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UV and fluorescence spectroscopy to monitor and predict PFAS, MIB, and emerging contaminant removal by activated carbon

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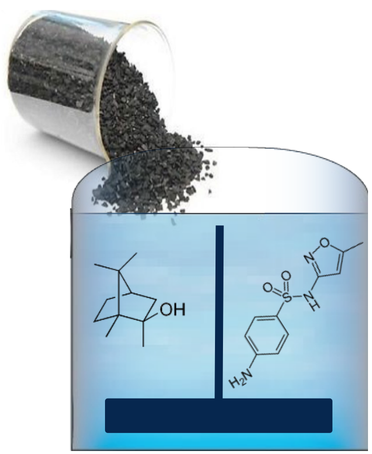
Presentation overview

Study #1

Powdered activated carbon (PAC) adsorption of MIB and Sulfamethoxazole

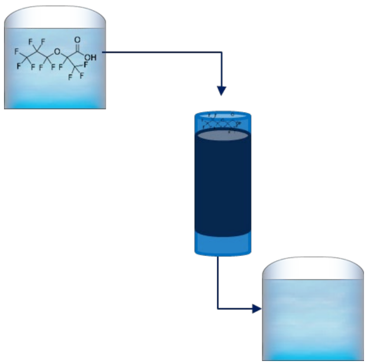


Study #2

Granular activated carbon (GAC) adsorption of short-chain PFAS:

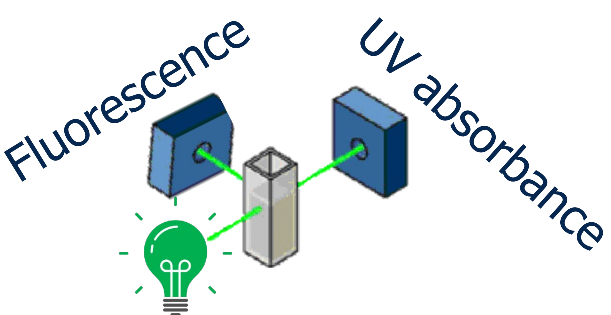
<8 carbon carboxylic acids

<7 carbon sulfonic acids



Common to both studies:

Predicting and monitoring contaminant adsorption with UV and fluorescence

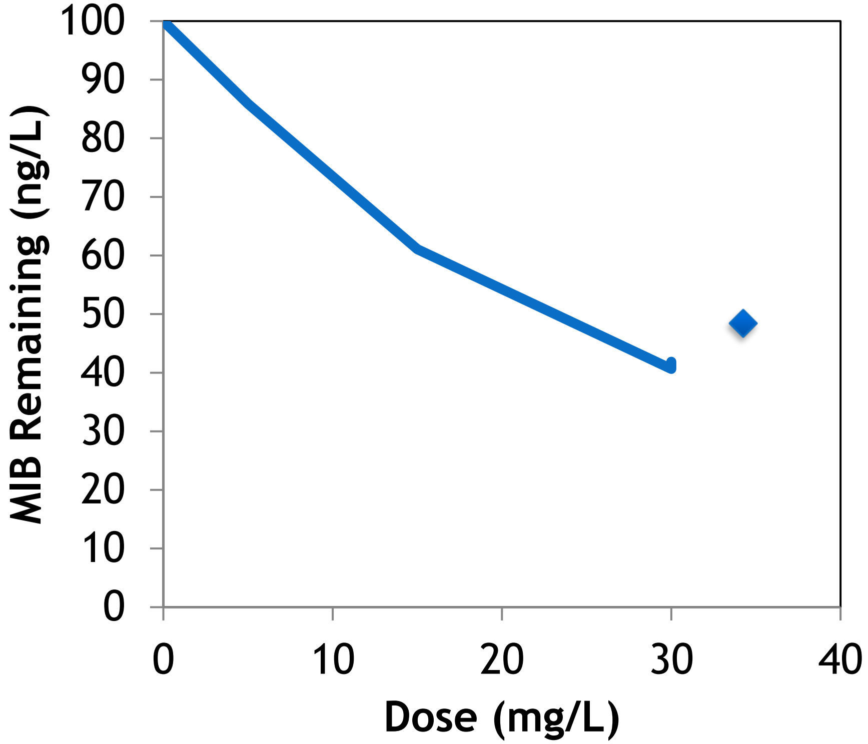


Study #1: PAC Adsorption of MIB and Sulfamethoxazole

Goal #1: Predict PAC performance

- Approach – Multiple linear regression

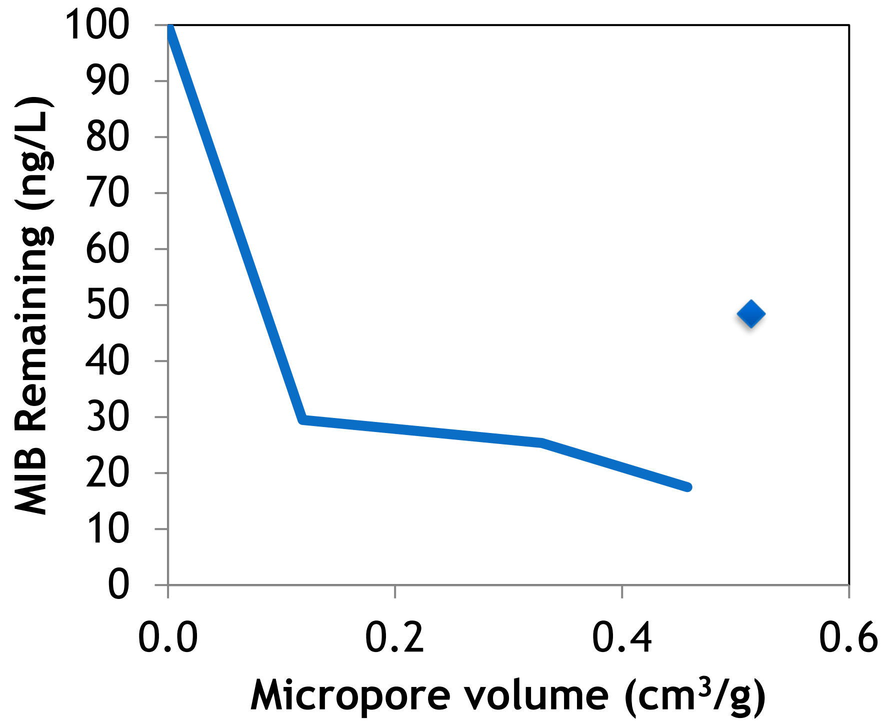
$$\text{MIB Remaining} = -a \times \text{PAC Dose}$$



Goal #1: Predict PAC performance

- Approach – Multiple linear regression

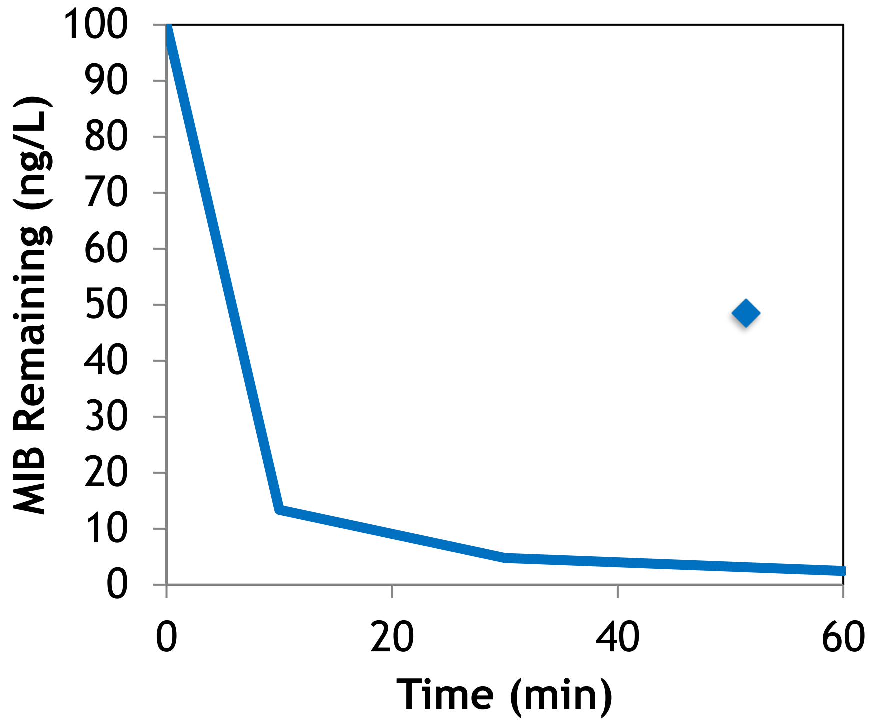
$$\text{MIB Remaining} = -a \times \text{PAC Dose} - b \times \text{micropore volume}$$



