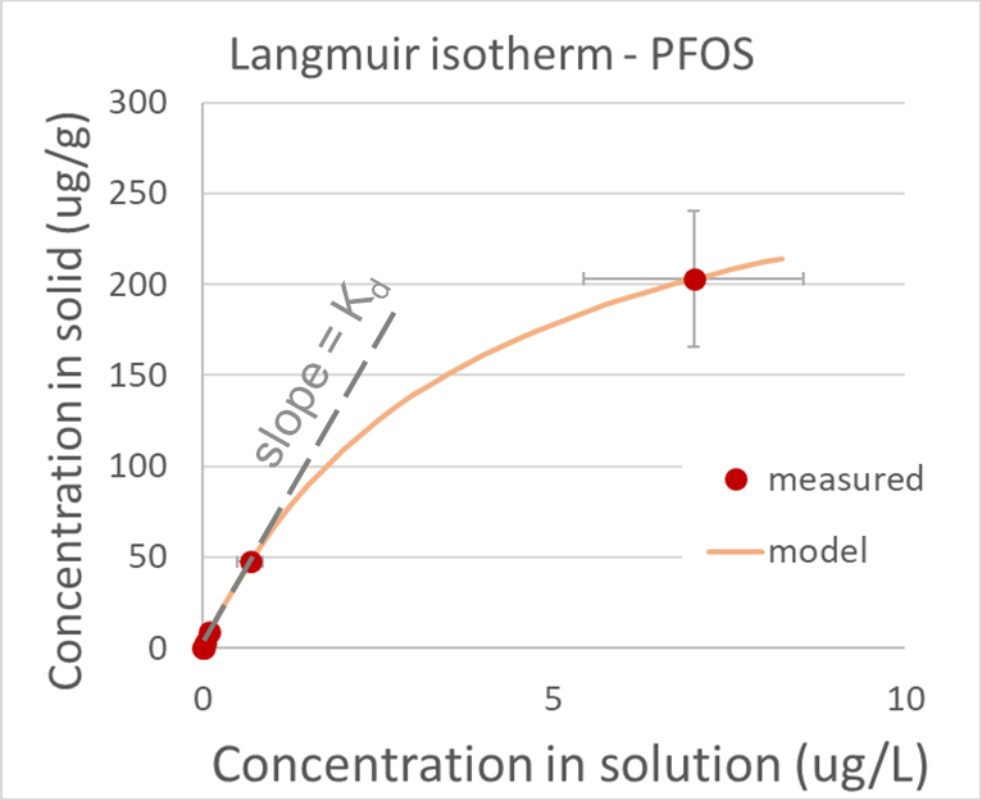
Determination of the solid-solution partition coefficient (K_d)

