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Removal of Complex Mixtures of Perfluoroalkyl Acids from Water Using Molecularly Engineered Coatings on Sand and Silica

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14. ABSTRACT
Rationally-designed organosilica adsorbents where synthesized to study the adsorption of perfluoroalkyl substances (PFAS) from water. The goals were to better understand mechanisms of adsorption and thus design optimal adsorbents to minimize costs of remediation. Swellable organically modified silica (SOMS) was used as a platform as it can be modified by use of different silane monomers and entrapped cationic polymers. Adsorbents were studied using a series of bench-scale isotherm and column experiments. Measurements were done in comparison to activated carbon and ion exchange resins currently used in water treatment. The best performing SOMS adsorbent was evaluated in a pilot test installed on a side stream at the Former Joint Reserve Base (JRB) Naval Air Station (NAS) Willow Grove. Data suggest that PFAS self-assemble into aggregates which enhances the adsorption of long-chain PFAS. This work advanced the field of PFAS adsorbents for remediation by providing insights into adsorption mechanisms and a new type of adsorbent.

15. SUBJECT TERMS
PFAS, adsorbents, organosilica, site remediation, technology for ex situ remediation

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1.3 List of Acronyms

AFFF:	Aqueous firefighting foam
ATR	Attenuated total reflectance
BET:	Brunauer–Emmett–Teller (isotherm)
BJH:	Barrett-Joyner-Halenda (pore size calculation method)
BTEB:	bis(trimethoxysilylethyl)benzene
CAS	Chemical Abstracts Services number
C_e	equilibrium concentration
CMC:	critical micelle concentration
DMDMS	dimethoxydimethylsilane
FT-IR	Fourier transform – infrared spectroscopy
GAC:	ranular activated carbon
HPLC	high pressure liquid chromatography
Iex	ion exchange
K_F	Freundlich constant
log K_{ow}	log base 10 of the octanol-water partition equilibrium constant
NOM	natural organic matter
q_e	adsorption capacity at equilibrium
QQQ	triple quadrupole (mass spectrometer)
PHC	porous hydrophobic coating
PFAA:	perfluoroalkyl acid
PFAS:	poly- and perfluoroalkyl substance
SOMS	swellable organically modified silica
TOP assay:	total oxidizable precursor assay

1.4 PFAS analyte list

PFAS Name	Acronym	Formula	CAS
perfluorodecanoic acid	PFDA	$C_{10}HF_{19}O_2$	335-76-2
perfluorononanoic acid	PFNA	$C_9HF_{17}O_2$	375-95-1
perfluorooctanoic acid	PFOA	$C_8HF_{15}O_2$	335-67-1
perfluoroheptanoic acid	PFHpA	$C_7HF_{13}O_2$	375-85-9
perfluorohexanoic acid	PFHxA	$C_6HF_{11}O_2$	307-24-4
perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	2706-90-3
perfluorobutanoic acid	PFBA	$C_4HF_7O_2$	375-22-4
perfluorooctanesulfonic acid	PFOS	$C_8HF_{17}O_3S$	1763-23-1
perfluorohexanesulfonic acid	PFHxS	$C_6HF_{13}O_3S$	355-46-4
perfluorobutanesulfonic acid	PFBS	$C_4HF_9O_3S$	375-73-5
perfluorooctanesulfonamide	PFOSA	$C_8H_2F_{17}NO_2S$	754-91-6
perfluorooctane sulfonamide quaternary ammonium	PFOSaAm	$C_{13}H_{13}F_{17}N_2O_2S$	13417-01-1

1.5 Keywords

PFAS, adsorbents, organosilica, site remediation, technology for ex situ remediation

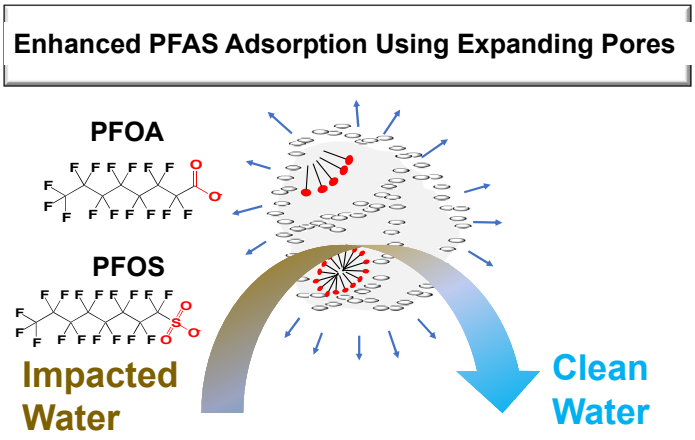
1.0 ABSTRACT

Introduction and Objectives. Rationally-designed organosilica adsorbents where synthesized to study the adsorption of perfluoroalkyl substances (PFAS) from water. The goals were to better understand mechanisms of adsorption and thus design optimal adsorbents to minimize costs of remediation. Swellable organically modified silica (SOMS) was used as a platform as it can be modified by use of different silane monomers and entrapped polymers. A unique feature of SOMS is the ability to volumetrically swell significant enlarging the microscale pore structure. Swelling enhances capacity and improves adsorption kinetics.

Technical Approach. A step-wise approach was used. First, a diverse set of SOMS materials adding fluoroalkyl groups and/or cationic groups to a hydrophobic resin were synthesized. Materials were then screened for PFAS adsorption using kinetics and adsorption isotherms. Adsorbents with optimal performance were further studied using a series of bench-scale column experiments. Measurements were done in comparison to activated carbon and ion exchange resins currently used in water treatment. Finally, the best SOMS adsorbent was evaluated in a pilot test installed on a side stream at the Former Joint Reserve Base (JRB) Naval Air Station (NAS) Willow Grove. Reversibility of the resins were also tested.

Results. Optimal PFAS adsorbents were found to be highly porous SOMS materials possessing hydrophobicity and cation groups. Cationic groups help to bind anionic PFAS. Data suggest that PFAS self-assemble into aggregates which enhances the adsorption of long-chain PFAS. SOMS is ideally suited to take advantage of PFAS self-aggregation since the resin has an expanded pore structure obtained via swelling. For purposes of evaluation, during the pilot test, poly-SOMS adsorbent developed in this study yielded an adsorption capacity of 2,600 µg/g of PFAS given an influent concentration of 40 µg/g total PFAS and a contact time of 1 minute.

Benefits. SOMS-based PFAS adsorbents have improved capacity over current technologies. Scale-up of SOMS was accomplished during the study making the material an option for full scale PFAS remediation activities. SOMS based resin has two benefits. First, it has higher capacity than ion exchange resin, especially in the presence of natural organic matter. Second, SOMS can be regenerated using a solvent rinse. Regeneration allows resins to be used and PFAS to be concentrated for residue management. The new adsorbent technology appears useful for economical remedial action to manage groundwater resources at DoD facilities.



2.0 OBJECTIVES

In this SERDP Proof-of-Concept Project we created SOMS adsorbents with pore structures and chemical functionality to study the adsorption of a wide suite of PFAS from water. Organosilica adsorbents in the form of SOMS were hypothesized to be a useful tool in studying PFAS adsorption in order to optimize affinity and capacity. First, the pore size can be expanded by swelling SOMS with a water miscible organic liquid prior to use. Several studies suggest that PFAS adsorbates aggregate to form micelles and hemi-micelles upon adsorption.[18–20] Wider pores would help to facilitate transport and accommodate PFAS aggregates.[21] Second, the surface chemistry of the organosilica was varied by polymerization of different silane monomer mixtures. Systematic addition of a fluoroalkyl group and a cationic (ion exchange) group to the pre-existing hydrophobic (aryl rich) pores was used to determine the effect on PFAS adsorption. In the absence of optimal silane precursors, a polymer was entrapped which has cationic groups for ion exchange and amide groups to participate in hydrogen bonding interactions with C-F groups.

Systematic research steps with the following tasks:

1. A wide set SOMS adsorbents of different compositions were synthesized and their physical properties characterized.
2. Adsorbents with acceptable porosity were screened using adsorption kinetics and adsorption isotherms in the ~200 ppb range.
3. Bench-scale columns tests were used to evaluate key adsorbents (200 ppb).
4. Simulated groundwater was used to test the best adsorbents vs. ion exchange at the ppt level to mimic field conditions. Water imported from field testing sites was used.
5. A pilot test was conducted at Former Joint Reserve Base (JRB) Naval Air Station (NAS) Willow Grove using one of the best adsorbents.
6. Regeneration was tested. These data combined treatment results and scale-up allows for a comprehensive assessment of whether SOMS-based adsorbents improved PFAS remediation.

3.0 BACKGROUND

Releases of PFAS are known or suspected at more than 300 DoD sites, and as of December 2016, DoD has spent more than $200 million in sampling, analysis, and remediation (DoD 2017). SERDP/ESTCP reported that the total number of impacted sites may reach the thousands.[1] Most PFAS are considered stable and persist in groundwater without significant biotic or abiotic degradation. As a result, natural attenuation is not a feasible remedial option and use of in situ technologies is limited by the chemical stability of PFAS. Thus, adsorbents are primary option for remediation. Improving the performance of adsorbents in a cost-effective manner is a key objective.

Here, polymeric organosilica materials based on a commercially developed platform were explored for PFAS absorption. This is inspired by the fact that both ion exchange and other polymeric adsorbents have shown improved adsorption capacity for PFOA and PFOS compared

to activated carbon. Examples of these polymeric media include crosslinked divinylbenzene polymer resins Dowex L493[2], Dowex V493[3], and Amberlite XAD4[2].

Mesoporous organosilica materials were hypothesized to be high capacity sorbents for PFASs. Organosilica adsorbents have been investigated by the Edmiston lab for the past 15 years inspired by the pioneering work by Cerveau and Corriu[4,5] and Loy and Shea[6] who demonstrated that MPOS could be prepared using the sol-gel polymerization processes where the characteristics of a porous material are tailored by controlling the kinetics of hydrolysis and condensation reactions of alkoxysilane precursors.[7,8] Using further modifications to the sol-gel method, our laboratory has designed porous materials for the selective adsorption and detection of vapor phase explosives[9,10] and aqueous chlorinated aromatic compounds.[11]

Careful selection of processing conditions has been used to create functional organosilica with controlled pore structures including mechanically flexible pore architecture to allow swelling up to 2.X in volume.[12] Termed "swellable organically modified silica" (SOMS, commercial name: Osorb®) these materials demonstrate capacity to adsorb both neat and dissolved phase organic molecules with very high capacity (>4 g/g).[13,14] The media has been successfully used in the treatment of stormwater[15] and produced water[16] and the development of passive samplers.[17] A key benefit of SOMS swelling is when acting as an adsorbent with natural waters where the flexibility to expand upon adsorption prevents blocking of adsorption sites by suspended solids or co-adsorption of natural organic matter.

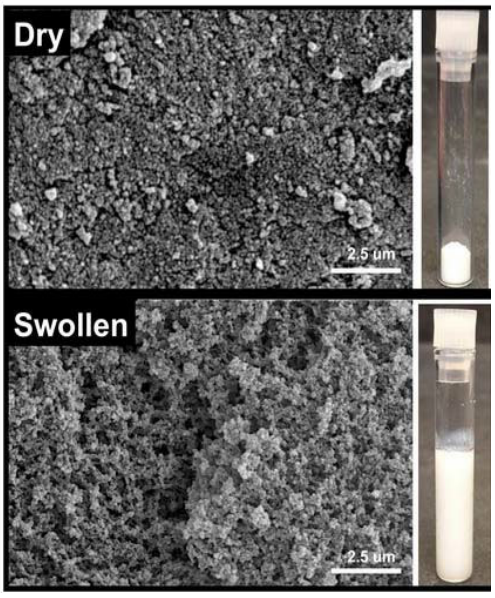


Fig 1: (Above) Photograph of SOMS which is a granular translucent adsorbent. The pores are continuous allowing diffusion of adsorbents throughout the entire particle.
(Right) Electron micrographs pair with photographs of SOMS unswollen (top) vs, swollen (bottom). Swelling induced by organic solvents expands the pores structure leading to a volumetric expansion of SOMS.

4.0 MATERIALS AND METHODS

4.1 Materials. Silane precursors **1**, BTEB; **2**, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-trimethoxysilane; and **3**, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (50% in methanol) were purchased from Gelest (Fig 2). Tetrabutyl ammonium fluoride (TBAF, 1.0 M solution in THF); 4, Luviquat™ FC 370 polymer, hexamethyldisilazane (HMDS), Norit® 1240W activated carbon, neat PFAS compounds, and all solvents were obtained from Aldrich. PFAS standards were obtained from Wellington Laboratories. Oasis® HLB (200 mg, 6 mL) solid phase extraction cartridges were obtained from Waters.