Goal #1: Predict PAC performance

- Approach – Multiple linear regression

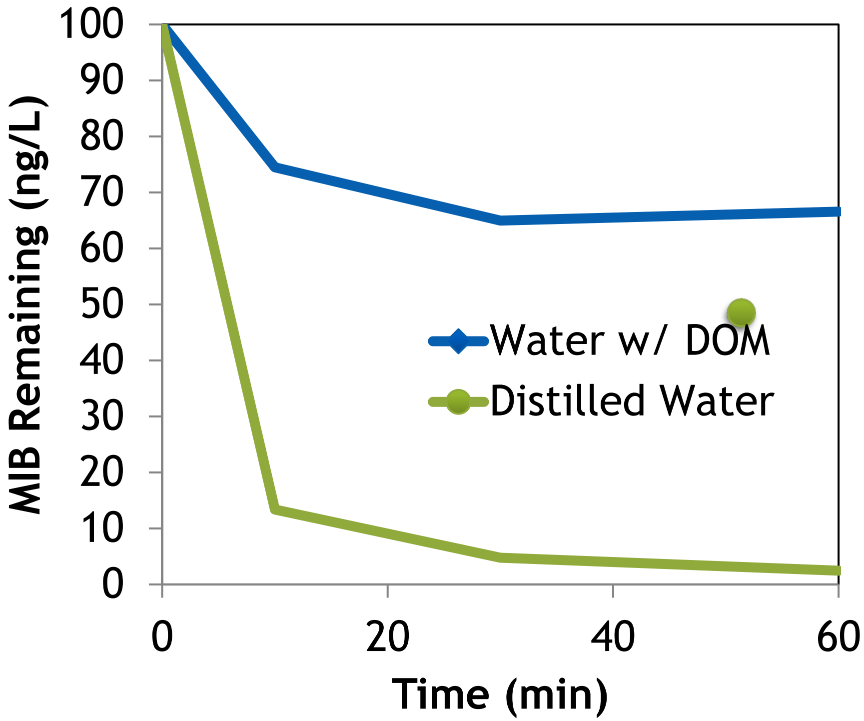
$$\text{MIB Remaining} = -a \times \text{PAC Dose} - b \times \text{micropore volume} - c \times \text{Contact Time}$$



Goal #1: Predict PAC performance

- Approach – Multiple linear regression

$$\text{MIB Remaining} = -a \times \text{PAC Dose} - b \times \text{micropore volume} - c \times \text{Contact Time} + d \times \text{Water Quality?}$$



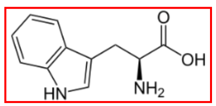
Goal #1: Predict PAC performance

- Approach – Multiple linear regression

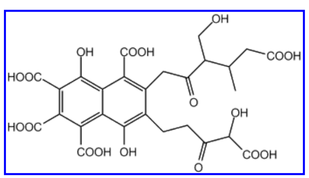
$$\text{MIB Remaining} = -a \times \text{PAC Dose} - b \times \text{micropore volume} - c \times \text{Contact Time} + d \times \text{Water Quality?}$$

  – Key water quality parameter is dissolved organic matter

Tryptophan

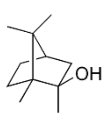


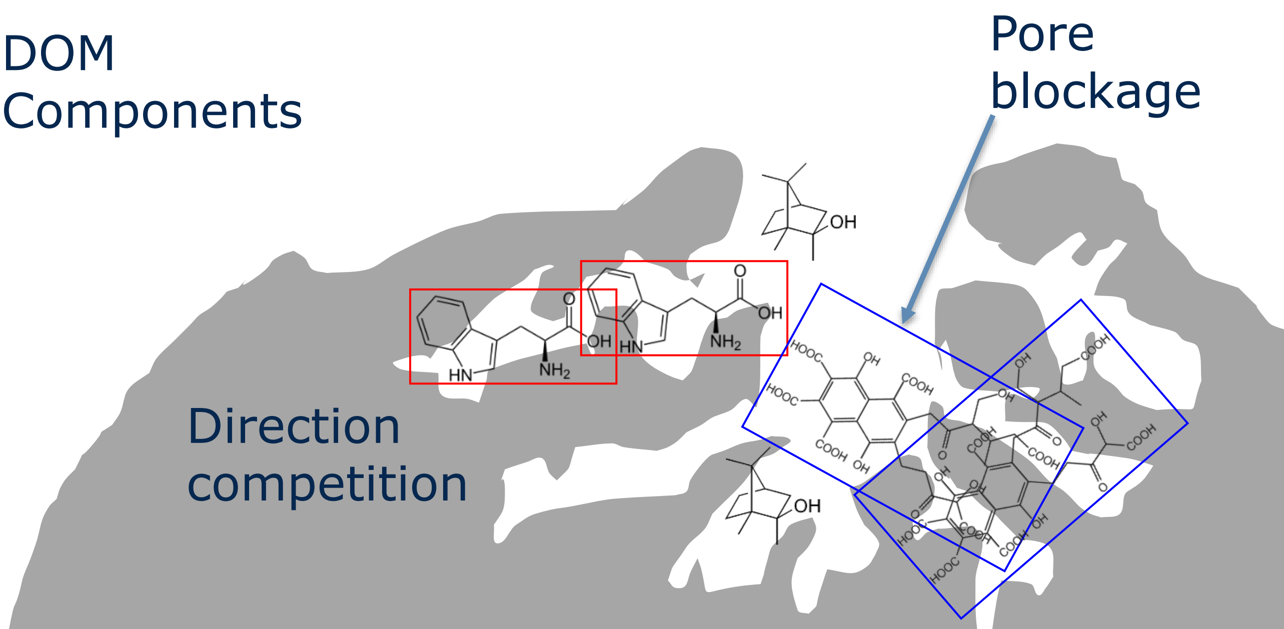
Model Fulvic acid



DOM Components

MIB



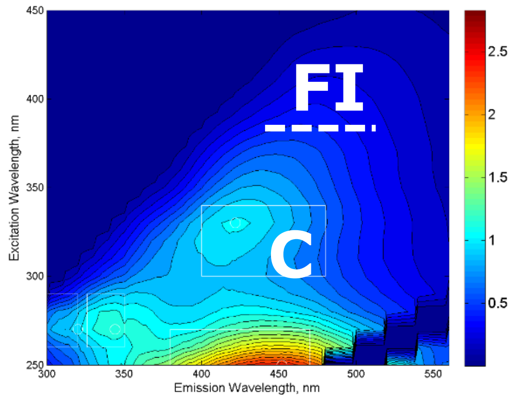


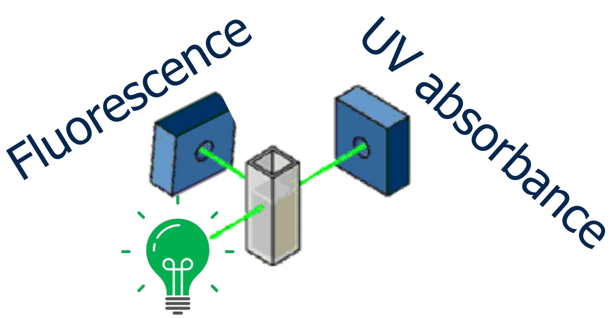
Goal #1: Predict PAC performance

- Approach – Multiple linear regression

$$\text{MIB Remaining} = -a \times \text{PAC Dose} - b \times \text{micropore volume} - c \times \text{Contact Time} + d \times \text{UVA}_{254,0} + e \times \text{FI}$$

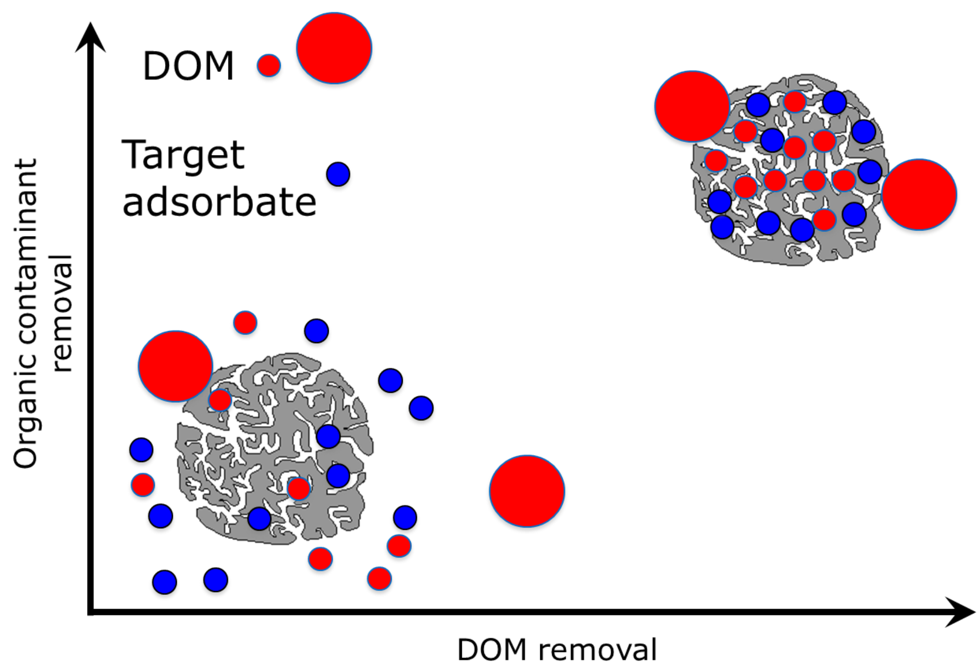
– Two common rapid, simple methods to characterize DOM are:
  - UV-absorbance at 254 nm (UVA_{254})
  - Fluorescence spectroscopy parameters, e.g.,:
    – Fluorescence index (FI) - slope of intensities at Em:470/520 nm @ Ex 370 nm
    – Peak C - intensity at Ex: 300-350 nm and Em: 400-480 nm