$$K_d = \frac{C_{solid}}{C_{solution}}$$

Typical units: L/kg





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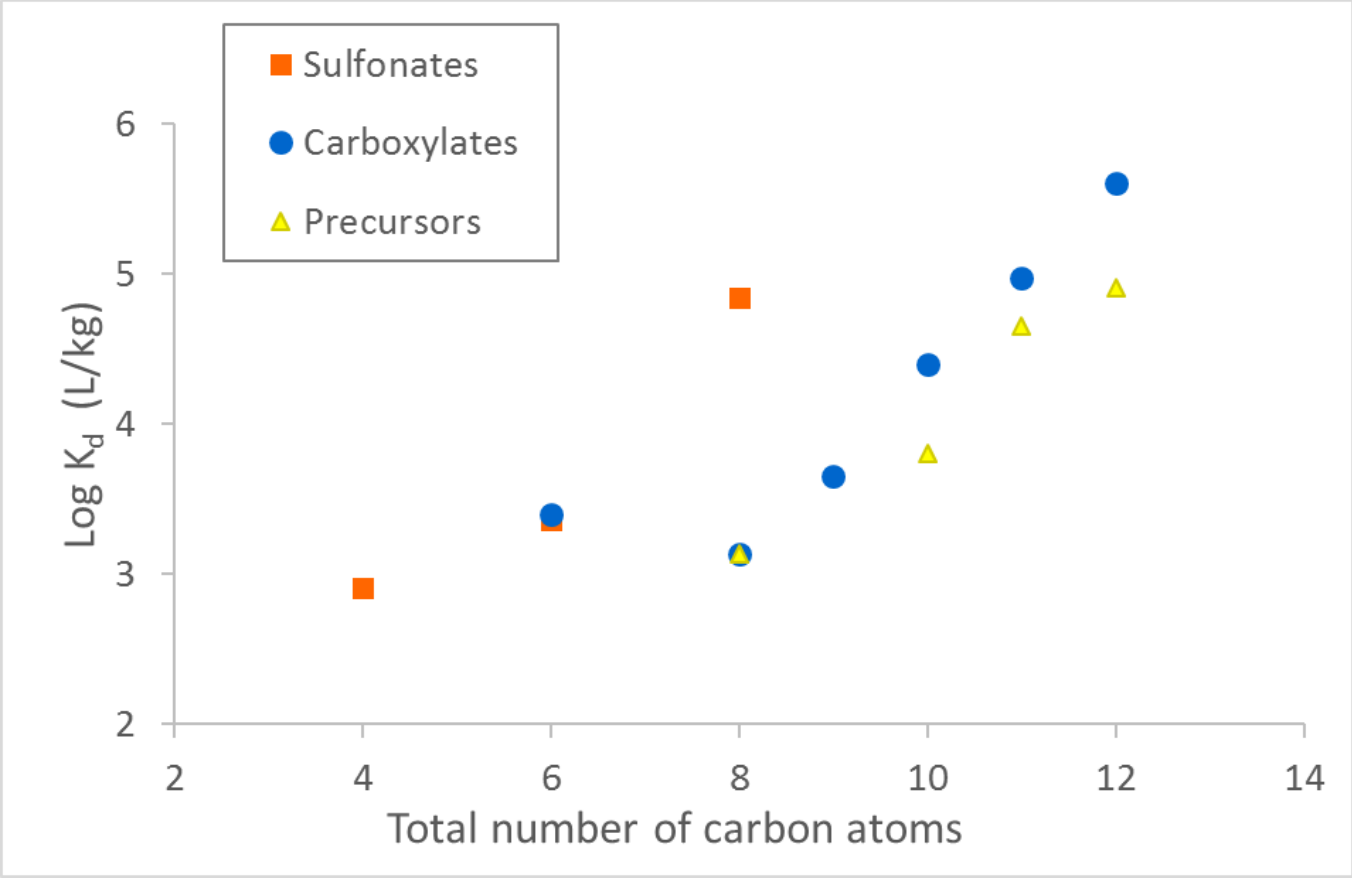
Partition coefficients (K_ds)

$$C_w = \frac{C_s}{K_d}$$

Analyte	Total # of carbons	K_d Sorbent 1	Log K_d Sorbent 1
Precursors			
6:2 FTS	8	1,380	3.14
8:2 FTS	10	6,415	3.81
NMeFOSAA	11	44,716	4.65
NEtFOSAA	12	80,145	4.90
Sulfonates			
PFBS	4	813	2.91
PFHxS	6	2,277	3.36
PFOS	8	69,709	4.84
PFDS	10	NA	NA
Carboxylates			
PFHxA	6	2,529	3.40
PFHpA	7	NA	NA
PFOA	8	1,355	3.13
PFNA	9	4,501	3.65
PFDA	10	25,253	4.40
PFUnA	11	93,725	4.97
PFDoA	12	400,567	5.60