4.2 Adsorbent Synthesis. SOMS exclusively comprised of **1** was prepared as described previously.[22] Fluoroalkyl-modified organosilica, "F-SOMS", was prepared by adding 3.0 g of **1** and 0.55 g of **2** to 14 mL acetone. Polymerization was catalyzed by the addition of 580 µL 0.225 M TBAF solution (90 µL 1M TBAF, 490 µL water) resulting in gelation. After aging for 6 days at 25°C, the gel was crushed into ~5-10 mm pieces, rinsed twice with acetone, and immersed in 20 mL of 5% v/v HMDS in acetone for 48 hr at 25°C. The gel pieces were thoroughly rinsed with acetone in using Soxhlet extraction, and dried at room temperature. The solid material was ground using a ball mill and sieved. Quaternary amine modified organosilica, "QA-SOMS", was prepared in the same manner as F-SOMS except 3.0 g of **1** and 800 µL of the vendor provided solution of **3** were combined to create the gel. SOMS with entrapped polymer, "poly-SOMS", was prepared by applying 10.0 mL of a 100 mg/mL of 4 in methanol to 5.0 g of SOMS which fully absorbed the solution. The methanol was evaporated at 25°C to dryness. The above procedures were modified by varying the ratio of silane precursors and polymer to create a series of materials. Porosity and PFOA binding affinity were characterized for each.

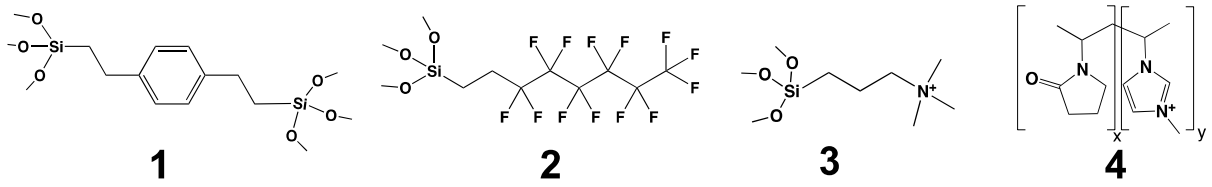


Fig 2. Structures of alkoxysilane precursors used for organosilica synthesis (**1-3**). Polymer (**4**) encapsulated in SOMS

4.3 Characterization. Surface area and pore volume were measured by N_2 adsorption at 77°K using a Beckman Coulter SA-3100 instrument. Samples were outgassed at 120°C for 120 min prior to measurement. Surface area was calculated using the BET method[23] and the pore size distribution was calculated using the BJH method.[24] Swelling capacity (mL of liquid absorbed per g SOMS) was measured by gravimetry after titrating the sorbent to the fully swollen state with neat acetone. The change in volume was measured by visible light microscopy using image analysis software (Image J). Scanning electron microscopy was conducted using Hitachi S-4700 after coating the samples with Pt. Imaging was done at 10.0kV. Reproducibility was tested by repeating measurements using the same sample and also by measuring adsorption by separate batches of material synthesized by the same procedure. FT-IR spectra of poly-SOMS were taking using a Perkin-Elmer FT-IR 2000 using KBr pellets whereas spectra for other materials were measured using a Nicolet 6700 FT-IR using a diamond-ATR accessory. Fluorine elemental analysis was conducted by Galbraith Laboratories.

4.4 Adsorption Kinetics and Isotherm Measurements. Adsorption kinetics was measured by adding 200 mg of adsorbent to 1 L high density polyethylene (HDPE) bottles. SOMS, F-SOMS, and QA-SOMS were pre-wetted by applying a minimal volume of ethanol (~500 µL) to the adsorbent. Next, 500 mL of 2000 µg/L solution of individual PFAS in DI water or 50 mM NaCl was added to the bottles which were shaken for 14 hours at 170 rpm with 2 mL aliquots taken at 0.25, 0.5, 1, 2, and 14 hr intervals. Sample aliquots were filtered with 0.45 µm cellulose acetate syringe filters, except for PFOSA and PFOSaAm, which were centrifuged to remove any adsorbent particles. Cellulose acetate filters were shown not to remove PFAS compounds except for PFOSA and PFOSaAm in separate experiments. Samples were immediately diluted with 50:50 with 100% methanol or 50:50 with 95%methanol / 5% ammonium acetate if the compound was a perfluorinated carboxylate. An additional control experiment was done by adding the polymer 4 to water containing PFAS solutes and measuring that the polymer did not lead to bias in the measurement, which was not observed. The concentration of PFAS was measured by LC-MS for each aliquot and the initial solution which was compared to a control which was a sample of filtered or centrifuged untreated solution. Internal standards and perfluoro-n-[1,2-$^{13}C_2$]octanoic acid (M2PFOA) and sodium perfluoro-1-[1,2,3,4-^{13}C4]octanesulfonate (MPFOS) were added prior to measurement to selected samples. Data was fit to an integrated a pseudo-second order kinetic model.[27]

$$\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (1)$$

where $q(t)$ is the amount adsorbed at time t, k_2 is the rate constant, and q_e=$q(t\rightarrow\infty)$, the equilibrium capacity. RStudio (Version 1.1.456) was used to fit isotherms and pseudo second order kinetics.

Adsorption isotherms were conducted for each individual PFAS at C_0 concentrations of 250, 500, 1000, 1500, and 2000 µg/L in either DI water or 50 mM NaCl using a 40 mg/L dosage of adsorbent. SOMS and F-SOMS were pre-swollen with ethanol prior to addition of aqueous PFAS solutions. Bottles were shaken for 14 hr and the PFAS concentration measured compared to control samples of the initial solution using the same procedures above. Data was fit to the Freundlich isotherm in the form:

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \qquad (2)$$

by linear regression using RStudio to determine $1/n$ and the Freundlich constant, K_F. All adsorption isotherms were run in duplicate.

4.5 Column Experiments. Adsorbents were pre-wetted either by vigorous agitation in water for GAC and poly-SOMS or swelling with ethanol for SOMS and F-SOMS. Continuous flow column experiments were performed by placing 500 mg of sorbent in 16 mm Pharmacia XK16 glass/polyamide-polyethylene column creating a bed height of approximately 1 cm. Polypropylene tubing was used for all fluid handling. Adsorbents were initially rinsed on the column with 250 mL of DI water at 2 mL/min. PFAS solutions were applied at 1.0 mL/min with a contact time of 2 min. Treatment columns were run with influent concentrations of either 2.0 or 200 µg/L. Effluent samples were collected periodically in conjunction with matched influent samples. Aliquots were immediately diluted 50:50 with either 100% methanol or 95% methanol/ 5% ammonium acetate solution and PFAS concentration measured by LC-MS. Internal standards were added to select samples for quality control. When analyzing effluent from 2.0 µg/L applied

PFAS concentration 500 mL aliquots were collected and concentrated using solid-phase extraction as previously described49,50. Surrogates sodium perfluoro-[$^{13}C_8$]-octanesulfonate (M8PFOS) and perfluoro-n-[$^{13}C_8$]octanoic acid (M8PFOA) were used to measure recovery.

Simulated groundwater with 2.0 ppb for each PFAS analyte was used to evaluate poly-SOMS vs. other commercial media. Water was prepared in 15L batches and spiked from the same stock solutions. Humic acid (1.0 ppm) was used as natural organic matter. Each batch is characterized to ensure consistency. Analytical measurements are made using the approved SOPs which use an individual mass labeled surrogate for each PFAS.

Table 1. Simulated Groundwater Composition

Solute	Concentration (mg/L)
Cations	
Ca^{2+}	10
Mg^{2+}	1.5
Na^{+}	14
Anions	
HCO_3^{-}	25
Cl^{-}	22
SO_4^{2-}	10
Natural Organic Matter	
Humic acid	1.0
pH	7.7
conductivity	128 µS

Table 2. PFAS Concentrations in Simulated Groundwater

Solute	Concentration (ng/L)
PFBA	750
PFPeA	750
PFHxA	1100
PFHpA	1200
PFOA	1200
PFNA	1200
PFBS	750
PFHxS	1200
PFOS	2000

4.6 Analytical measurements. PFAS concentrations were analyzed by LC-MS using an Agilent 1200/6410 HPLC-MS (QqQ) with using Infinity Lab C18 Poroshell 120 21x100 mm column, particle size 2.7 µm and PEEK tubing is used for solvent flow. Mobile phases were A: 5 mM ammonium acetate in water B: 95% methanol + 5 mM ammonium acetate with a flow rate of 0.300 mL/min at temperature of 35°C. Injection volumes were 5 µL. Single PFAS analytes with expected concentrations >2 µg/L were measured using direct injection with isocratic elution with MRM detection utilizing both a quantitative and qualitive transitions of analytes and internal standards (See Appendix A- Standard Operating Procedures). SPE extracts were of single component samples were run in the same procedure. Mixtures of PFAS compounds were run using gradient elution. A laboratory reagent blank and laboratory control sample was run before each set of samples and several times during each daily worklist. A laboratory control was run with each sample sub-set or experimental method or set of samples. The limit of quantitation of the HPLC-QqQ was 0.65-6.5 µg/L in direct injection mode (See Appendix A- Standard Operating Procedures) with replicate precision <3%.

Note: The MRLs and DLs reported in Appendix A are for the instrument measurement itself and do not account for pre-concentration via solid-phase extraction. For guidance the concentration factor for most extractions was 500-1,000X meaning the LODs were ~10^3 lower .

4.7 Pilot test. Poly-QA (open) was manufactured at the kg scale for testing at Former Joint Reserve Base (JRB) Naval Air Station (NAS) Willow Grove. 10 kg was successfully manufactured. Two media cartridges were filled with 0.5 kg of poly-SOMS each. Due to back-pressure, only one cartridge was operated at 0.36 gal/min for 28 days (15,100 gal water total). Samples were taken initially and after at 7-day intervals after start-up. Sample splits were sent to EuroFins for third party testing. The TOP assay was used to characterize each sample in addition

4.8 Summary of Adsorbents Tested

Table 3: Bulk adsorbents tested

Adsorbent	Precursors	Description	Forms*	
			"Dry" unswollen	"Open" swollen
SOMS	1	Hydrophobic pores	yes	yes
F-SOMS	1,2	Hydrophobic with fluoroalkyl groups	yes	yes
QA-SOMS	1,3	Hydrophobic with cationic groups	yes	yes
poly-SOMS	1,4	Hydrophobic, entrapped cationic polymer	yes	yes
GAC	-	Norit® 1240W type GAC	n/a	n/a
Ion exchange	-	Marathon	n/a	n/a

* SOMS materials can be in the collapsed dry unswollen state or swollen pore expanded state. It was found that the swollen state improved PFAS adsorption.

Table 4: Bulk adsorbents tested

Adsorbent	Precursors	Description
PHC-Silica	1	hydrophobic organosilica film on filter sand
F-PHC-Silica	1,2	hydrophobic organosilica film with fluoroalkyl groups on filter sand

Coated films or similar composition on standard water filtration sand to produce a lower cost adsorbent.

5. RESULTS & DISCUSSION

5.1 Adsorbent Synthesis and Characterization. The overall goal of the project is to develop and test porous organosilica based adsorbents in removing a wide range of PFASs from water. The hypothesis is that addition of fluoroalkyl groups to the surface of organosilica sorbents would improve the affinity and selectivity to adsorb perfluoroalkyl compounds from water. Adsorbents would be created using the swellable organically modified silica (SOMS) system which provide a highly porous material that expands up to 3X via a flexible microstructure. Finally, the adsorption mechanism is to be studied both empirically by measuring adsorption of a wide range of PFASs under different solution conditions and directly by FT-IR-ATR spectroscopy.

Synthesis of adsorbents was done using a modified sol-gel process where alkoxysilane precursors are polymerized under mild conditions to spontaneous form a porous solid network. Overall, 16 different SOMS materials were created varying the amounts of three precursors: i) BTEB, **1**, that creates a flexible hydrophobic porous network ii) precursor **2** which adds fluoroalkyl groups to the pore network, and iii) precursor **3** which adds cationic binding sites in combination with the surface chemistries above (Fig 2).

All materials prepared were successful in forming solid porous materials which were characterized by measuring the dry state surface area and pore volume, the microscale morphology by SEM, and composition by FT-IR (Tables 5&6). In further investigations it was determined that a porous network could not be obtained if the amount of BTEB dropped below 40% mol/mol. BTEB appears to be the structure directing precursor and when used in insufficient amounts precludes gel formation. As the mol fraction of the fluyoroalkyl precursor was increased the porosity decreased. Despite some differences in the porosity the microscale texture of the adsorbents with and without fluoro groups as introduced using fluoroalkyl precursor **2** were relatively similar as examined by SEM (Appendix B). As the amount of fluoroalkyl increased some mesopore formation was apparent. Swelling capability as measured by the amount of absorption of acetone liquid was increased when moderate amounts of fluoroalkyl precursor was used.