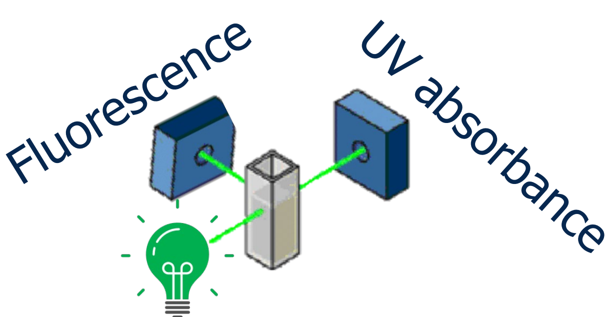




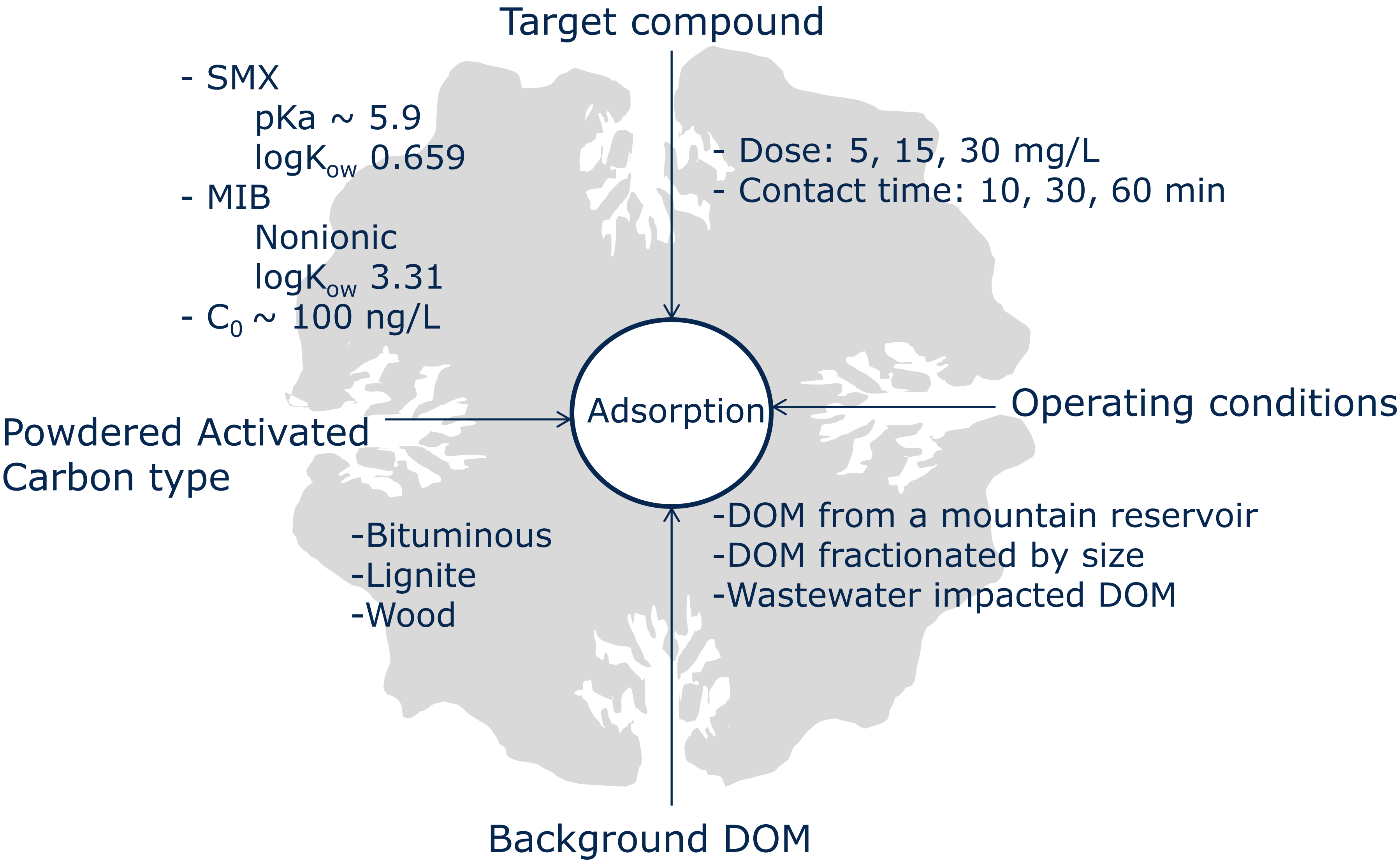
Goal #2: Monitor PAC performance

- Approach – Develop a relationship between DOM optical property removal and MIB and SMX removal
  - Trace organic contaminant analysis is expensive
  - UV_{254} and fluorescence peak C can be measured quickly, in the field, and at a relatively low cost





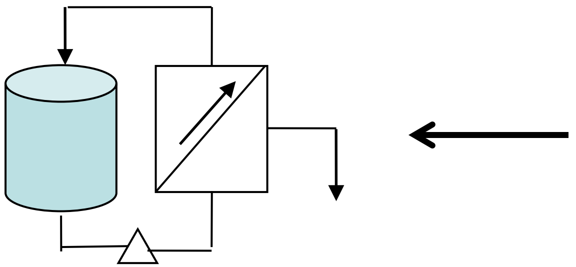
Study #1: Materials and Methods



Study #1: Materials and Methods

Identifier	Source	TOC (mg/L)
BEM 3 mg/L	DOM concentrate from mountain reservoir #1	3.2
BEM 7 mg/L	DOM concentrate from mountain reservoir #1	6.8

Reverse Osmosis

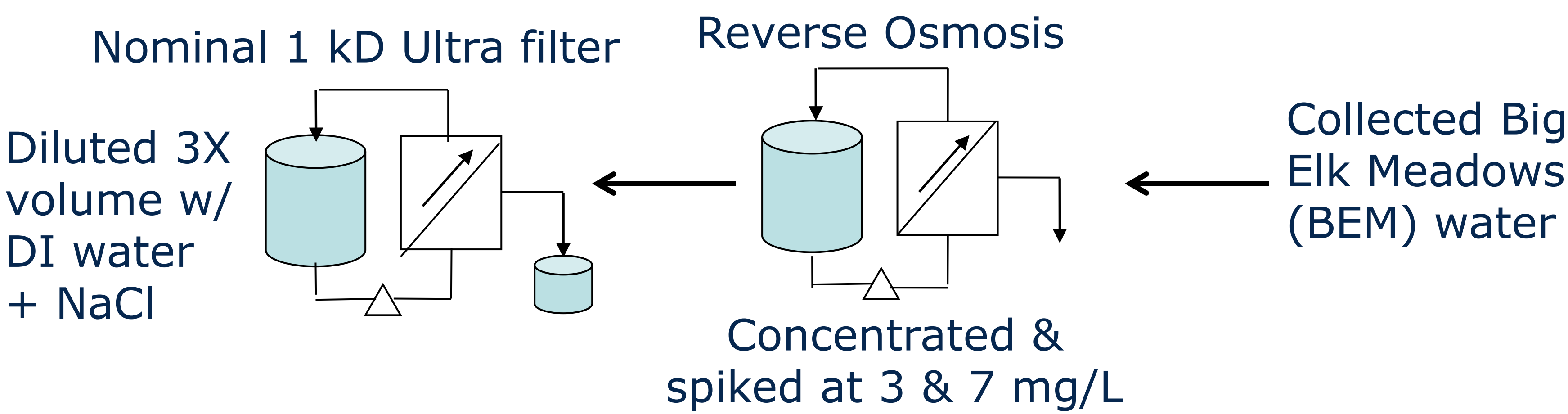


Collected Big Elk Meadows (BEM) water

Concentrated & spiked at 3 & 7 mg/L

Study #1: Materials and Methods

Identifier	Source	TOC (mg/L)
BEM 3 mg/L	DOM concentrate from mountain reservoir #1	3.2
BEM 7 mg/L	DOM concentrate from mountain reservoir #1	6.8
>1kD BEM	Large fraction from mountain reservoir	3.2
<1kD BEM	Small fraction from mountain reservoir	3.1



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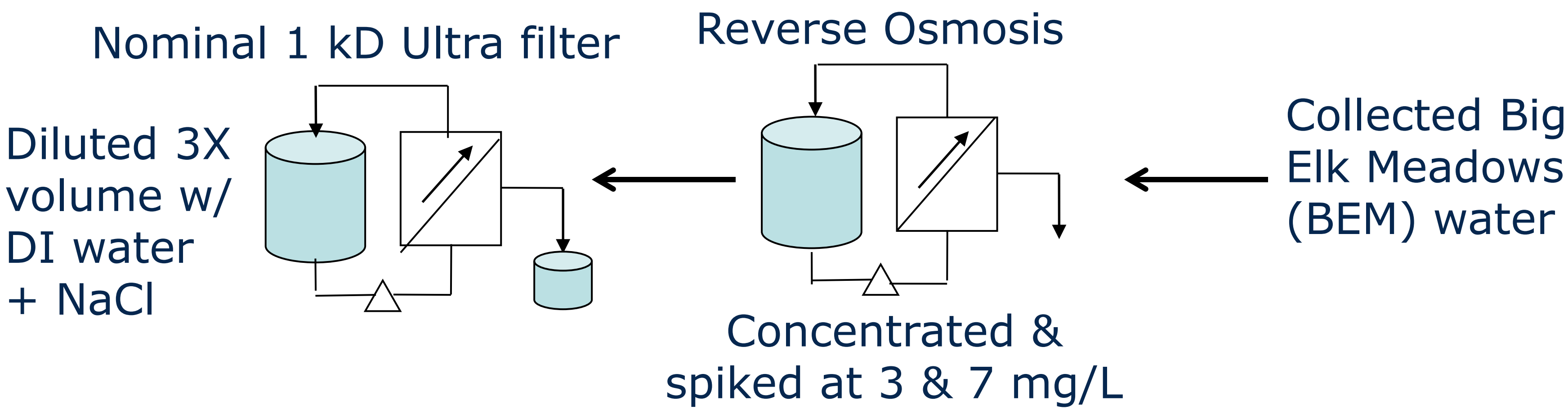
BEM 7 mg/L	DOM concentrate from mountain reservoir #1	6.8
>1kD BEM	Large fraction from mountain reservoir	3.2
<1kD BEM	Small fraction from mountain reservoir	3.1
Barker	Mountain reservoir #2	3.0
Boulder Creek	Wastewater impacted stream	6.9
Barr 4 mg/L	Wastewater impacted lake	3.8
Barr 8 mg/L	Wastewater impacted lake	8.3