Sorbent 1



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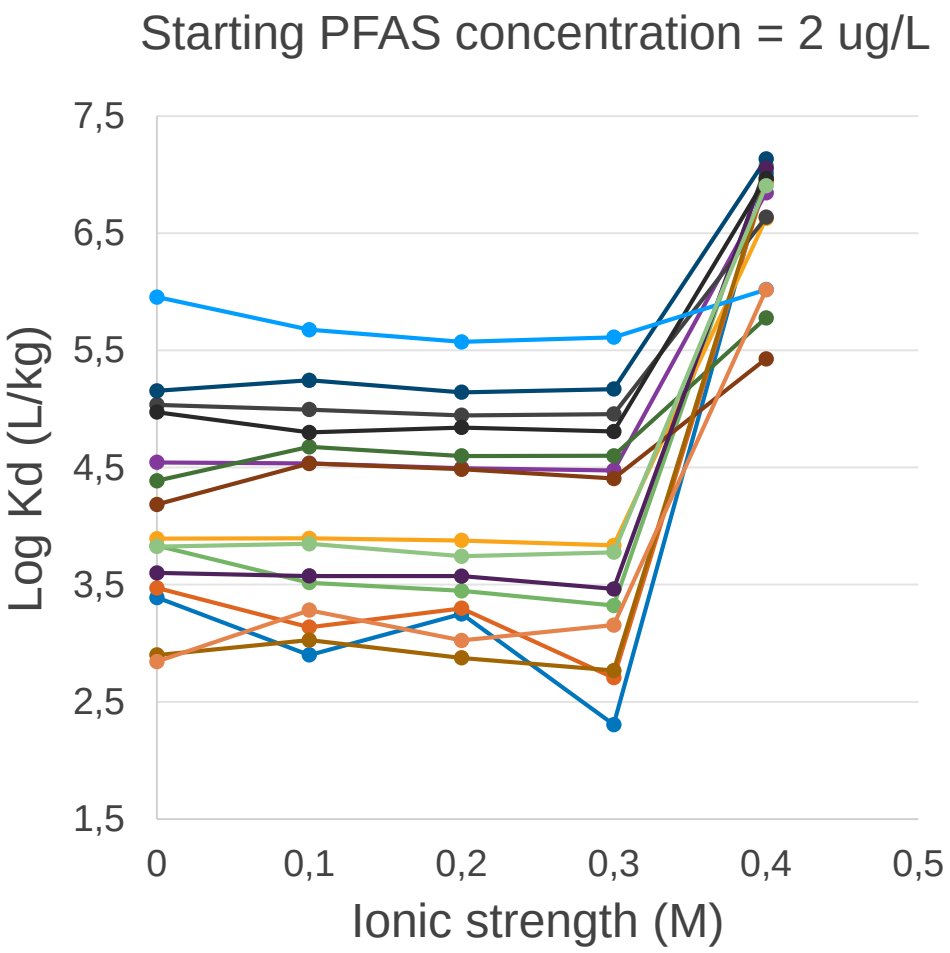