Table 5: Characteristics of fluoroalkyl modified adsorbents

ID	Mole Ratio Precursor 2	Surface area (m^2/g)	Pore volume (mL/g)	Swelling capacity (mL/g)	Pore diameter distribution (%)			PFOS Removal %
					<6 nm	6-80 nm	>80 nm	
A1	**0**	646	1.03	6.1	29	69	2	65
A2	**0.07**	621	0.80	7.0	58	41	1	71
A3*	**0.13**	660	1.04	6.6	30	69	1	69
A4	**0.19**	500	0.60	6.3	71	26	3	41
A5	**0.31**	420	0.54	6.2	64	34	2	60
A6	**0.47**	283	0.50	6.0	28	63	9	30
A7	**0.57**	212	0.36	3.8	particle size could not be maintained			
A8	**0.66**	85	0.18	2.9				

*Material used in subsequent measurements as **F-SOMS**.

Table 6: Characteristics of fluoroalkyl/quaternary amine derived adsorbents

ID	Mole Ratio Precursor 3 (cationic)	Mole Ratio Precursor 2 (fluoroalky)	Surface area (m^2/g)	Pore volume (mL/g)	Swelling capacity (mL/g)	Pore diameter distribution (%)			PFOS Removal %
						<6 nm	6-80 nm	>80 nm	
A9	**0**	**0**	679	1.06	6.8	30	68	2	>99
A10	**0.07**	**0**	418	0.88	5.4	12	81	7	>99
A11	**0.07**	**0.07**	365	0.78	4.1	14	61	15	>99
A12*	**0.14**	**0**	500	0.60	6.3	71	26	3	>99
A13	**0.14**	**0.07**	420	0.54	6.2	64	34	2	>99
A14	**0.21**	**0**	192	0.74	6.0	28	63	9	>99
A15	**0.21**	**0.07**	212	0.60	6.7	10	84	6	>99
A16	**0.42**	**0**	405	0.84	5.3	29	65	6	>99

*Material used in subsequent measurements as **QA-SOMS**.

The full group of prepared materials was screened for the adsorption of PFOS as a baseline determination of effectiveness of adsorption. All materials prepared removed PFOS from water, however, the affinity of adsorption decreased as the amount of fluoroalkyl precursor mole ratio exceeded 0.19. The decrease could be due to the reduced porosity, for example, **A4** had a porosity of 500 m^2/g vs. **A7** which was prepared with 3X more **2** had a porosity of only 212 m^2/g. As a result, **A3** (**F-SOMS**) was chosen as the material with optimal amount of fluoroalkyl precursor based on the following criteria: i) good porosity, ii) ability to swell, iii) effective PFOS adsorption, and lowest amount of fluoroalkyl precursor. FT-IR spectroscopy indicated that the Si-O-Si region from 950-1200 cm^{-1} were similar for SOMS and F-SOMS. F-SOMS showed an increase in peak area at 1250 and 1100 cm^{-1} due the introduction of C-F stretching modes52. Determining the extent of incorporation of the fluoroalkyl precursor (2) in the final material was difficult to quantitate using FT-IR due to the overlap of the C-F bands with the Si-O-Si region from 1100-1250 cm^{-1}. Elemental analysis found that F-SOMS was composed of 13.6% fluorine by weight representing 80% theoretical incorporation of 2 in the final material, assuming complete polycondensation. Full condensation is unlikely, thus, there was substantial incorporation of the fluoroalkyl group.

QA-SOMS materials prepared with precursor **3** (quaternary amine) required over 5 min to reach a gel state during polymerization compared to <1 min for SOMS. QA-SOMS was more friable and became a powder during the synthesis process, whereas SOMS and F-SOMS remained a monolithic material until being ground to granular form prior to testing. The reduction in gel time and reduced hardness may be due to charge-charge repulsions during polymerization that reduce crosslinking. Spectroscopic evidence for reduced crosslinking of QA-SOMS is correlated with the appearance of a band at 890 cm^{-1} characteristic of Si-O with a non-bridging oxygen[25] and reduction in the shoulder at 1080 cm^{-1} of the primary Si-O-Si band (see Appendix C).

In addition to bulk organosilica materials, two types of adsorbents were created by coating silica with a sol-gel derived organosilica film. The materials were comprised of films made from BTEB (PHC-Silica) and films made of 0.87/0.13 mol ratio of **1**/**2**. Deposition was done by pour solutions of polymerized, but non-gel precursor solutions in acetone onto silica supports and then evaporating off the acetone at 80°C. The mass of the organosilica adsorbent coating was 0.8% of

the total mass. Despite the success of synthesizing coated-sand the PHC-Silica adsorbents were discontinued from further study due the small film thickness (~ 200 microns) limiting adsorption capacity (Appendix D).

The friability of QA-SOMS was predicted to limit full scale commercial production and usage of the adsorbent. Thus, alternative methods to add cationic groups to SOMS were explored. The ability of the cationic polymer **4** to remain encapsulated in **poly-SOMS** upon rinsing with water was tested. A sample of poly-SOMS was rinsed with 500 volumes of DI water over 20 min collecting the flow through. After drying, the mass of the poly-SOMS decreased 14±3% post water rinse. Confirmation via mass balance was achieved by evaporating the water to dryness and measuring the residue for polymer by gravimetry and FT-IR. The non-volatile residue was determined to be polymer equivalent to the mass lost upon rinsing. Poly-SOMS was hydrophilic prior to rinsing, however, the granular material became hydrophobic after rinsing. The data suggest that a minor fraction of the polymer remained on the surface during the swell-dry encapsulation process which was readily removed by water rinse. Remaining polymer appeared to be fully encapsulated and not removed by water rinse. Encapsulation was also verified by measuring the amount of polymer in poly-SOMS before and after use in column experiments using FT-IR. Recently, we have determined a method to permanently fix the polymer to make a stable poly-SOMS.

Notes about SOMS swelling and adsorption. The ability of SOMS to swell allows two distinct forms of the adsorbent: either an unwetted-unswollen form or material that is pre-swollen to expand the pores. Adsorption of PFAS by either unswollen or swollen SOMS was evaluated through batch equilibrium experiments starting with a concentration of C0=2,000 ug/L. It was found that when unswollen the adsorption of PFAS compounds >C4 was significantly reduced. For example, the extent of adsorption pf PFOA and PFOS after 14 hr using swollen-SOMS was 91%, respectively, compared to 29% and 8% if SOMS was unswollen (see Appendix D). In contrast, PFBA adsorption was higher when using unswollen SOMS: 46% removal vs. 0% removal when SOMS was swollen. The ability of unswollen SOMS to adsorb PFBA may be due to the adsorbate's smaller size which allows entry into the collapsed air filled pores of the hydrophobic SOMS matrix. Unswollen SOMS has previously shown good capacity to adsorb volatile organic solutes, including short chain carboxylate acids, from water.[26] For all subsequent experiments, SOMS and F-SOMS were pre-swollen prior to measurement of adsorption by adding a volume of ethanol just sufficient to open the pores and wet the interior surfaces. Absorbed ethanol was displaced by water by dilution when the material added to aqueous samples. After ethanol displacement the pores remain open. Pore collapse only occurs when capillary forces by entrained solvent constrict SOMS during evaporation.

5.2. Final characterization. Organosilica adsorbents were characterized by scanning electron microscopy (Appendix E), FT-IR, and porosimetry (Table 7). F-SOMS, which introduced 0.13 mol/mol of 2 relative to 1 which was used exclusively in previous work, had little impact on the microstructure. Both SOMS and F-SOMS swelled upon addition of acetone: 6.8 vs. 6.5 mL acetone/g adsorbent, respectively resulting in a 2.5x change in volume. In contrast, the surface area and pore volume of QA-SOMS was reduced (Table 2).

Table 7: Physical properties of adsorbents

Adsorbent	Description (Precursor)	Particle Size (μm)	BET Surface Area (m^2/g)	Pore Volume (mL/g)	Pore Diameter Distribution (%)			Swell* (mL/g)
					<6 nm	6-80 nm	>80 nm	
SOMS	swellable modified silica (**1**)	250-450	650	1.03	29	69	2	6.1
F-SOMS	fluoroalkyl modified (**1**, **2**)	250-450	660	1.04	30	69	1	6.6
QA-SOMS	quaternary amine modified (**1**, **3**)	50-150	500	0.60	71	26	3	6.3
poly-SOMS	entrapped cationic polymer (**4**)	250-450	155	0.21	35	63	1	6.1
GAC	Norit® 1240W	450-600	975	0.52	55	39	6	-
IEx	Dowex® Marathon™ MSA Cl	500-600	dry adsorbent non-porous					

* volume of liquid acetone absorbed per gram of sorbent.

Table 8. Second order rate constants for PFAS adsorption and the associated error.

	k_2 (g adsorbent/mgPFAS•hr)									
	ionic strength = 0 mM					ionic strength = 50 mM				
PFAS	**SOMS**	**F-SOMS**	**QA-SOMS**	**poly-SOMS**	**GAC**	**SOMS**	**F-SOMS**	**QA-SOMS**	**poly-SOMS**	**GAC**
PFDA	5.6±3.1	1.9±0.4	0.7±0.2	1.1±0.2	0.8±0.2	>20	19.0±1.2	5.3±0.2	1.2±0.3	1.4±0.5
PFNA	1.0±0.3	0.7±0.3	4.9±0.7	1.2±0.6	0.9±0.2	8.2±1.7	4.0±0.9	10.5±6.1	1.4±0.3	1.4±0.4
PFOA	10.4±3.8	6.9±1.8	2.5±1.0	1.1±0.3	1.6±0.7	6.5±1.8	>20	1.9±0.6	0.6±0.1	0.7±0.3
PFHpA	6.3±0.8	3.2±0.5	0.4±0.1	1.0±0.2	0.2±0.1	3.2±0.8	8.8±2.6	2.4±0.3	0.7±0.1	0.4±0.2
PFHxA	1.7±0.4	2.4±0.5	0.3±0.2	0.7±0.1	1.0±0.5	3.1±2.3	3.6±1.8	2.1±0.7	0.2±0.2	0.4±0.3
PFPeA	5.0±3.8	*no ads*	1.1±0.5	0.9±0.1	0.4±0.1	>20	*no ads*	0.8±0.1	1.3±0.2	0.6±0.2
PFBA	*no ads*	*no ads*	1.0±0.5	1.0±0.1	0.7±0.1	*no ads*	*no ads*	0.7±0.3	2.2±0.2	0.8±0.3
PFOS	7.8±6.5	5.9±0.6	>20	1.9±0.1	0.2±0.1	14±0.8	26.3±3.5	20	3.1±0.7	22±7.6
PFHxS	4.0±2.2	2.4±0.7	>20	0.7±0.1	0.1±0.01	>20	8.7±1.0	16±3	0.9±0.3	10±0.1
PFBS	11±30	*no ads*	*n/m*	0.1±0.1	0.1±0.04	>20	*no ads*	*n/m*	0.7±0.2	0.6±0.2
PFOSA	5.2±1.3	2.6±1.3	>20	5.6±1.8	0.6±0.3	3.9±1.3	6.3±2.6	20	2.3±0.4	0.4±0.2
PFOSaAm	1.9±1.0	0.2±0.3	>20	1.1±0.6	0.3±0.06	20±0.3	0.3±0.1	12±3	1.6±0.2	1.4±0.4

5.3. Adsorption Kinetics. The rate of adsorption of individual PFAS solutes was measured by batch depletion experiments at pH 6.6. The adsorption kinetics for PFOA (Fig. 3) were typical where SOMS materials had a faster rate of adsorption compared to GAC. Adsorption to QA-SOMS was the most rapid, however, the particle size of the material was much smaller and cannot be directly compared. Most of the kinetic data fit well to a pseudo-second order rate equation to calculate k_2. Overall, the rate of adsorption to SOMS and F-SOMS were 3-10x faster compared to poly-SOMS or GAC. (Table 8, see Appendix F for complete data sets). Faster rates of adsorption to SOMS is attributed to the open swollen pore structure. In contrast, adsorption to poly-SOMS was slower, presumably since it was a porous matrix collapsed around polymer. The rate of adsorption to poly-SOMS was generally constant across the range of PFAS compounds regardless of chain length suggesting that diffusion into the polymer filled pores does not depend strongly on PFAS size. For SOMS and F-SOMS, a reduction in adsorption rate for longer-chain compounds was observed, with a 10-fold reduction in adsorption rate for PFNA relative to PFOA.

Increasing the ionic strength led to and an approximately 2-fold increase in the rate of adsorption of PFAS solutes to SOMS and F-SOMS (Table 8). Ionic strength had little impact on the rate of adsorption to poly-SOMS or GAC, with the exception of PFOS adsorption which was more rapid in the presence of 50 mM NaCl. Overall, the kinetic data indicate that there may be distinct differences in the barriers to mass transport and/or adsorption mechanisms depending on adsorbent type. Adsorption to SOMS and F-SOMS appears to be facilitated by the open pore system via hydrophobic interactions since minimal adsorption of short -chain PFAS was observed.