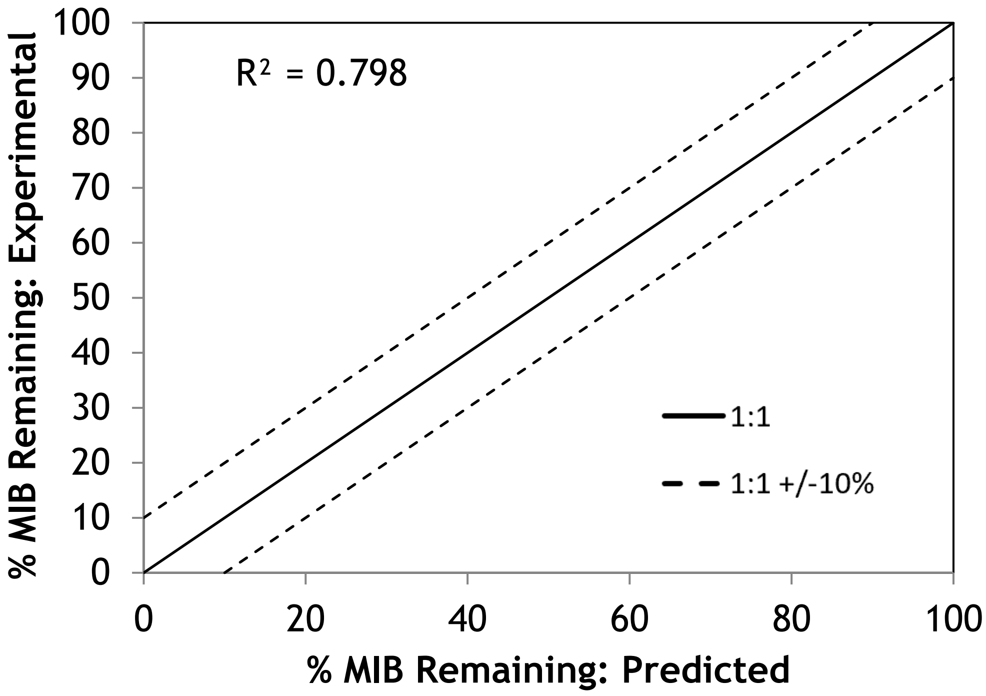
Study #1: Materials and Methods

- Phips and Bird Jar Tester
- Liquid scintillation counting
  - $[^{14}C]$-MIB and $[^{3}H]$-SMX
- HORIBA FluoroMax-4
  - Ex: 240-450 (10nm incr.), Em: 300-560nm (2nm incr.), Slitwidth: 5nm, Integration time 0.25s, Sc/Rc mode
  - Corrected EEMs by: Blank subtraction, Raman normalization, Inner filter correction (Cary 100 Bio), Instrument-specific corrections

Study #1: Results – Predicting PAC Performance

- Regression without FI: MIB

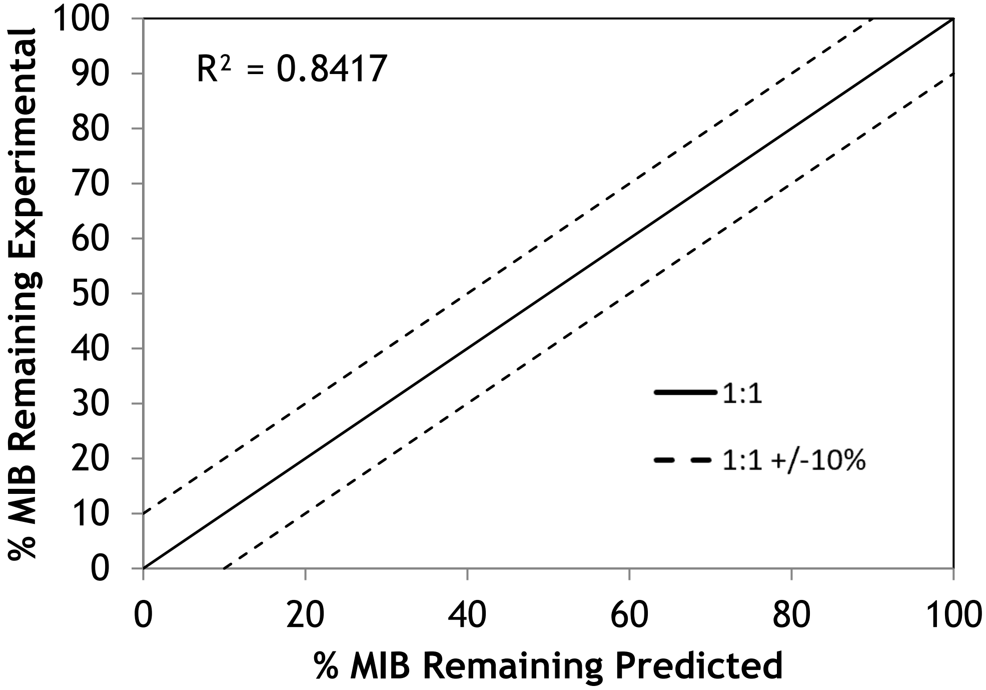
$$\text{\% MIB Remaining} = -19 \times \text{PAC Dose} - 4.2 \times \text{micropore volume} - 2.7 \times \text{Contact Time} + 84 \times UVA_{254,0} + 83$$



Study #1: Results – Predicting PAC Performance

- Regression with FI: MIB

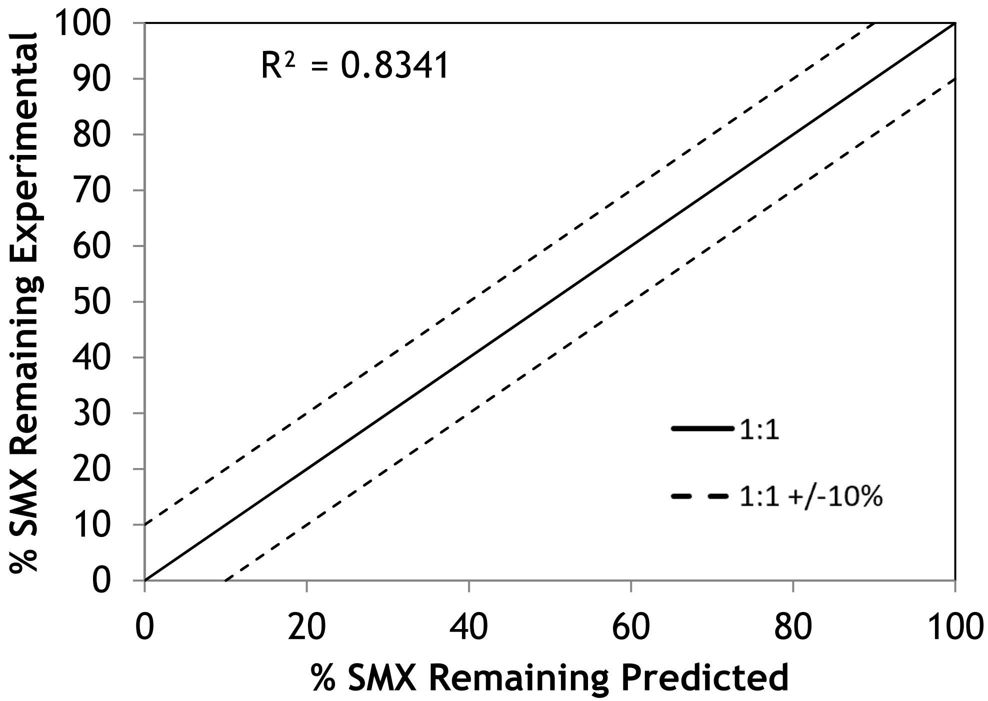
$$\%\,\text{MIB Remaining} = -16 \times \text{PAC Dose} - 3.2 \times \text{micropore volume} - 5.8 \times \text{Contact Time} + 78 \times UVA_{254,0} + 5.2 \times FI + 68$$



Study #1: Results – Predicting PAC Performance

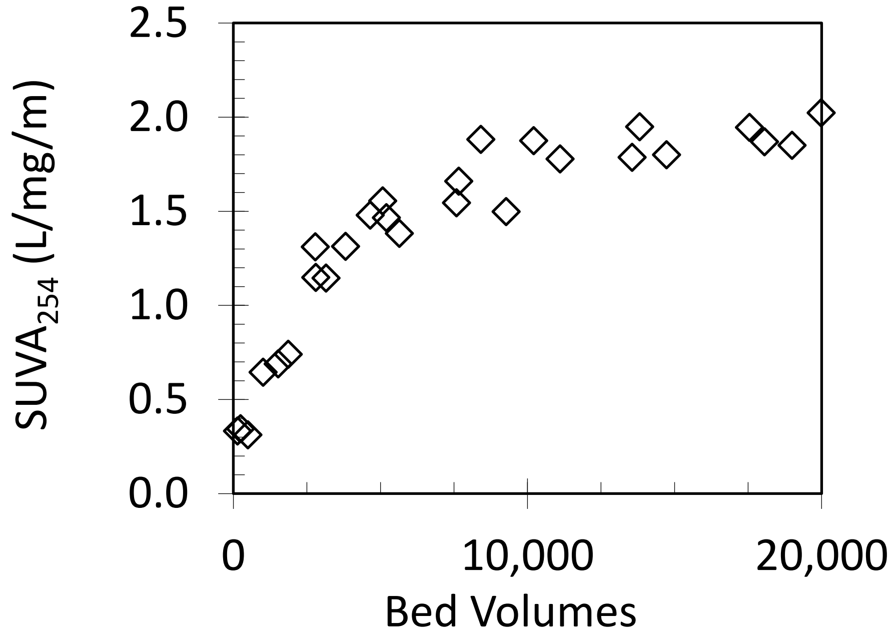
- Regression with FI: Sulfamethoxazole (SMX)

$$\begin{matrix}\text{\% SMX} \\ \text{Remaining}\end{matrix} = -16 \times \begin{matrix}\text{PAC} \\ \text{Dose}\end{matrix} - 1.4 \times \begin{matrix}\text{micropore} \\ \text{volume}\end{matrix} - 6.5 \times \begin{matrix}\text{Contact} \\ \text{Time}\end{matrix} + 83 \times UVA_{254,0} + 8.2 \times FI + 61$$