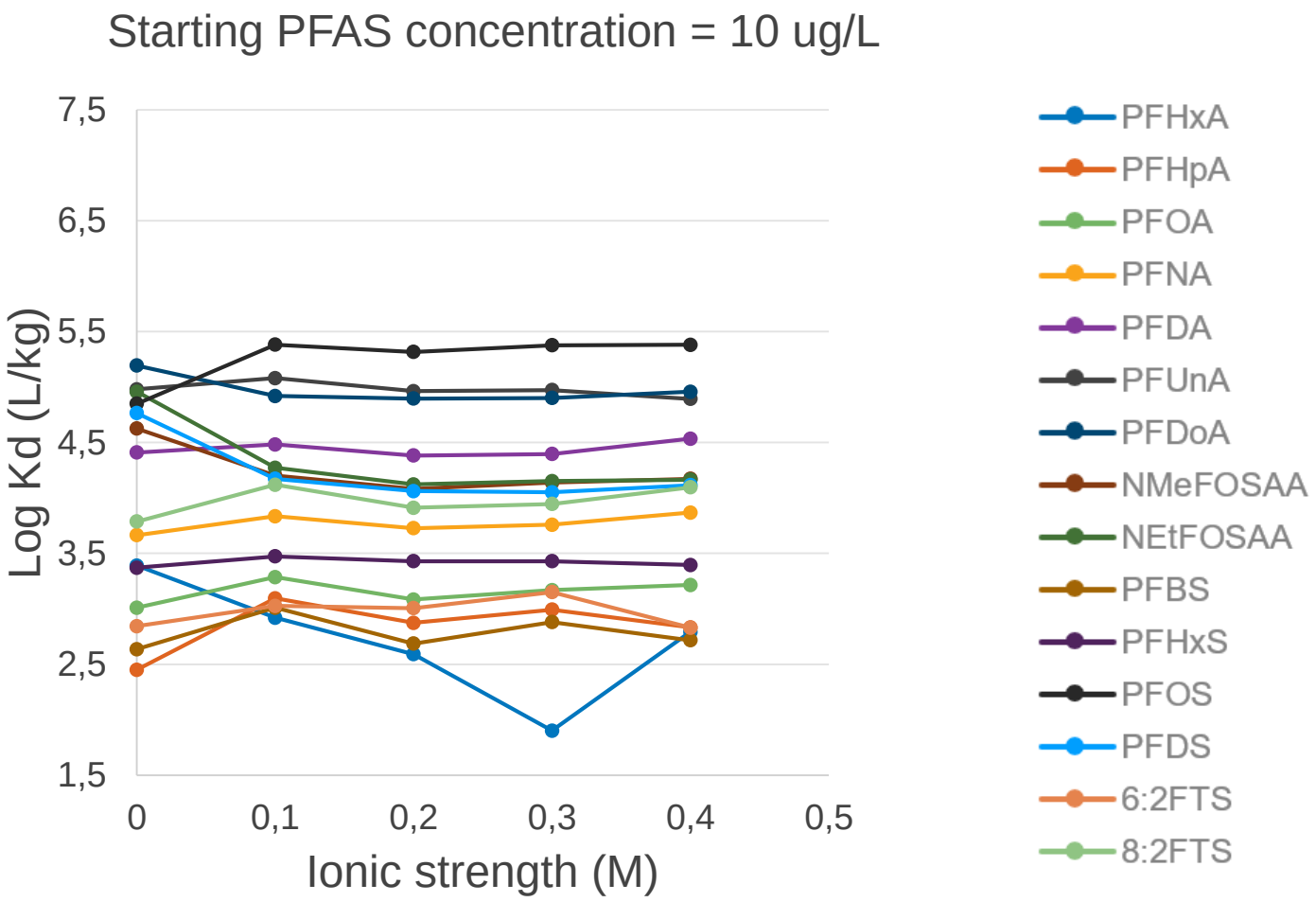
Effect of Ionic Strength on K_d