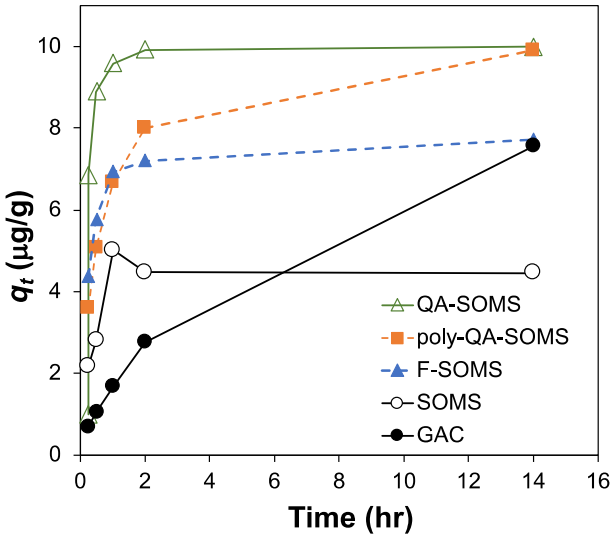


Fig 3. Adsorption kinetics of PFOA uptake using SOMS (○); F-SOMS (▲); QA-SOMS (△); poly-SOMS (■); and GAC (●). Dosage 200 mg/L, temperature 25°C, constant agitation, DI water.

The affinity of PFAS adsorption, as measured by the adsorption capacity at equilibrium (q_e), varied depending on the adsorbent (Appendix F). Hydrophobic adsorbents SOMS and F-SOMS showed negligible adsorption of short-chain PFAS solutes including PFBS and PFBA suggesting that the degree of affinity between the fluoroalkyl groups and the adsorbent is too weak. The presence of fluoroalkyl groups in F-SOMS did not lead to a substantial increase in affinity of

other PFAS solutes compared to SOMS putting into question the hypothesized improvement of affinity due to specific interactions with fluoroalkyl groups.

GAC and poly-SOMS showed broad effectiveness to adsorb PFAS compounds regardless of chain length and polar group. Poly-SOMS had the highest affinity demonstrating near complete removal of all PFAS solutes except for the cationic PFOSaAm compound which was presumably hindered due to like-charge repulsion. Elevated ionic strength had a deleterious impact on the adsorption of shorter chain compounds to poly-SOMS including PFBA, PFBS, and PFPeA. Overall, GAC, and in particular poly-SOMS, show consistent performance in term of adsorption rate and capacity for a wide range of PFAS solutes.

5.4. Adsorption Isotherms. Individual adsorption isotherms for all 12 PFAS compounds binding to SOMS, F-SOMS, poly-SOMS, and GAC were measured at ionic strengths of 0 mM and 50 mM NaCl, pH 6.6. Poly-SOMS was found to have on average the highest capacity across the set of PFAS solutes tested (Fig. 4 for representative compounds PFBA, PFBS, PFOS, PFOS; Appendix G.). Adsorption isotherms for poly-SOMS typically did not reach saturation under the conditions tested. The lack of saturation in the adsorption to poly-SOMS was unusual given that the pore volume of 0.21 mL/g was the lowest for all the adsorbents (Table 7). It is hypothesized that swelling of poly-SOMS induced by adsorption of PFAS provides a mechanism to generate additional pore volume.

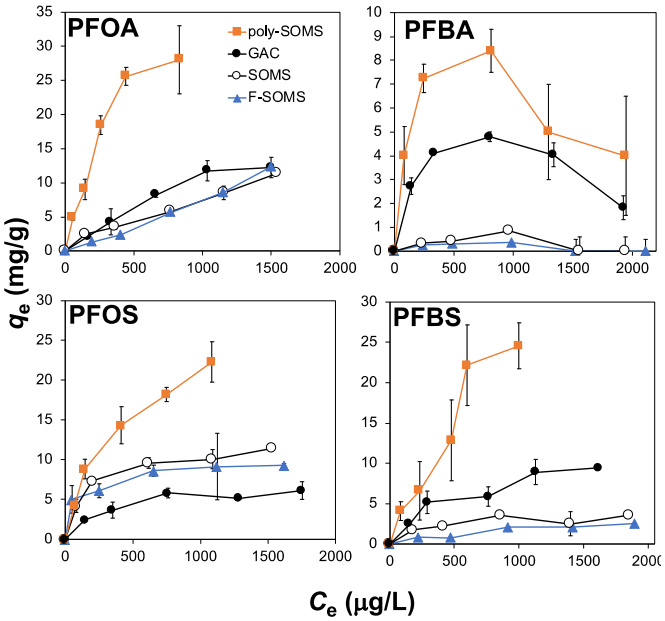


Fig 4. Adsorption isotherms for PFBA, PFBS, PFOA, and PFOS to SOMS (○); F-SOMS (▲); poly-SOMS (■); and GAC (●). Dosage: 40 mg/L, 14 hr contact time, constant agitation, DI water.

PFBA yielded isotherms that differed from other PFAS solutes (Fig. 4). First, adsorption to SOMS and F-SOMS was minimal, as also observed in the kinetics measurements. Second, adsorption of PFBA to poly-SOMS and GAC from DI water reaches a maximum and then decreases at higher concentrations. The unusual shape of the isotherm may be due to the substantial fraction of PFBA in solution altering the equilibrium for adsorption. Such behaviour

may be important in understanding the challenges in removing PFBA from water. A standard isotherm for PFBA was observed at elevated ionic strength (see Appendix G).

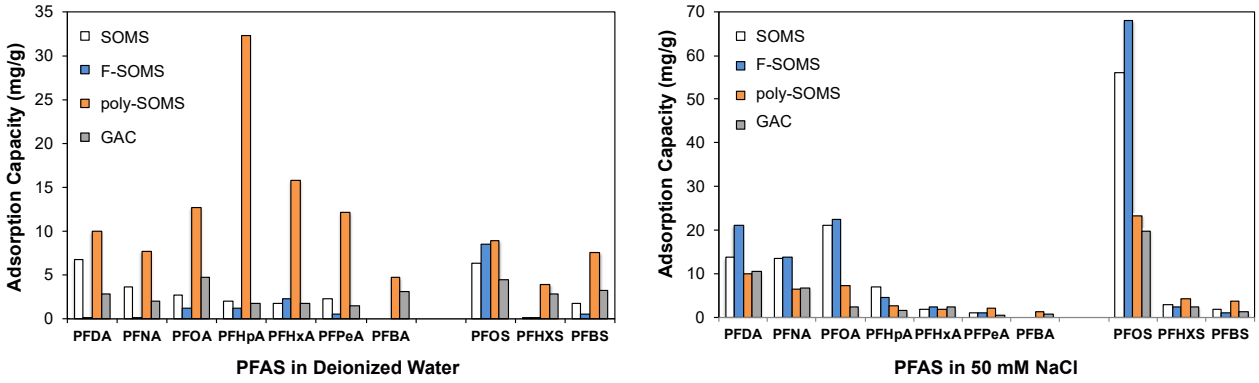


Fig 5. Adsorption capacities for anionic PFAS by organosilica compounds and GAC in DI water (*left*) and 50 mM NaCl (*right*). Error ± 6%.

Adsorption isotherms were fit to the Freundlich isotherm (for complete data set see Appendix G). Based on the fitted equations to the Freundlich model, capacity at C_e = 200 µg/L was calculated (Fig. 5). The C_e value was selected because the concentration is near environmental relevance and was within the measured equilibrium concentration range of all data sets. Several notable results were observed. Both poly-SOMS and GAC showed broad adsorption performance across the entire set of PFAS. Poly-SOMS generally had 2-5x the capacity compared to GAC at equilibrium and was the best performing adsorbent in DI water reaching a maximum adsorption capacity of 22.8±0.6 mg/g for PFHxA. In contrast, SOMS and F-SOMS were less effective in adsorbing short-chain PFAS compounds from DI water indicative that interactions with the fluoroalkyl group are insufficient to provide removal when the chain length is smaller. Thus, the hypothesis that the introduction of fluoroalkyl groups would increase affinity of PFAS adsorption is not supported by the data. In general, F-SOMS and SOMS have similar capacity for each individual PFAS compound. Hydrophobic surfaces appear to be sufficient to promote adsorption of long-chain PFAS compounds regardless of surface composition assuming the fluoroalkyl groups added by co-polymerization are accessible to make adsorbate interactions. These results differ from previous reports where organofluorine modified adsorbents[33] have demonstrated better performance to the adsorption of PFOA and PFOS. What is unknown is whether modification with fluoroalkyl groups leads to greater selectivity in adsorption of PFAS compounds in mixtures with non-fluorinated organic solutes. Selectivity will be tested in the future to fully understand whether there are benefits to creating fluoroalkyl-modified adsorbents.

Addition of fluoroalkyl groups to SOMS was further explored by varying the amount of fluoroalkyl content by varying the relative amounts of precursor **1** to **2** from 0-0.47 mol/mol **2**. The BET surface area, pore volume, and capacity to adsorb PFOS were measured (see supplementary information Table S8). Results show that the affinity of PFOS remains constant for mole fractions of **2** between 0-0.13 mol/mol. As the fraction of fluoroalkyl precursor increases beyond 0.13 mol/mol, PFOS capacity decreases with a concomitant decrease in surface area and pore volume of the adsorbent. These data suggest that a more open pore structure provides for additional capacity. The material prepared with 0.13 mol/mol **2** was chosen as F-

SOMS since the surface area, pore volume, and swelling was equivalent to SOMS while possessing the maximum amount of fluoroalkyl groups.

The adsorption capacity of neutral and cationic PFAS solutes was also evaluated. GAC and poly-SOMS yielded capacities equivalent to short chain anionic PFAS (Table 9). Adsorption capacity of poly-SOMS for the cationic PFOSaAm was measurable, but lower than any other PFAS including PFBA. Adsorption of PFOSA and PFOSaAm by SOMS and F-SOMS was substantial. F-SOMS had adsorption capacity at C_e = 200 µg/L of >30 mg/g for both compounds. F-SOMS showed a 2-fold increase in capacity for PFOSA over SOMS (35 vs 17 mg PFOSA/g adsorbent). As a result, there may be improved affinity upon the addition of fluoroalkyl groups in the absence of adsorbate charge.

Table 9: Adsorption capacity for neural and cationic PFAS.

PFAS	Adsorbent	Capacity (mg/g) *Ce* = 200 µg/L*
PFOSA	SOMS	17.7
(neutral)	F-SOMS	34.9
	poly-SOMS	8.8
	GAC	5.1
PFOSaAm	SOMS	35.5
(cationic)	F-SOMS	36.7
	poly-SOMS	2.0
	GAC	4.9

*Error ± 5%. Dosage: 40 mg/L, 14 hr contact time.

Ionic strength was varied to determine the effect on adsorption. Under conditions of elevated ionic strength (50 mM NaCl) SOMS and F-SOMS had enhanced adsorption capacity for PFOA and especially PFOS (Fig 5). For example, adsorption capacity of PFOS was 67±3 mg/g adsorbed to F-SOMS at C_e 200 = µg/L, which is 4x what was observed for GAC under the same conditions. Enhancement of adsorption of PFAS to hydrophobic SOMS in the presence of salt occurred for only longer-chain compounds ≥C7 and thus may be attributable to the "salting out effect" where the partitioning onto the adsorbent is enhanced in presence of dissolved ions because the water is more ordered and compressible and the cavity volume available to accommodate an in situ fluoroalkyl group is reduced.[54] Higher capacities observed for longer chain PFAS may also be due to enhancement of adsorbate-adsorbate interactions, with one explanation being that higher ionic strength screens ion-ion repulsions of the PFAS headgroups resulting in micelle formation once the concentration in the pores becomes high enough. When examining the effect of elevated ionic strength on the performance of GAC, addition of salt generally improves adsorption of longer-chain PFAS, but negatively impacts adsorption of short chain compounds such as PFBA. Reduction in adsorption of short-chain compounds suggests that the ability of GAC to adsorb PFAS made be due in part to ion exchange. The effect of ionic strength on the adsorption of poly-SOMS shows a strong dependence on the length of the PFAS chain length (Fig. 6). Adsorption isotherms for longer chain compounds such as PFDA, PFNA,

and PFOA show no dependence on ionic strength, suggesting that adsorption of poly-SOMS by these compounds is driven primarily by interactions of the fluoroalkyl groups with the sorbent and themselves via adsorbate-adsorbate interactions. In contrast, the addition of salt reduced affinity of short chain PFAS compounds to poly-SOMS, suggesting that ionic interactions with polymer quaternary amine groups may be the predominant interaction. Overall, the data suggest that successful adsorption of a wide range of PFAS compounds requires multiple types of interactions: ionic interactions to capture short chain compounds and hydrophobic interactions to promote association of long-chain compounds. Regardless of PFAS compound, poly-SOMS yielded higher capacity than carbon at either ionic strength condition.