Study #1: Results – Predicting PAC Performance

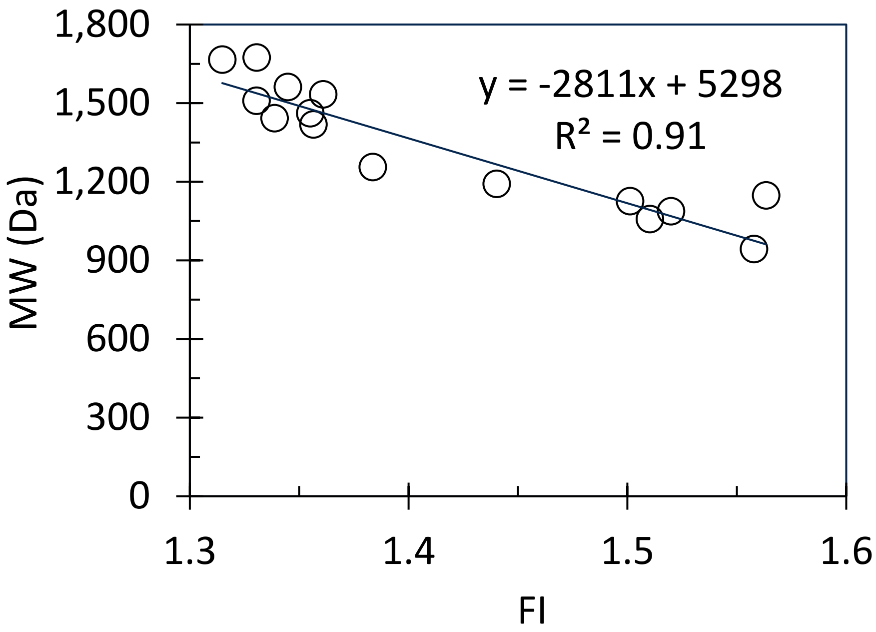
- Why does UVA_{254} correlate to MIB and SMX removal?
  1. UVA_{254} and TOC are correlated
  2. UVA_{254} detects aromatic DOM
     - Aromatic DOM is more adsorbable than aliphatic DOM



Shimabuku, K.K., Kennedy, A.M., Mulhern, R.E., Summers, R.S. (2017) Evaluating activated carbon adsorption of DOM and micropollutants using fluorescence spectroscopy. *Environmental Science and Technology*, 51 (5) 2676–2684.

Study #1: Results – Predicting PAC Performance

- Why dose FI correlate to MIB and SMX removal?
  1. Larger FI indicates lower MW DOM
  2. Smaller DOM is more competitive for adsorption sites



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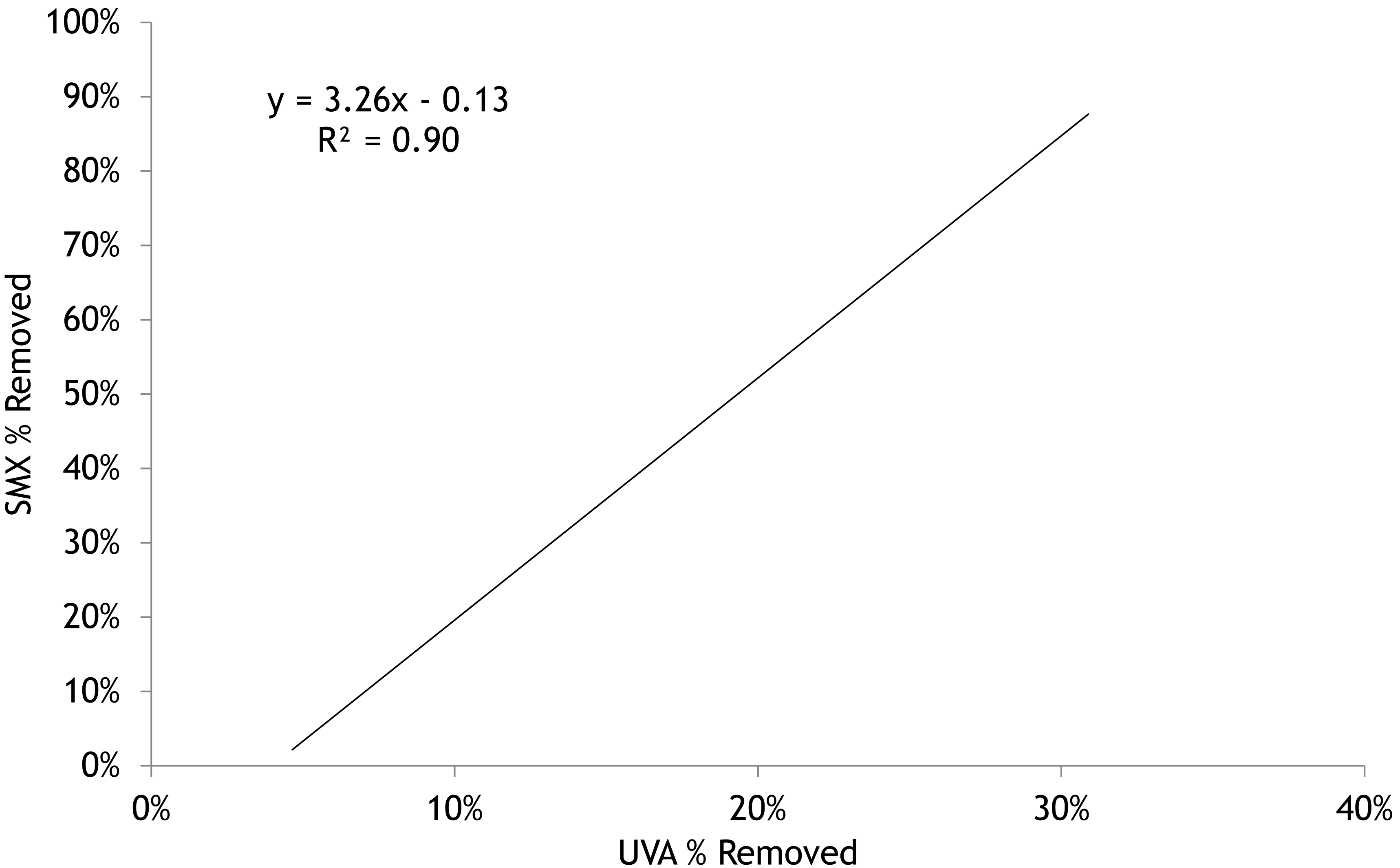
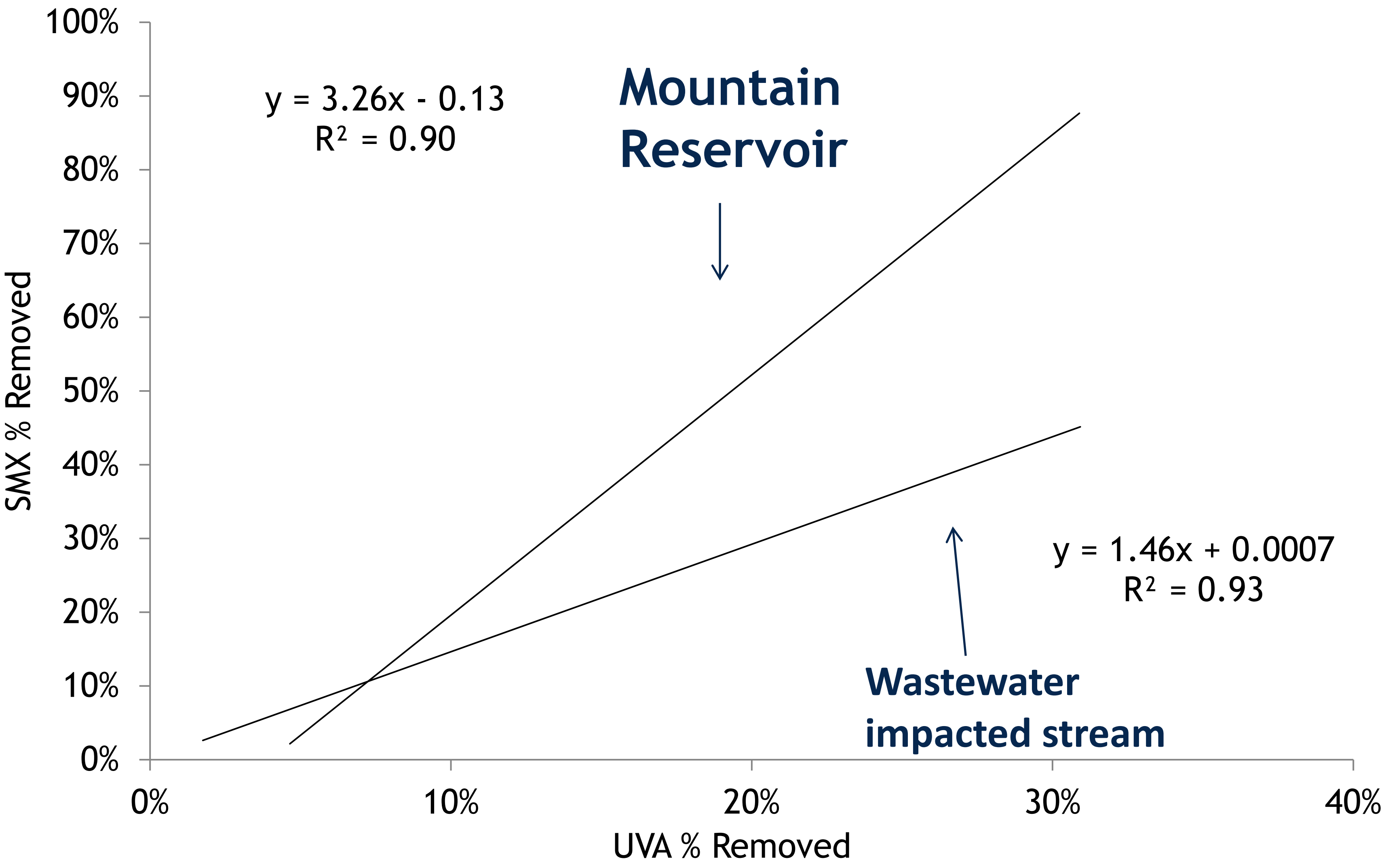
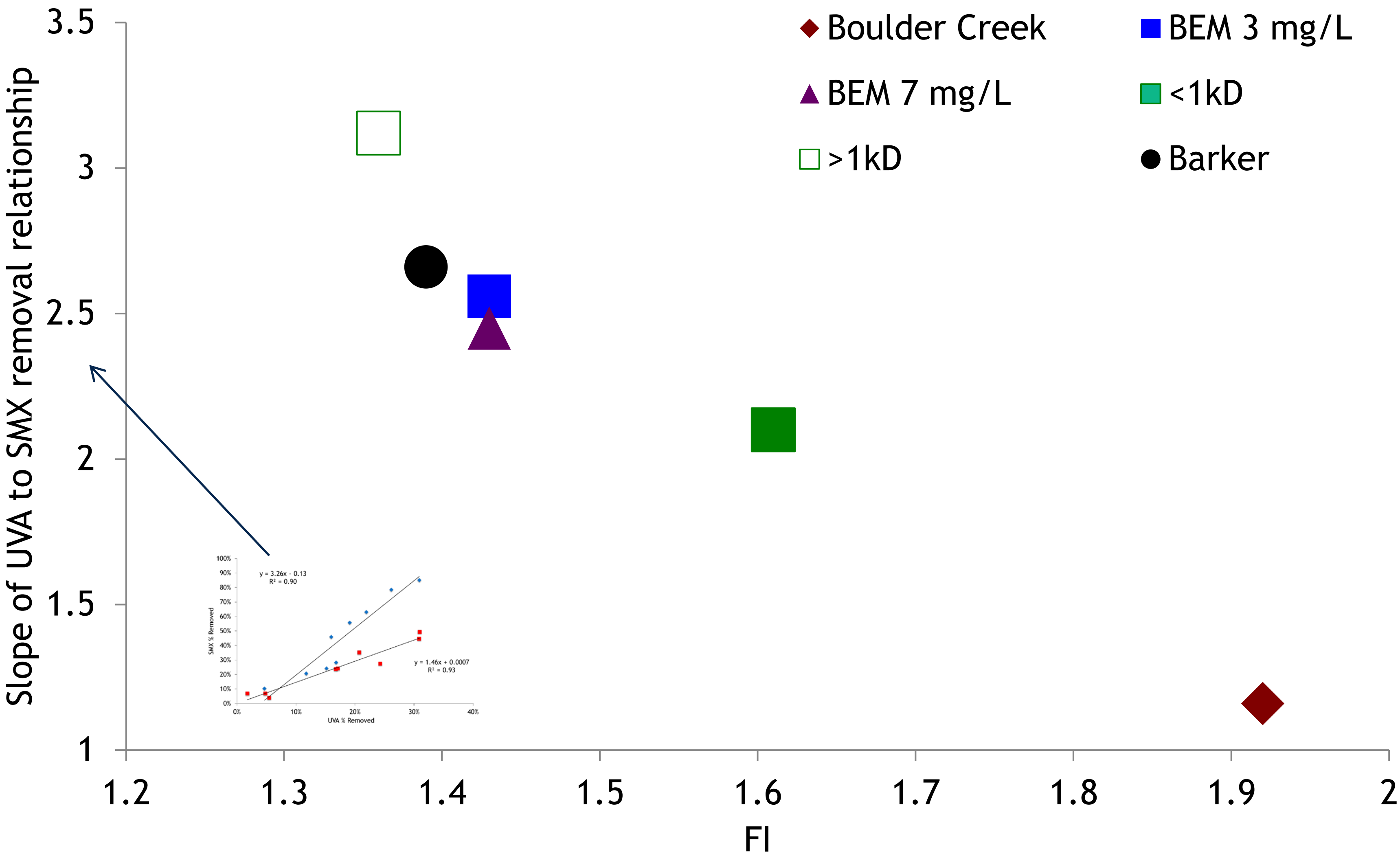
Study #1: Results – Monitor PAC Performance