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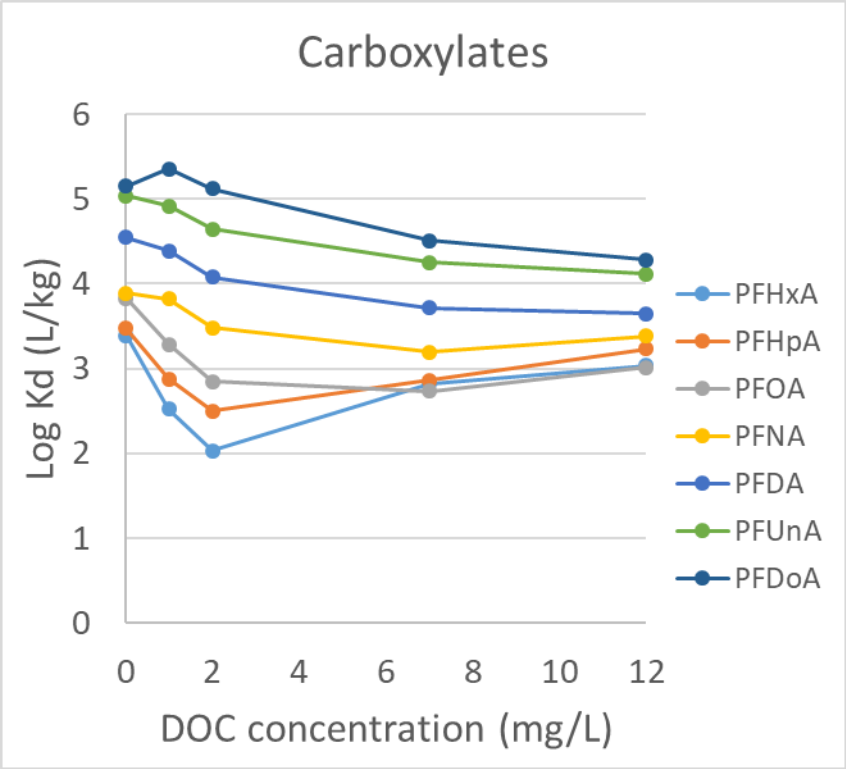
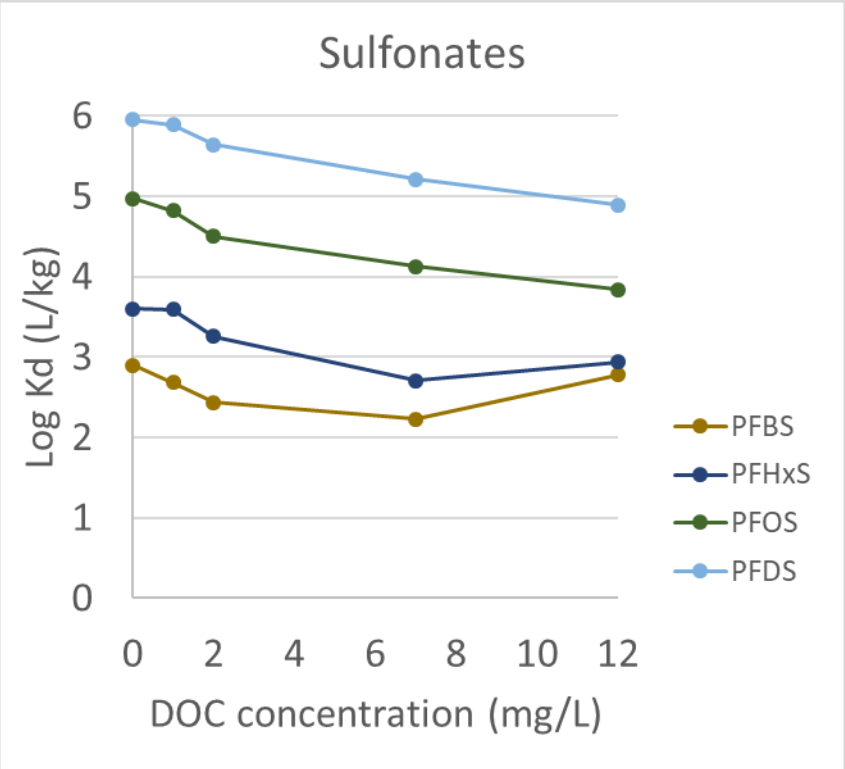
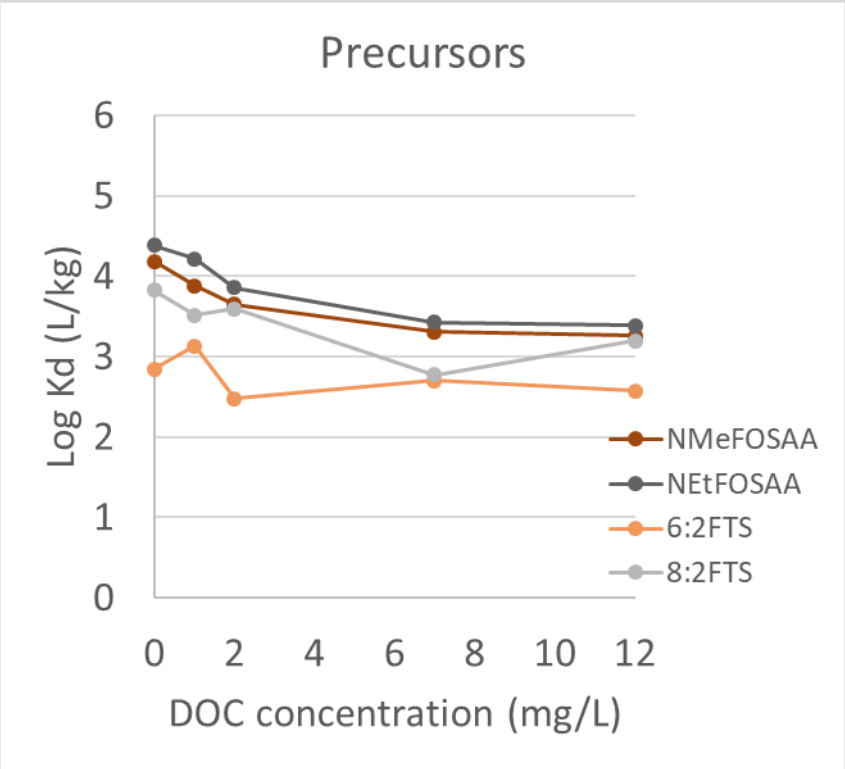
Effect of Dissolved Organic Carbon (DOC) on K_d