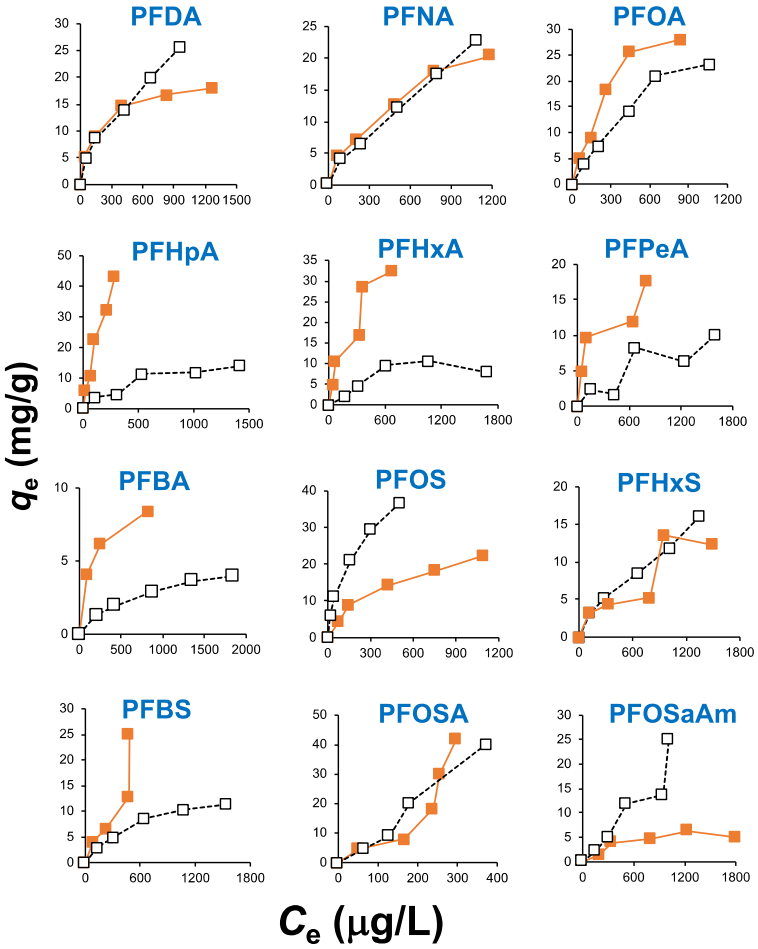


Fig 6. Adsorption isotherms of PFAS solutes to poly-SOMS in DI water (■) and 50 mM NaCl (□).

Modification of SOMS by the addition of fluoroalkyl groups or quaternary amine groups was useful in that the effects due to differences of surface chemistry could be evaluated independently of morphology by using an equivalent organosilica scaffold with similar pore structure. The pores can be expanded by swelling which presumably aids mass transport further reducing differences in adsorption to changes in pore size. Longer-chain PFAS compounds were adsorbed to hydrophobic SOMS. Adsorption of the full range of anionic PFAS of all chain lengths appears to require adsorbents that are hydrophobic and possess cationic groups. GAC was generally effective across the full range of PFAS compounds suggesting that the surface is also heterogeneous (hydrophobic, ionic) and/or that smaller pores assist in adsorption of short-chain PFAS.

5.5 Bench-Scale Column Experiments. Adsorption isotherms showed that F-SOMS and poly-SOMS were the two adsorbents with highest capacity and where selected for further experiments. Here, performance was compared to GAC and IEx resins. In addition, the swelling state of poly-SOMS was also evaluated for the first time. Three type of column experiments were performed:

Table 10: Column experiment parameters.

Column Experiment	PFAS analyte(s)	PFAS concentration	Water Matrix
Single PFAS	Single PFAS	200 µg/L	DI water
Mixed PFAS	12 PFAS analytes	200 µg/L each	DI water
Groundwater	12 PFAS analytes	1-2 µg/L each	Simulated groundwater

Single PFAS columns were used to evaluate the relative capacity of individual PFAS analytes to a specific resin. A concentration of 200 µg/L (ppb) was selected as it was high enough to make measurements by direct injection while still being environmentally relevant.

Mixed PFAS columns were used to evaluate performance for a suite of analytes in tandem. Data could be sued to evaluate relative breakthrough volumes. A mixture is environmentally relevant and a concentration of 200 µg/L was again chosen (well below critical micelle concentration).

Groundwater columns were the most comparable to actual field conditions in that they had dissolved solids and concentration in the low ppb. Water was either provided from Willow Grove or was simulated in the lab. Lab simulated water used PFAS concentrations of 2 µg/L or less. Samples were evaluated using solid phase extraction to achieve detect limits around 2 ng/L. Humic acid was used as NOM in simulated water.

Note: A white paper was drafted by the PI discussing how bench-scale testing of adsorbents could be harmonized so that data across projects can be cross-compared. The white paper is provided in Appendix H.

5.5.1 Single PFAS Columns. Granular adsorbents were packed into beds and used to treat water containing PFAS compounds to evaluate treatment performance. Single component solutions were applied to F-SOMS, poly-SOMS, and GAC at an effluent concentration of C_0 = 200 µg/L. Single PFAS compounds were tested to evaluate how equilibrium adsorption isotherms match data obtained from column experiments where the contact time is significantly shorter (see Appendix I for breakthrough curves). For all PFAS compounds tested (PFOS, PFOA, and PFBA) SOMS, F-SOMS, and GAC demonstrated a capacity at breakthrough that was less than the equilibrium capacity at C_e=200 µg/L (Fig 5 vs. Table 11). For example, F-SOMS had a capacity of 0.7 mg PFOS/g at column breakthrough $C_{effluent}$ = 40 µg/L vs. 8.5 mg PFOS/g at C_e =200 µg/L as measured using an adsorption isotherm. The comparatively lower capacity at breakthrough is expected since the breakthrough point was determined when the effluent is 5x lower than 200 µg/L (i.e. pre-equilibrium). In addition, and the contact time on the column was less compared to batch experiments used to measure the isotherm (2 min vs 14 hr). Interestingly, the capacity values at column breakthrough for poly-SOMS were much higher and exceeded the capacity as measured for C_e=200 µg/L using the adsorption isotherm. For example, 47 mg PFOA/g was adsorbed at the

breakthrough concentration of $C/C_0 < 0.2$ (40 ug/L) as compared to 12 ± 1 mg/g at C_e=200 µg/L on the isotherm. A possible explanation for the higher adsorption capacity of poly-SOMS during continuous long-term flow is that 14 hr was insufficient for equilibrium to be established in batch experiments. It is hypothesized that during the time of column flow, PFOA was strongly adsorbed to poly-SOMS and able to diffuse into the polymer filled pores. Due to the process of inward diffusion, the PFAS adsorbates may become deeply sequestered. Swelling may also contribute to the increased capacity in continuous flow experiments where adsorption may have triggered matrix expansion and addition sites to adsorb PFOA (see below, mechanisms). The increase in capacity for PFAS removal under continuous flow is fortuitous since using a granular media bed is the practical way such material would be used for treatment.

Table 11: Adsorption capacity at breakthrough for PFOA, PFOS, and PFBA, C_0= 200 µg/L

	Capacity at Breakthrough (mg/g)				
	Matrix: DI water			Matrix: 50 mM NaCl	
PFAS	F-SOMS	poly-SOMS	GAC	F-SOMS	GAC
PFOS	0.7	78	2.2	14.2	0.5
PFOA	0.9	36	1.5	9.9	0.5
PFBA	0	11	0.1	n/m	n/m

Overall, poly-SOMS showed significantly higher capacity for PFAS compared to GAC. F-SOMS only showed performance gains relative to GAC at elevated ionic strength.

5.5.2 Mixed PFAS Columns. A mixture of all 12 PFAS compounds (C_0=200 µg/L each) was applied to a poly-SOMS column in order to test the removal of in the presence of co-solutes. Breakthrough for each PFAS compound was distinct for each substance with shorter chain compounds (ex. PBFA) eluting first (Fig. 7A) similar to results seem previously for GAC and ion exchange resins.[13] Interestingly, the poly-SOMS showed a temporary improvement in treatment performance after 15,000 applied bed volumes resulting in a dip in the breakthrough curve. The cause of the temporary increase in PFAS affinity is unknown, but may a manifestation of adsorbate-induced swelling. (Note: Backpressure increased 5-10% during the course of the experiment which may be a manifestation of loss of intra-particle bed volume.) After 65,000 applied bed volumes 11/12 PFAS compounds had reached breakthrough. Neutral PFOSA was still being fully removed and long-chain PFDA and PFOS compounds also showed strong removal at the 65,000 bed-volume mark. Displacement of PFBA and PFPeA began to occur at the 50,000-bed volume mark at the time PFOA reached breakthrough. The contact time for all columns was 1 min. The total amount of adsorbed PFAS to poly-SOMS was 80 mg/g at 65,000 bed-volumes (mL/g).

Poly-SOMS was tested in both the dry unswollen form and the swollen state where the pores were open by pre-treatment with methanol (Fig 7B). The open pores allow for faster adsorption kinetics as demonstrated by the improved treatment efficiency and capacity. The total amount PFAS adsorbed to open poly-SOMS was 180 mg/g at 130,000 bed-volumes (mL/g).

GAC and IEx resin was tested in the equivalent conditions: 12 PFAS compounds C_0=200 µg/L each, contact time 1 min (Fig 7 C&D). Both GAC and IEx resin showed reduced kinetics compared

to poly-SOMS and especially open-poly-SOMS. Due to the reduced kinetics PFAS breakthrough C/C_0=0.2 happened relatively quickly compared to poly-SOMS. The total amount of PFAS bound to IEx resin was 57 mg/g.

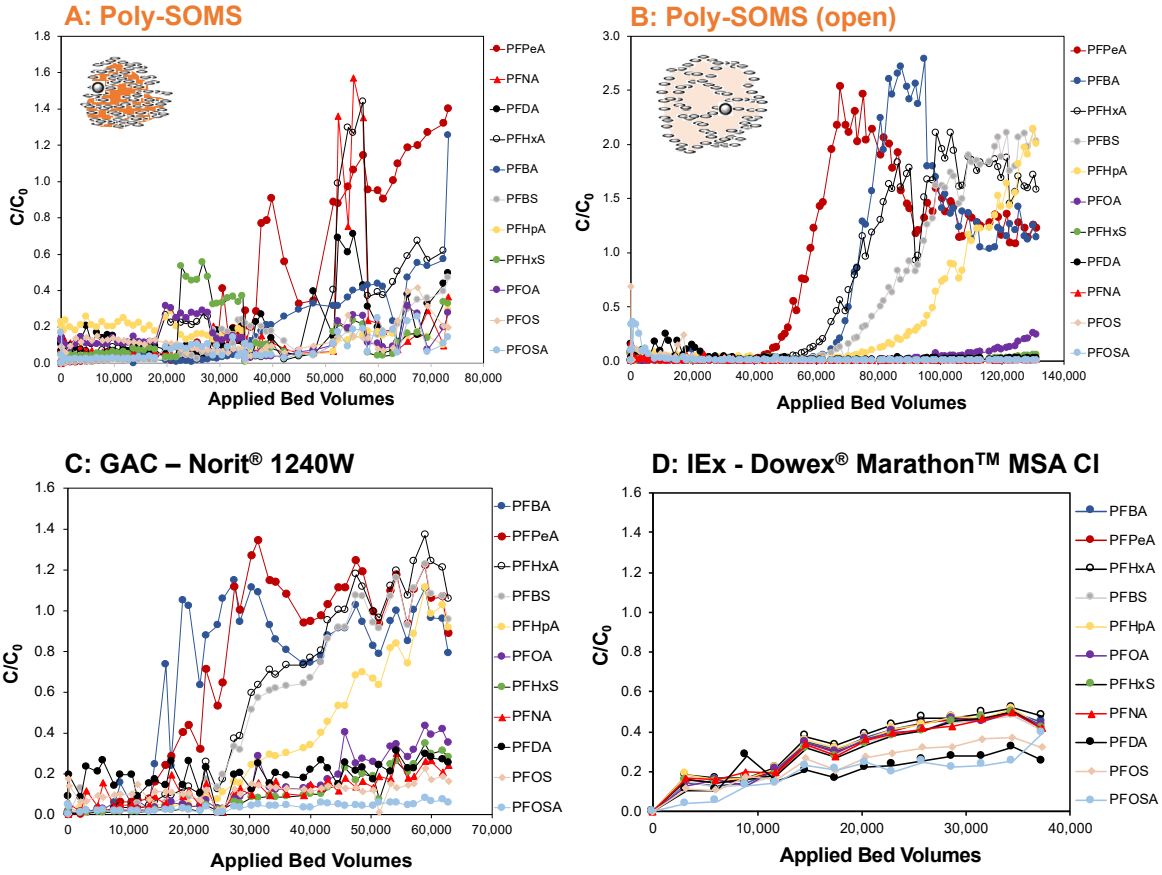


Fig 7: Mixed PFAS bench-scale column breakthrough curves for A: poly-SOMS; B: pore expanded poly-SOMS (open); C: GAC; and D: ion exchange (IEx) resin to 12 component PFAS mixture 200 μg/L each. Contact time: 1.0 min. Bed volume defined as mL applied volume per g of adsorbent. Temperature 25°C, deionized water matrix.