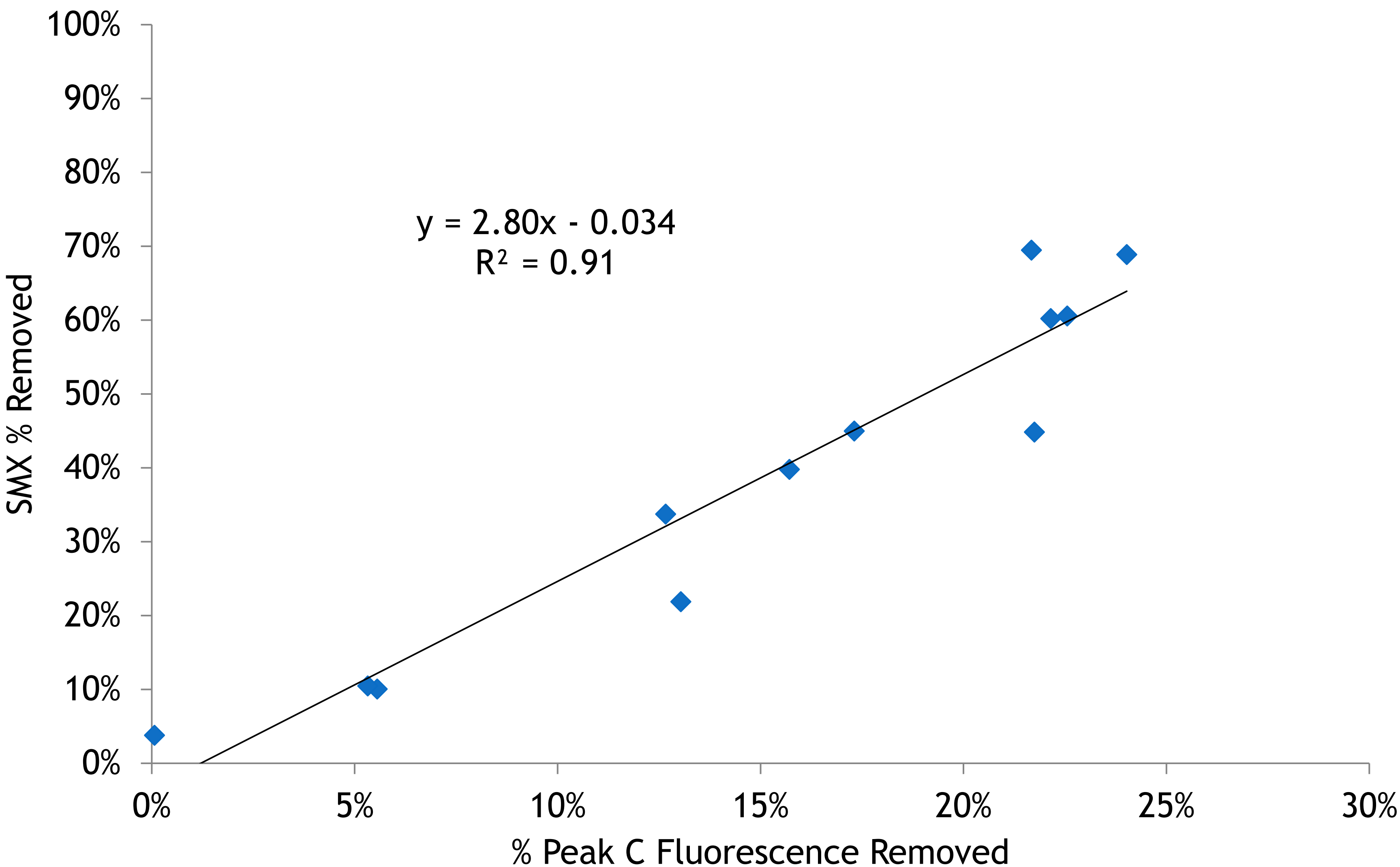
Study #1: Results – Monitor PAC Performance



Study #1: Results – Monitor PAC Performance



Study #1: Results – Monitor PAC Performance



Study #2: GAC adsorption of short-chain PFAS

Study #2: Overview

- Overarching Goal: Model GAC adsorption of a mixture of 11 short-chain PFAS using optical properties…

Compound class	Chemical name	Abbreviation	Carbon chain length
sulfonate	Perfluorobutanesolufonate	PFBS	C4
sulfonate	Perfluoropentanesulfonate	PFPeS	C5
sulfonate	Perfluorohexanesulfonate	PFHxS	C6
carboxylate	Perfluoropentanoate	PFPeA	C5
carboxylate	Perfluorohexanoate	PFHxA	C6
carboxylate	Perfluoroheptanoate	PFHpA	C7
ether	perfluoro-2-methoxypropanoate	PMPA	C4, branched
ether	perfluoro-2-ethoxypropanoate	PEPA	C5, branched
ether	hexafluoropropylene oxide-dimer acid (perfluoro-2-propoxypropanoate)	GenX	C6, branched
ether	perfluoro-3-methoxypropanoate	PFMOPrA	C4, linear
ether	perfluoro-4-methoxybutanoate	PFMOBA	C5, linear

…in three waters with different DOM characteristics

Test water	DOC (mg/L)	SUVA (L/mg-m)	FI
Groundwater	2.8	1.6	1.71
Surface water	4.5	5.2	1.49
Wastewater	5.8	3.0	2.23

Aung, M. T., Shimabuku, K. K., Soares-Quinete, N., & Kearns, J. P. (2022). Leveraging DOM UV absorbance and fluorescence to accurately predict and monitor short-chain PFAS removal by fixed-bed carbon adsorbers. Water Research, 213, 118146.