Starting PFAS concentration = 2 ug/L







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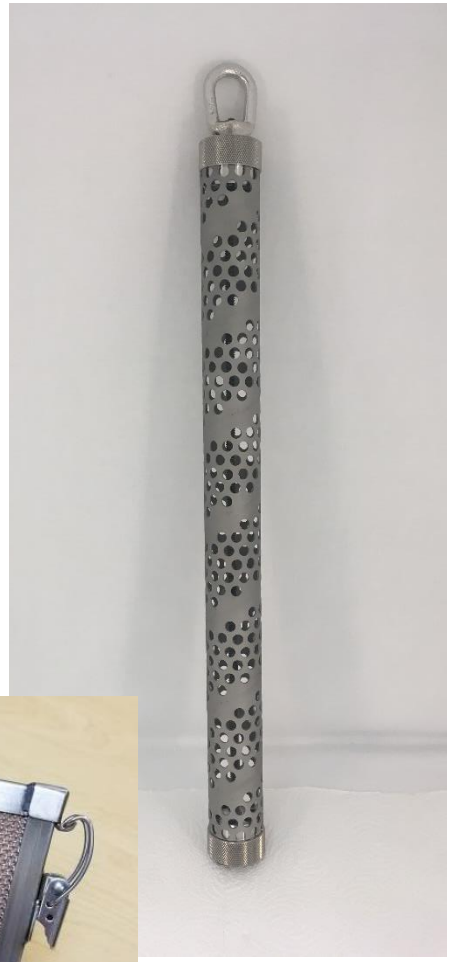
Hardware Design and Field Deployments

- Two types of hardware were designed to meet the needs of both surface water and groundwater deployments.
- First round of field demonstration-validation PFAS Insight™ samplers retrieved from the field last week and submitted for analysis.
- More field samples to be collected in the near future to allow performance assessment.



Summary

Adsorption

- Equilibrium achieved in < 1 week for most analytes.
- Strong preconcentration of anionic and neutral PFAS.
- Adsorption strongest and fastest for longer chains, sulfonates, and precursors.

Extraction efficiency

- Extraction efficiencies were similar for all solvents tested.
- Extraction procedures optimized to achieve an average of 94% recovery with one overnight and two short extractions.

Matrix influence

- Increasing ionic strength did not affect partitioning of PFAS except for low PFAS concentration and highest ionic strength (0.4 M) treatment, where increase in K_d was observed.
- The effect of DOC correlated with PFAS chain length, but generally caused decrease in K_d by up to ~ 1 log unit.

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For more information on PFAS at Battelle visit
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