FT-IR spectrometry taken before use and after recovery of poly-SOMS from the column, determined that >85% of the initial polymer, **4**, remained after 65,000 bed volumes (Appendix J). The distinct amide band at 1650 cm^{-1} of **4** was used for quantitation. Loss in the polymer was likely due to rinsing off residues from the surface that was unentrapped during preparation. Recent work has led to a mechanism where polymer is not leached.

5.6 Adsorption mechanism: macro-aggregation. Scanning electron microscopy was used to examine poly-SOMS as synthesized compared to poly-SOMS recovered after application of 65,000 bed volumes of 200 ug/mL each PFAS as a mixture (Fig 8). Prior to treatment the surface of poly-SOMS generally resembled SOMS with a general morphology of interconnected organosilica colloids particles (Fig 8A). Polymer comprising 8% w/w of poly-SOMS may be evident by some of the pores being less distinct than SOMS (Fig. 2A). After PFAS adsorption the surface of the poly-SOMS particles was much smoother with >1μm globular structures adhering to various places on the surface (Fig 8B). It is presumed that these structures are comprised of

accumulated PFAS as there were no other solutes in the water. Similarly, macro-aggregates of PFAS have been observed by transmission electron microscopy in spent ion exchange resins.[17] Poly-SOMS particles were fractured by short duration grinding to expose the interior pore structures (Fig 8C&D). Electron microscopy revealed a generally similar pore morphology between as synthesized poly-SOMS versus resin removed from the column, although after PFAS adsorption appearance of residues in some regions was observed (Fig 8D). Based on the microscopy, there is evidence that PFAS accumulates at or near the surface of poly-SOMS in multi-layer or macro-aggregate structures. The hypothesis that swelling was involved in enhancing capacity was not supported by electron microscopy as the pore sizes are generally equivalent between fresh and used resin. Instead, capacity may be influenced by PFAS interacting with co-adsorbates. The displacement of short-chain PFBA during the mixed PFAS column experiment may be due to replacement of PFBA with a long-chain PFAS compound in regions of accumulated PFAS. This hypothesis will be further tested in future work.

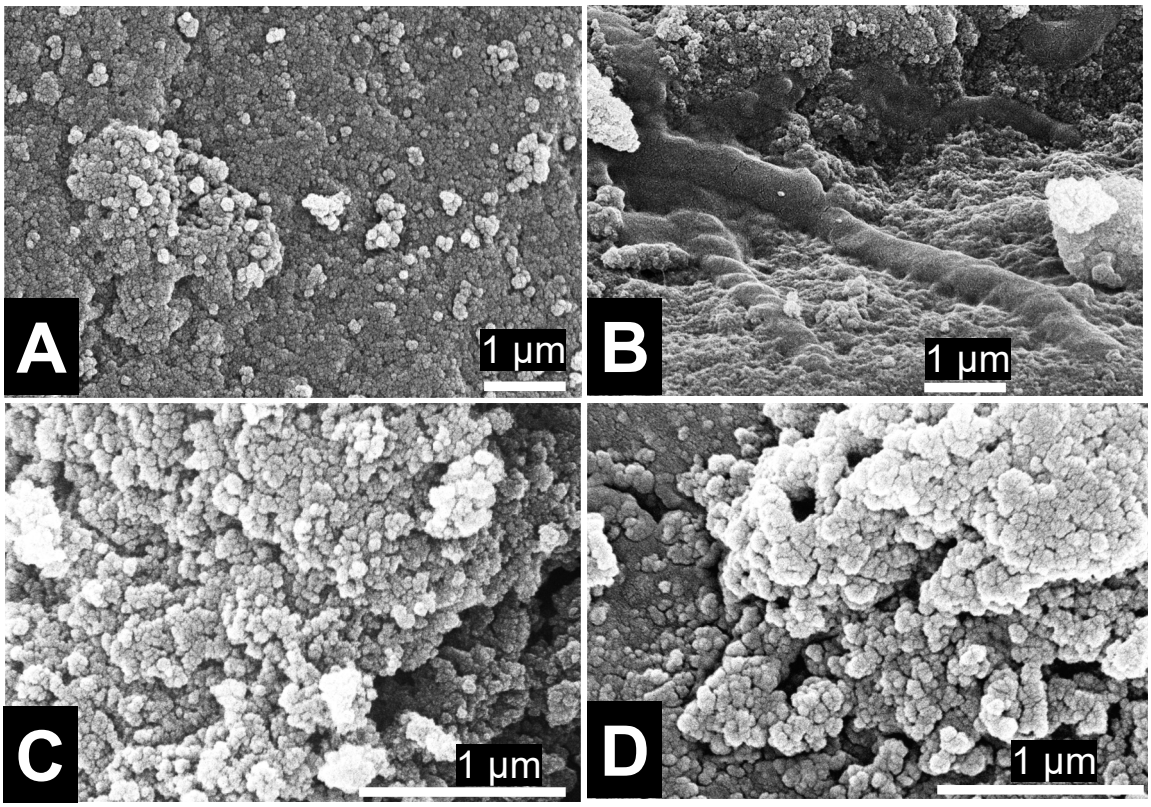


Fig. 8. SEM micrographs of poly-SOMS as synthesized (A &C) vs. after recovery from column mixed PFAS post-breakthrough (B & D). A &B are images of the surface of the adsorbent particles. C & D are the interior of the adsorbents accessed via grinding.

5.7 Treatment at low PFAS concentrations. Measurement of treatment performance at low PFAS concentrations was used to determine if SOMS-based adsorbent had sufficient affinity to achieve effluent <70 ng/L given an environmentally relevant input concentration of 2.0 µg/L. The breakthrough point (C/C_0=0.2) for 2.0 µg/L PFOS on a SOMS column with an ionic strength of 50 mM occurred at 12,000 column volumes (see supplementary information Table S9). The PFOS effluent concentration was 72 ng/L for SOMS and 37 ng/L for F-SOMS averaged over the

first 4,000 column volumes indicating that the fluoroalkyl-modified material may yield higher affinity at low concentrations. Overall, initial results show that SOMS materials have the capability to treat water to meet guidelines.

5.8 Simulated groundwater testing: Bench-scale (pre-pilot). Column testing was done with PFAS mixtures. Two tests were performed. First, water was sampled from Willow Grove and used for bench-scale column testing. The results were very good and demonstrated at large amounts of water (100 gallon) would be needed to do complete breakthrough studies, even with only using 2 grams of adsorbent. Thus, secondly, simulated groundwater was prepared spiked with ~1 µg/L of each PFAS analytes to run long-term breakthrough measurements. Humic acid (1.0 mg/L) was added to the simulated groundwater to provide a background of natural organic matter.

5.8.1 Bench-scale columns: Willow Grove water. Water was obtained from Former NAS JRB Willow Grove on February 18, 2019. 8x1L bottles were collected for adsorption isotherms and a 20L HDPE carboy was filled for column testing. Field sampling was done by professionals at Arcadis located in eastern PA. Testing began immediately upon arrival of the sample water.

F-SOMS and poly-SOMS were tested in column breakthrough experiments using granular material (~60 mesh, 0.25 mm diameter particles). The variables included type of media and contact time (Table 12, Appendix L) by changing the type and volume of the bed. Overall, good treatment performance was noted, with poly-SOMS having an expected better removal rate of the short PFAS solutes compared to F-SOMS (98.4% vs. 64%). Effluent can be treated to meet EPA guidelines when the contact time was 2.5 min (0.4 bed vol/min). Sufficient site water was collected to conduct an initial breakthrough study using poly-SOMS with a contact time of 1.0 min (i.e. 1.0 bed vol/min). A total of 11,000 bed volumes was applied. Treatment performance was generally good with C/C_0 at 0.1 after 11,000 bed volumes (Fig 9). There was a preference for perfluorinated sulfonates over carboxylates.

Displacement of PFHpA (which was at relatively lower concentrations) was observed. The mechanism of PFAS aggregation upon adsorption may explain this behavior as longer chain PFAS compounds with lower critical micelle concentrations "swap places" with previously adsorbed shorter chains. In experiments above, we observed that after sufficient numbers of longer chain PFAS compounds continue to adsorb, affinity for short-chain species is regained over time.

Adsorption isotherms and column experiments were used to test the effectiveness of treating site-water. Adsorption isotherms were measured for F-SOMS, poly-SOMS, and GAC (Appendix K). Isotherms were measured by adding increasing dosages of the adsorbent with a treatment time of 14 hr under agitation to ensure equilibrium. All adsorbents removed the PFAS solutes present at various extents. It was found that for GAC the percent removed remained fairly constant with increasing dosages. In contrast, organosilica adsorbents had overall better treatment effectiveness which further improved at higher dosages. Overall, the adsorption capacity for SOMS materials was about 2X compared to GAC.

Table 12: Lab-scale column treatment performance using Willow Grove site water.

Compound	Concentration (µg/L)			
	Site Water (Influent)	Effluent – Composite 0-1800 applied bed volumes (Percent Reduction)		
		F-SOMS (2 bed vol /min)	Poly-SOMS (2 bed vol/min)	Poly-SOMS (0.4 bed vol/min)
PFBS	0.96± 0.07	0.369 (61.7)	0.015 (98.4)	0.001 (99.8)
PFHxS	7.6± 0.3	0.280 (59.4)	0.140 (98.1)	<0.001 (99.99)
PFOS	40.7± 0.3	0.537 (98.7)	0.279 (99.3)	0.010 (99.9)
PFHpA	0.30 ± 0.01	0.040 (86.7)	0.020 (93.5)	0.002 (99.3)
PFOA	0.84± 0.5	0.050 (94.0)	0.053 (93.7)	0.004 (99.5)
Total PFOS + PFOA	42	0.588	0.332	0.014

Bed volume definitions: 2 bed volume per minute is 0.50 g of adsorbent at a flow rate of 1.0 mL/min (~0.5 min contact time) 0.4 bed volume per minute is 2.5 g of adsorbent at a flow rate of 1.0 mL/min (~2.5-3 min contact time)

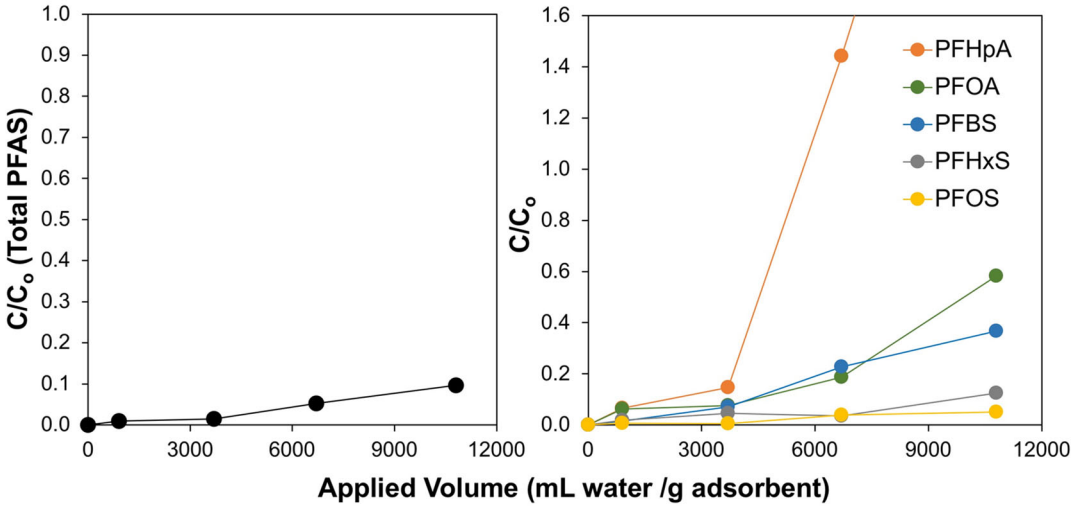


Fig 9: Breakthrough curve for site water using poly-SOMS at a flow rate of 2 bed volumes per minute. *Left.* Total PFAS concentration. *Right.* Breakthrough curves for individual PFAS analytes. Note: PFOS is the compound in highest concentration.

5.8.2 Bench-scale columns: simulated groundwater. Rapid small-scale column testing developed by Schaefer et al. was used to test adsorbents. Even with small scale testing, the volume of applied groundwater was estimated to be 200-500 L for 5 g columns of poly-SOMS, because of the high capacity of the adsorbent. As a result, we simulated groundwater from NAS JRB Willow Grove. Water was prepared in 15L batches and spiked from the same stock solutions. The PFAS concentration for each batch was measured to ensure consistency. Analytical measurements are made using the approved SOPs which use an individual mass labeled surrogate for each PFAS. A duplicate column of ion exchange media was run side-by-side with the poly-SOMS (Fig 10 A&B, see Appendix M for data).