Study #2: Methods

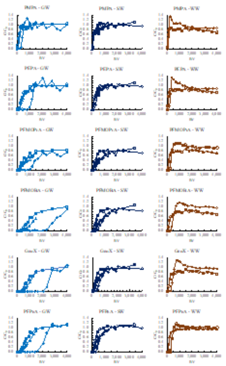
- Performed pilot, CD-RSSCT, and PD-RSSCT column tests with a GAC made inhouse

column	Bed dia. (cm)	d_p (mm)	EBCT (min.)
full-size	7.04	1.29 (8x30 US std. sieve)	30
pilot	2.54	1.29 (8x30 US std. sieve)	30
CD-RSSCT	0.953 (3/8")	0.196 (60x100 US std. sieve)	0.695
PD-RSSCT	0.476 (3/16")	0.108 (100x200 US std. sieve)	2.52

- Liquid chromatography coupled with Quadrupole Time-of-flight mass spectrometer (QTOF/MS)
- Same DOM characterization in Study #1

Study #2: Overview

- Goal 1: (Not the focus here) assess the ability to model the sum of PFAS (ΣPFAS) adsorption as an individual constituent



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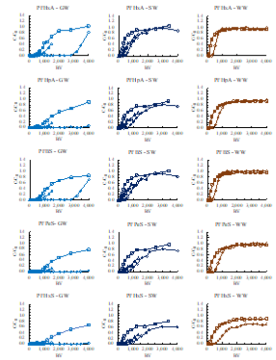

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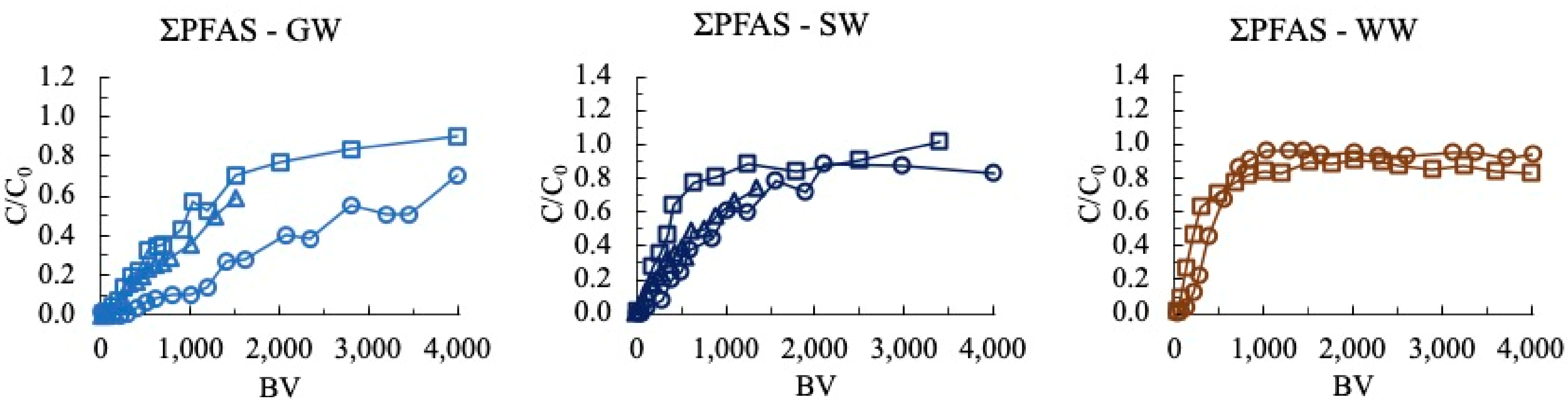
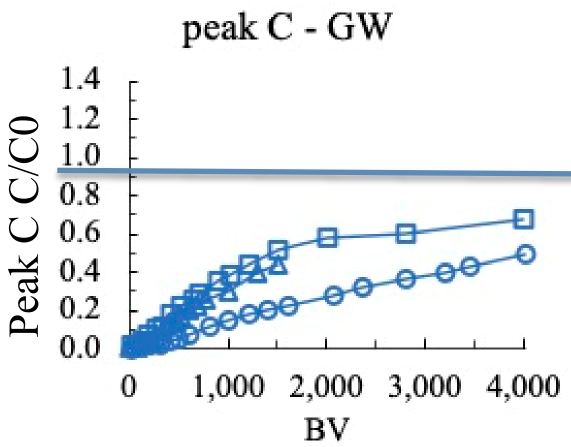
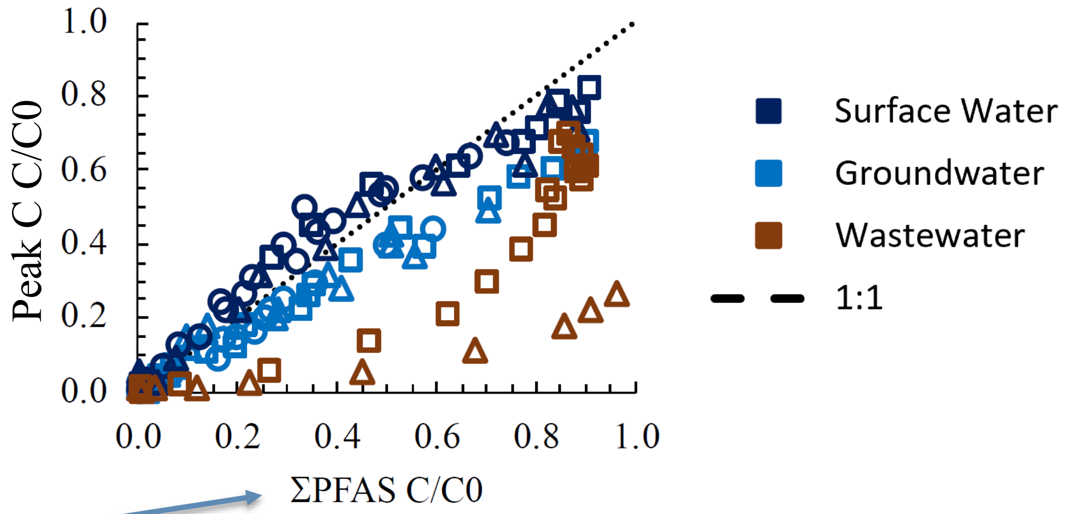
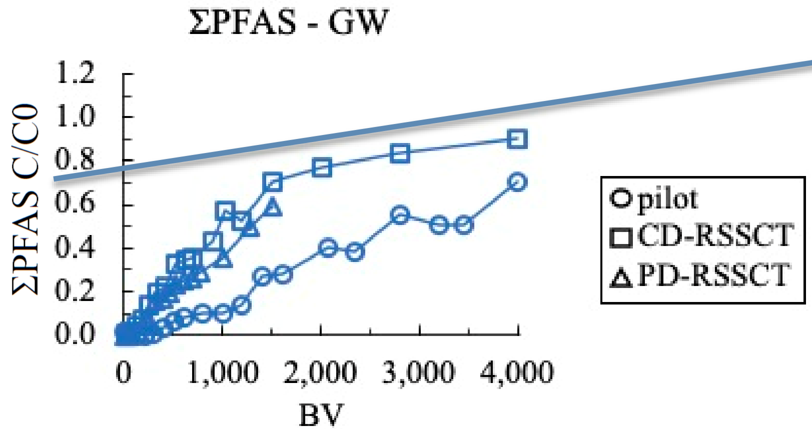


Study #2: Overview

- Goal 2: Monitor ΣPFAS breakthrough based on optical parameter breakthrough



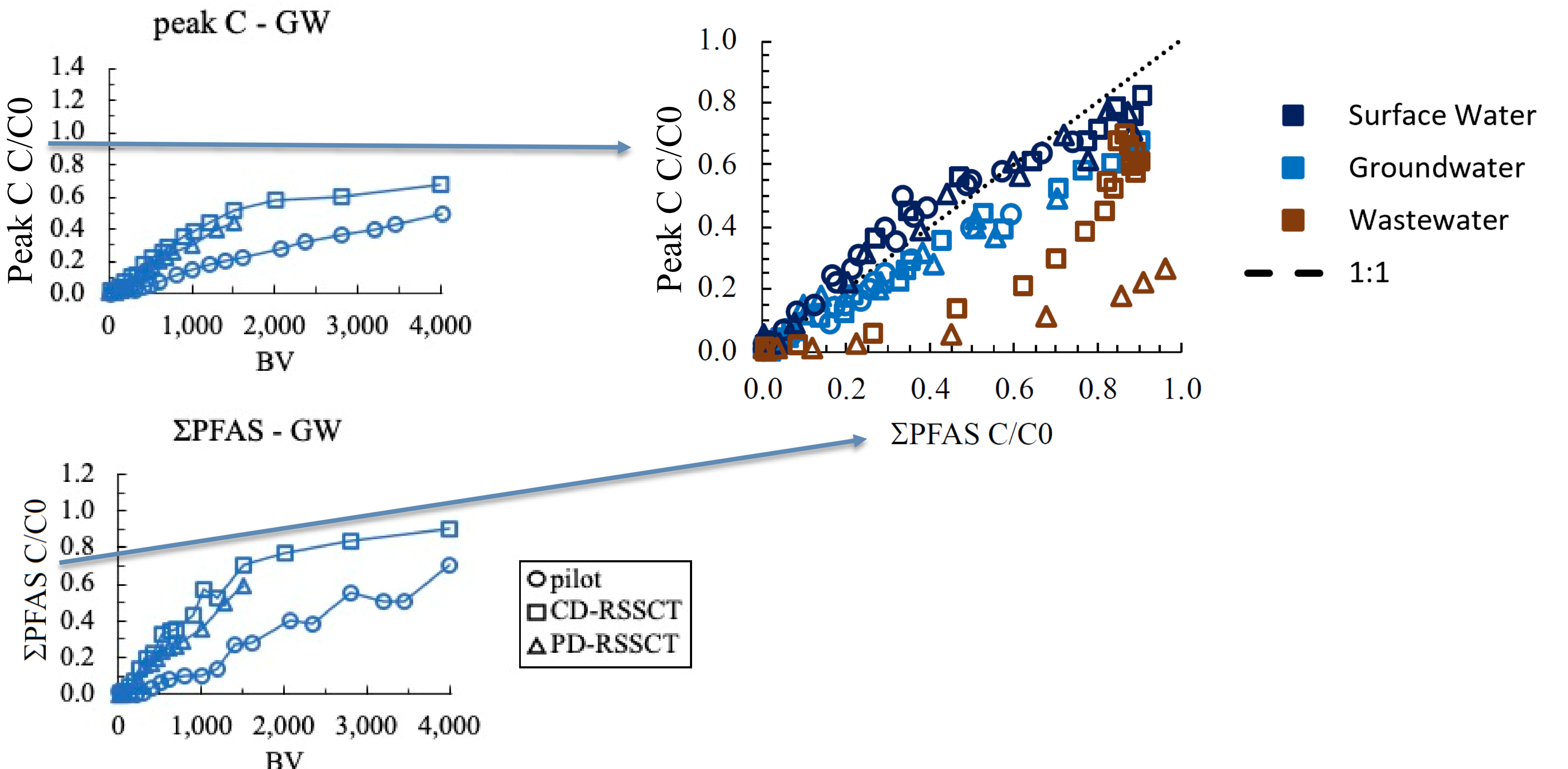




– Incorporate raw water optical parameter data to correct to a 1:1 correlation in all waters

Study #2: Overview

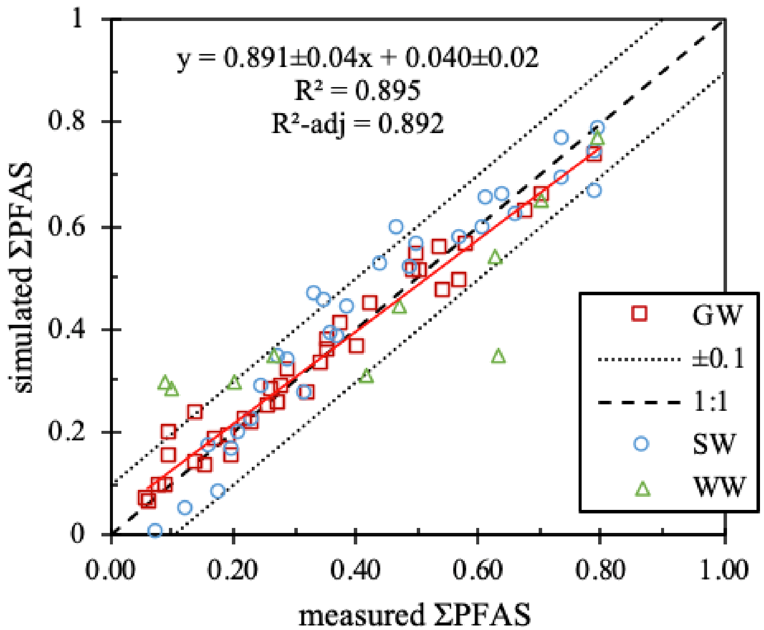
- Goal 3: Use the constant relationship between Peak C and ΣPFAS breakthrough in pilot and RSSCTs to predict ΣPFAS breakthrough at pilot-scale



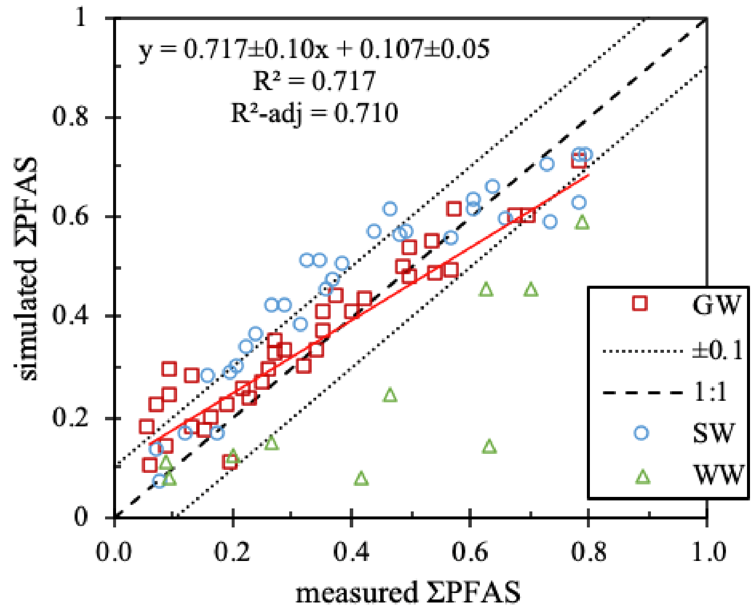
Study #2: Monitoring PFAS Breakthrough

- Incorporating raw water optical parameters improved the ability of optical property breakthrough to monitor ΣPFAS breakthrough
- Fluorescence based parameters were more effective than UV-based parameters
  - Most likely because fluorescence parameters captures DOM competition and adsorbability better than UV parameters

$\Sigma PFAS = -0.894 + 1.252 \text{ peak } C/C_0 + 0.526 \text{ } FI_0$

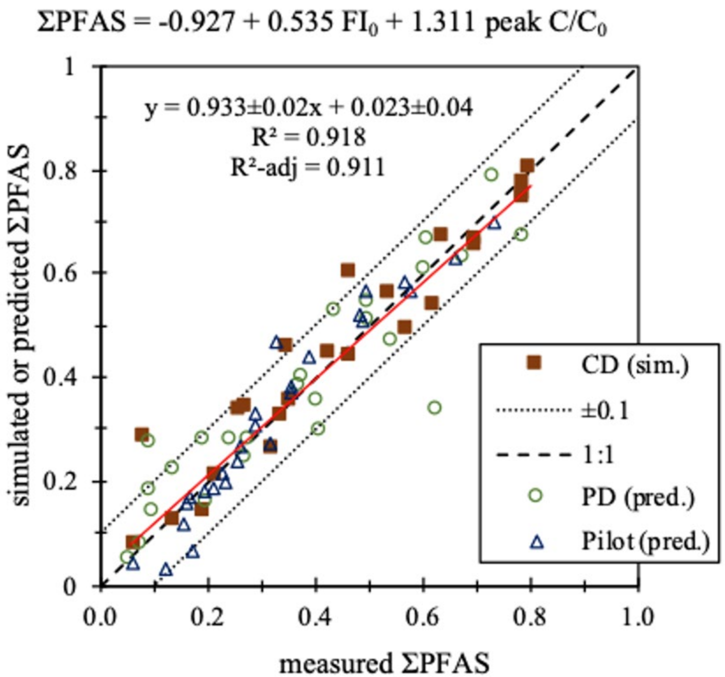


$\Sigma PFAS = 0.0428 - 0.671 \text{ } UVA_0 + 1.045 \text{ } UVA/UVA_0$



Study #2: Predicting PFAS Breakthrough in Pilot Columns

- Fitting the model to one RSSCT data set could effectively predict breakthrough in the other RSSCT and pilot datasets
- Suggests an approach to RSSCT scaling could be developed by:
  1. Making a relationship between Peak C and PFAS breakthrough with an RSSCT
  2. Monitoring Peak C at full-scale to estimate PFAS breakthrough



Conclusions

- Fluorescence and UV-absorbance a simple, rapid, and relatively low-cost methods that can facilitate activated carbon adsorption modeling
- Predictive multiple linear regressions for MIB and SMX removal by PAC benefit from incorporating UV_{254} and FI
- A simple empirical relationship can be derived between micropollutant and DOM removal measured by UVA
  - The slope of the relationships change with differences in DOM character
- Peak C and UV_{254} can be used to monitor PFAS breakthrough in GAC filter adsorbers
  - Can also facilitate scaling between RSSCT and full-scale media containing adsorbers

Thank you!

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