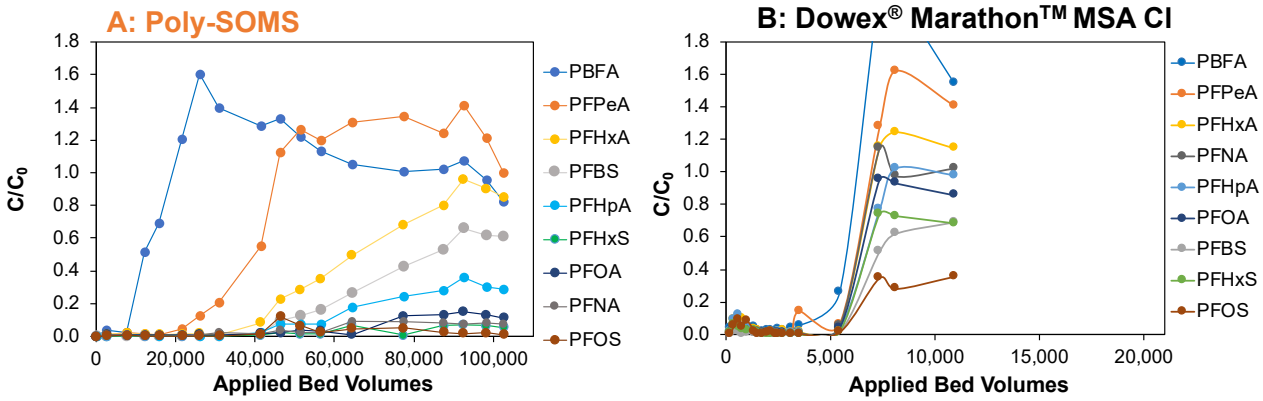


Fig 10. Lab-scale groundwater columns for A: poly-SOMS and B: IEx resin. Influent PFAS concentrations were 1 µg/L (1 ppb) for each PFAS analyte (see methods section). Contact time was 2 min. Water contained dissolved solids and 1 ppm humic acid. Bed volume defined as mL applied volume per g of adsorbent.

For ion exchange resin all the PFAS analytes broke through at the same time around 5,000 bed volumes. This suggests that binding to IEx may be due to charge-charge interactions and at breakthrough available ion exchange sites were filled and/or blocked by co-adsorption of humic acid. In contrast, for poly-SOMS breakthrough of short chain PFAS compounds occurred before longer chain species. In fact, PFOS and PFNA with poly-SOMS did not breakthrough even after 100,000 bed volumes. These data suggest that although poly-SOMS does contain numerous cationic sites the adsorption mechanism us different that Dowex IEx resin. It is hypothesized that the open and swellable pore structure of SOMS provides room for PFAS aggregation. Long chain PFAS more readily participate in aggregation and are strongly adsorbed, and in fact, may displace short chain adsorbates. This hypothesis is supported by SEM evidence for these aggregates (see above) and the fact that the number of PFAS adsorbates exceeds the number of theoretical cation exchange sites. Thus, poly-SOMS appears to provides a space for PFAS to "concentrate and self-assemble" where the cationic groups help thermodynamically to neutralize accumulated negative charge.

5.9 Pilot Test – Willow Grove. A 0.5 gpm side-stream pilot test system was designed and built for an installation Former Joint Reserve Base (JRB) Naval Air Station (NAS) Willow Grove. It was constructed with off-the shelf parts and was relatively simple in design (Appendix N). The pilot unit consisted of two media cartridges holding 0.5 kg of poly-SOMS (open) each. Flow rate and pressure was controlled by a pump in front of the media cartridges. A booster pimp was located after the cartridges to return effluent to the main line. After operating both cartridges for

a few days, one cartridge was removed to ensure pressure did not exceed tolerances. Afterwards, the system ran steady and uninterrupted for 26 days at a flow rate of 0.36 gal/min.

The pilot test was run stream system for 4 weeks with weekly sampling of influent and effluent. Water samples at weeks 2 and 4 were sent splits sent to Eurofins for 3rd party analysis. Eurofin 3rd party data has yet to be received. Samples were tested by HPLC-MS/MS and the TOP assay. The completed data set is located in Appendix O. Despite 0.5 kg treating over 18,000 gal of water over 28 days, poly-SOMS was still absorbing PFAS (Fig 11).

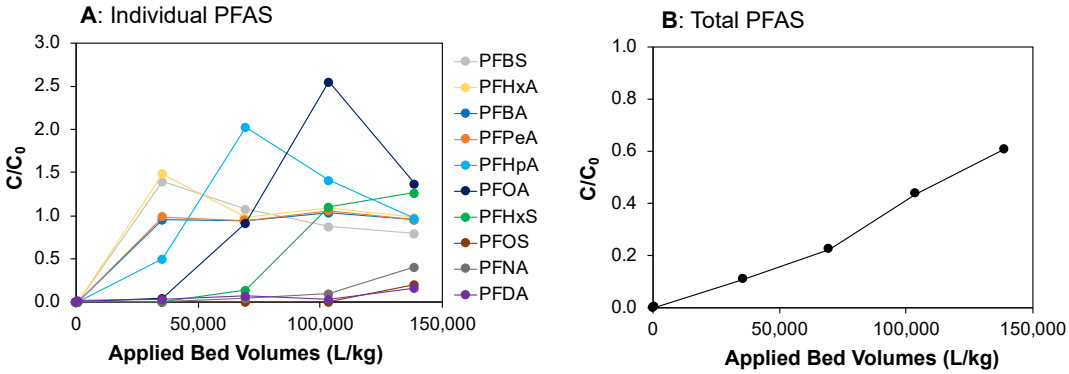


Fig 11. Breakthrough curves for PFAS during Willow Grove Pilot using poly-SOMS. A: Individual PFAS analytes. B: Total PFAS as measured by HPLC-MS/MS. Contact time: 1 min. Input PFAS concentration was ~40 µg/L.

Similar to the bench data, short chain PFAS break through before longer chain. Interestingly, PFOS removal was still >99% even after 100,000 column volumes demonstrating the affinity for longer chain PFAS. Contact time was 1 min so kinetics of adsorption were relatively fast. After 28 days of operation the loading of PFSA was 2.6 g/kg (2,600 µg/g), which compares favorably with other adsorbents.

5.10. Regeneration. Regeneration was tested using various solvents by placing 100 mg of SOMS or poly-SOMS in a solid-phase extraction cartridge. Next, 100 mL of a solution containing 11 PFAS analytes (200 µg/L each) was applied to the cartridge. The flow through was collected and the amount perfluorinated carboxylates and sulfonates were analyzed to determine the amount adsorbed. To test regeneration, 3 applications of 5 mL of solvent were then applied to the adsorbent in the cartridge, collected separately, and the PFAS solutes measured to determine the percent recovery by calculating the mass balance. The total desorbed mass was calculated.

Regeneration of SOMS was best achieved using 100% methanol or 80% methanol. Regeneration of poly-SOMS was best achieved with 80% methanol or 80% methanol containing 1M NaCl. One aspect of regenerating poly-SOMS is the potential that the solvent would swell the SOMS leading to the desorption of the encapsulated quaternary amine polymer. Polymer desorption was tested using UV spectrometry. It was found that 100% methanol rinse removed >50% of the encapsulated polymer from poly-Osorb during regeneration. Mixture of methanol water was determined to be an optimal rinse solvent to preserve polymer entrapment.

Regeneration of SOMS (open) and poly-SOMS was tested in a solid-phase extraction (SPE) experiment. First, 200 mg absorbent (SOMS or poly-SOMS) was added to an empty SPE cartridge. After conditioning, 100 mL of 100 ppb PFAS solution was passed through cartridge at

1 mL/min and the effluent collected. Removal efficiency was measured be comparing the influent and effluent concentrations.

After each adsorption run the media was regenerated with 3 x 5 mL rinses of regeneration fluid (methanol). Switch out falcon tubes and add another 5 mL regeneration fluid. The amount of PFAS desorbed was measured to complete the mass balance. The adsorbent was rinsed with water and a 100 mL aliquot of 50 ppb PFAS solution was applied. This process was repeated through multiple regeneration cycles measuring the ability to adsorb PFAS (Figs 12 & 13). See appendix P for data.

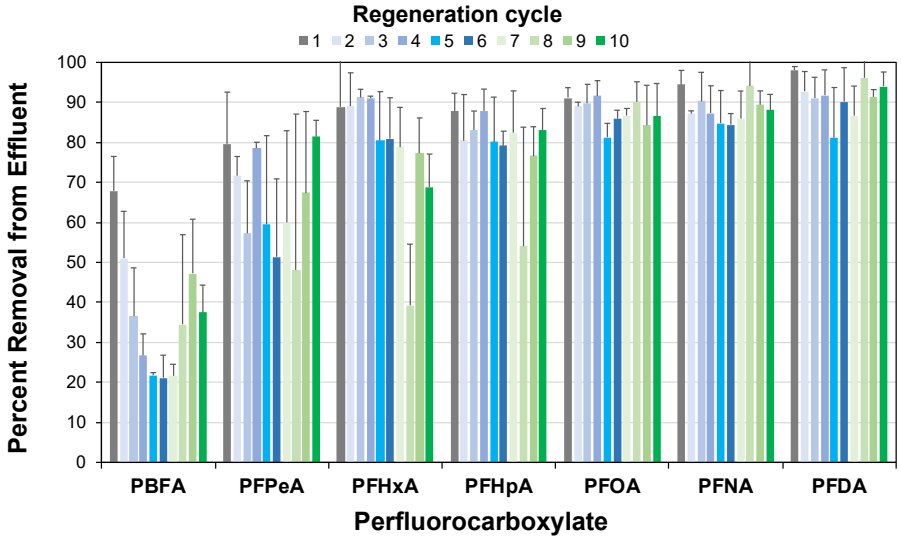


Fig 12. Percent PFAS removal vs. 10 regeneration cycles using **SOMS** adsorbent. PFAC concentration 50 μg/L each perfluorocarboxylate.

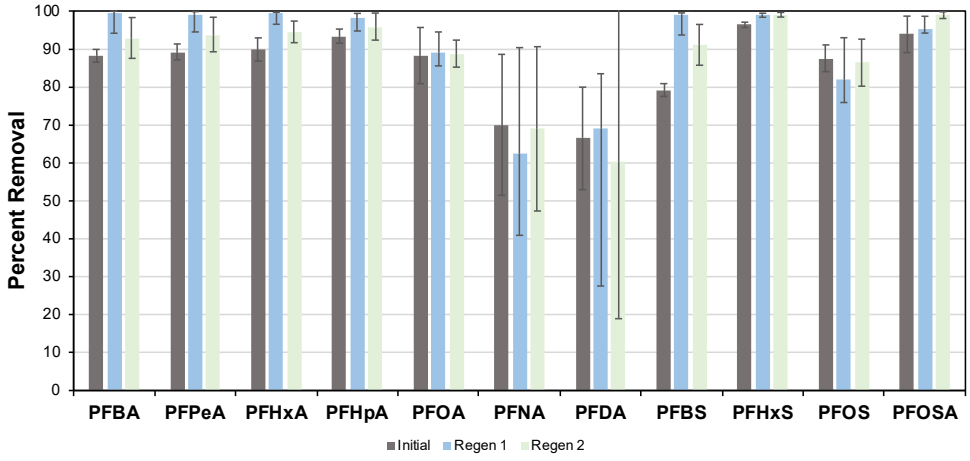


Fig 13. Percent PFAS removal vs. 2 regeneration cycles using poly-SOMS adsorbent. PFAS concentration 50 μg/L each perfluorocarboxylate.

6.0 CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH

Summary. PFAS adsorption was studied using organosilica adsorbents of well-defined composition and structure. It was found that PFAS adsorption is best facilitated by larges pores that are hydrophobic and contain cationic groups. The mechanism of adsorption is likely ion exchange and/or hydrophobic interactions which lead to subsequent self-assembly of PFAS compounds within the pores. The result is high capacity adsorbents. Poly-SOMS was found to be the material that has the highest adsorption.

Scale-up of poly-SOMS was demonstrated in this SEED project since SOMS is commercially available as Osorb®. As a result, larger-scale pilot testing can be envisioned immediately. It is hypothesized that poly-SOMS would be a high capacity adsorbent to compliment treatment trains or be useful adsorbent in other remediation options, especially those that require fast kinetics or extended capacity.

Observations during pilot test. Conducting in field tests is extremely useful in measuring performance and understanding practical aspects of real-world performance. By several measures the pilot testing was successful. However, two limitations were noted that could be addressed in future research.

Earlier breakthrough by short-chain PFAS. Short chain PFAS compounds are typically bind with lower affinity and capacity to adsorbents and similar behavior was seen with poly-SOMS. For instance, PFBA broke through after a few days whereas PFOS did significantly show breakthrough until after 3 weeks. Based on our current understanding of mechanism, it is seen that PFAS capacity is increased by self-association likely through interaction of the fluoroalkyl groups. Since PFBA has such a short fluoroalkyl group hydrophobic interaction and self-association modes of binding are limited. Thus, capture of short-chain PFAS must rely more in an ionic mode interaction with the adsorbent. Guided by this finding, we have an idea how to increase the charge density of the poly-SOMS to enhance short-chain PFAS adsorption.

Hydraulic performance of poly-SOMS. During the pilot test, approximately 90 psi of backpressure was observed across a 1 kg standard media canister. High pressure would not be suitable in scale-up operations, especially if higher pressures occur with larger bed sizes. Although hydraulic performance of regular SOMS is generally well understood and is suitable in larger systems, the bed characteristics of poly-SOMS are not well understood. There are notable differences between SOMS and poly SOMS: 1) poly-SOMS is “pre-expanded” to open the pore structure allowing for some degree of elastic deformation of the resin beads; and 2) poly-SOMS is filled with polymer that may lead to interparticle adhesion.

When the columns from the pilot test were returned to the laboratory they were carefully unpacked to examine the bed. It was found that the media was quite compacted in the plastic media canisters requiring significant “scraping” to dislodge. There was no evidence of preferred paths nor break-up of the particles as the particle size was unchanged by sieving. Given the ad hoc nature of the engineering it is anticipated that the pressure problem can be resolved by improved understanding of the properties and improved packing in a bed. It has been suggested that packing poly-SOMS in combination with sand would lead to increased void fraction and

decreased pressure drop. This could be systematically studied in the lab prior to further field testing.

Analytical capabilities. A question arose in review of the Final Report v1 if HPLC-QqQ provides sufficiently low limits-of-detection for PFAS measurement. The answer is yes. The MRLs reported in the Appendix are for the instrument and do not account for gains made in pre-concentration of analytes during solid-phase extraction. Given the excellent recovery via SPE (Appendix A) and concentration factor of 500-1000 our actual detection limits using SPE-HPCL-MS/MS (DoD QSM Table B-15) are 5-10 ng/L. In terms of reporting MRLs the methodology is much more sound testing standard solutions and measuring true instrument performance.

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Appendix
Final Report: ER18-1300

Removal of Complex Mixtures of Perfluoroalkyl Acids from Water Using Molecularly Engineered Coatings on Sand and Silica

Revision 1

PI: Paul L. Edmiston
The College of Wooster

Appendix A

Standard Operating Procedures v.3
ER18-1300: Removal of Complex Mixtures of Perfluoroalkyl Acids from Water Using Molecularly Engineered Coatings on Sand and Silica

This document provides the procedures and analytical methods used in the project ER18-1300. V.3 adds additional method information and responses to comments.

MATERIALS. Pure substances for batch adsorption tests and column are obtained from Sigma-Aldrich and used as received. Sulfonates were obtained as their sodium salts. Standards for analytical measurements and isotopic dilution are obtained from Wellington Labs.

Table 1: Analyte List (12 Compounds)

Analyte Name	**Acronym**	**CAS**
perfluorodecananoic acid, C_{10}	PFDA	375-95-1
perfluorononanoic acid, C_9	PFNA	335-67-1
perfluorooctanoic acid, C_8	PFOA	375-85-9
perfluoroheptanoic acid, C_7	PFHpA	307-24-4
perfluorohexanoic acid, C_6	PFHxA	2706-90-3
perfluorpentanoic acid, C_5	PFPeA	375-22-4
perfluorobutanoic acid, C_4	PFBA	375-95-1
perfluorooctanesulfonic acid, C_8	PFOS	1763-23-1
perfluorohexanesulfonic acid, C_6	PFHxS	355-46-4
Perfluorbuatanesulfonic acid, C_4	PFBS	375-73-5
perfluorooctanesulfonamide, C_8	PFOSA	754-91-6
perfluorooctane sulfonamide quaternary ammonium, C_8	PFOSaAm	13417-01-1

General Solution Preparation & Liquid Handling Procedures

PFAS SOLUTION PREPARATION. Pure substances are weighed and dissolved in methanol to create stock solutions of at least 2,000 ppm. Aqueous solutions are prepared by diluting the stock solution in water obtained from a Barnstead NANOpure DIamond Water Purification System verified to be free of PFASs by LC-MS. If necessary, the ionic strength can be adjusted with reagent grade NaCl. All aqueous solutions must be used with 24 hr of preparation. Standards for LC-MS are prepared in methanol and stored at 4°C in HPLC vials.

PFAS LIQUID HANDLING. All solutions are prepared in HDPE labware including volumetric flasks and bottles. Adsorption PFAS to HDPE labware was measured and found to be minimal with the HDPE containers obtained for the project. All adsorption measurements are conducted in HDPE containers. All labware is to be exclusive used for PFAS measurements.

Separating adsorbents from aqueous test solutions requires a physical means to remove adsorbent particles from solution. Filtration using syringe filters is a convenient method. However, adsorption to filters can lead to systematic errors. In order to evaluate the losses from filtration and create optimal SOPs, each analyte was evaluated to determine the % loss with either 0.44 um nylon, PTFE, or cellulose filters (Appendix I).

Based on findings, filtration with cellulose filters is acceptable for PFOS and PFHxS, and shorter chain perfluoroalkyl carboxylic acids: PFHxA, PFPeA, PFBA. For all other PFASs, centrifugation of the solution must be used to separate adsorbent from water in place of filtration. Nylon or PTFE filtration cannot be used in any instance.

Experimental Procedures to Evaluate PFAS Adsorption

A. Adsorption Kinetics

1. 100 mg of adsorbent is added to a 1L HDPE bottle.
2. Organosilica adsorbents are swollen with 100-200 uL of ethanol.
3. 500 mL of 2,000 ppb solution of a PFAS is added and the solution agitated on a platform shaker. Two ionic strength conditions are: 0 mM (DI water) and 50 mM NaCl. pH can be carried with addition of HCl
4. A control comprising a 500 mL of PFAS solution in HDPE bottles, but no adsorbent is also prepared and agitated on a platform shaker.
5. 2 mL aliquots are removed from both the control bottle and bottle with adsorbent at time = 0, 15, 30, 60, 120, and 840 min and either filtered with cellulose filters (see above) or centrifuged.
6. The concentration of PFAS is measured by LC-MS. If the measurement is to be conducted within 4 hr of sampling, the aqueous aliquot can be added to an HPLC vial and promptly measured. If the LC-MS assay is to be done >4 hr after sampling, the aqueous aliquot is diluted 1:1 with methanol and measured to prevent losses upon adsorption to glass HPLC vials.
7. Reduction is calculated relative to C_0 taken from the control.

B. Adsorption Isotherms

1. 100 mg of adsorbent are added to a 1L HDPE bottle.
2. Organosilica adsorbents are swollen with 100-200 uL of ethanol.
3. 500 mL of 2,000, 1,500, 1,000, 500, or 250 ppb (μg/L) PFAS solution is added to the bottle at either and the solution agitated on a platform shaker for 20 hr. Controls where the same solution is shaken in a HDPE bottle without adsorbent.
4. Aliquots are filtered or centrifuged depending on the identity of the
5. The concentration of PFAS is measured by LC-MS. If the measurement is to be conducted within 4 hr of sampling, the aqueous aliquot can be added to an HPLC vial and promptly measured. If the LC-MS assay is to be done >4 hr after sampling, the aqueous aliquot is diluted 1:1 with methanol and measured to prevent losses upon adsorption to glass HPLC vials.
6. Adsorption capacity is calculated from the reduction from C_0 measured from controls without added adsorbent.

Lab-Scale Column Experiments

Equipment. Continuous flow column experiments are conducted using medium pressure Pharmacia FPLC systems using P-500 pumps allowing flow rates between 0.1-10 mL/min. The pumps are solvent resistant reciprocal piston pumps. All tubing is polyethylene. Adsorbents are housed Pharmacia XK16 glass/polyamide-polyethylene medium pressure columns. Effluent is collected in 15 mL polyethethylene tubes using a Pharmacia fraction collector. Four separate column scale systems are used: (3) for experiment where PFASs influents are 2,000 ppb and (1) for water with influents are 2 ppb or less.

Breakthrough measurements: influent = 200 ppb

1. 500 mg of adsorbent is loaded in to a XK16 column (~2 mL bed volume).
2. Ethanol is added (~1 mL) to the organosilica to induce swelling.
3. Columns are flushed with at least 10 bed volumes of DI water.
4. Water with 2,000 ppb is applied at 10 mL/min.
5. Effluent fractions are continuously collected. Influent concentration (C_0) is sampled and measured after every 2-3L of applied PFAS solution to validate the concentration.
6. The concentration of PFAS in aliquots of effluent is measured by LC-MS. If the measurement is to be conducted within 4 hr of sampling, the aqueous aliquot can be added to an HPLC vial and promptly measured. If the LC-MS assay is to be done >4 hr after sampling, the aqueous aliquot is diluted 1:1 with methanol and measured to prevent losses upon adsorption to glass HPLC vials.
7. The column is run until adsorbents reach breakthrough.
8. The columns is cleaned with ethanol after use.

Breakthrough measurements: influent = 2 ppb

1. 500 mg of adsorbent is loaded in to a XK16 column (~3-5 mL bed volume).
2. Ethanol is added (~1 mL) to the organosilica to induce swelling.
3. Columns are flushed with at least 10 bed volumes of DI water.
4. Water with 2 ppb is applied at 10 mL/min.
5. Effluent fractions are continuously collected. Influent concentration (C_0) is sampled measured after every 2-3L of applied PFAS solution to validate the concentration.
6. Aliquots of effluent are collected and concentrated using solid-phase extraction. At least 100 mL of effluent is applied to an Oasis HLB 300 mg solid phase extraction cartridge pre-conditioned by rinsing with 3 mL of methanol and 15 mL of NanoPure water. PFASs are eluted from the column using 5 mL methanol into polyethene tubes. The methanol is evaporated under nitrogen stream and the sample reconstituted in 1 mL of methanol prior to measurement by LC-MS.

Regeneration Experiments

Solvent regeneration procedure

1. 200 mg of adsorbent is loaded in to solid-phase extraction cartridge and pre-wetted/expanded with 5 mL ethanol followed by 20 mL of water.
2. Exactly 100 mL of a solution containing 200 ppb of all 12 PFAS analytes is applied and all the effluent is collected. The concentration pre- and post- application is measured to determine the amount adsorbed. Effluent through a blank cartridge is measured as a control.
3. Regeneration solvent (5mL) is applied and the solution collected and PFAS measured. A mass balance is made to calculate the % adsorbed that was eluted.
4. The adsorbent is flushed with 20 mL of water and steps 2-3 are repeated at least 5 times to measure amount of adsorption and the amount regenerated.

Analytical Methods

EQUIPMENT. All measurements are made using an Agilent 1200/6410 HPLC-MS/MS(QqQ) using a dedicated InfinityLab Poroshell 120 EC-C18, 2.1 x 100 mm, 2.7 μm column. PEEK tubing is used for solvent flow.

Table 2: HPLC Parameters

Mobile phases	A: water + 5 mM ammonium acetate B: 95% methanol + 5 mM ammonium acetate
Flow rate	0.300 mL/min
Injection volume	5 μL
Column temperature	35°C

ANALYTICAL METHOD 1: Measurement of Single Compounds by Direct Injection
Measurement of PFAS concentration is measured with this method when conducting adsorption kinetics, isotherms, and column experiments performed using single a PFAS solution with concentrations > 2 μg/L. All samples tested in this protocol are laboratory prepared with a known starting concentration. Isotope dilution is not used.

MOBILE PHASE COMPOSITIONS AND MS/MS PARAMETERS. Isocratic HPLC-MS/MS methods were developed that would quantitate a single PFAS for these experiments with direct. The MRM transitions, MS settings and mobile phase compositions are given in Table 3.

Table 3: Optimized MS(QqQ) Parameters

Compound	**MRM Transition (*m/z*)**		**MS Voltages**		**Mobile Phase**	
	precursor	product(s)	Fragmentor	CE	A%	B%
PFBA	213	168.9	50	8	70	30
PFPeA	263	218.9	60	8	53	47
PFHpA	362.9	319	72	0	37	63
		169		12		
PFHxA	313	268.9	70	8	44	56
		119		18		
PFOA	413	369	69	4	30	70
		169		12		
		80		41		
PFNA	462.96	419	80	9	27	73
PFDA	513	469	69	8	23	77
		218.7	100	16		
		219	80	13		
PFHxS	398.9	99	90	75	36	64
		80		41		
PFBS	298.9	98.9	69	32	52	48
		79.9		44		
PFOS	498.9	99	100	50	27	73
		80				
PFOSA	497.9	77.9	69	40	21	79
		47.9	100	100		
PFOSaAm	599	SIM	135		23	77

CALIBRATION. Calibration curves are measured for each compound using a 17-point curve with standard solution concentrations ranging between 0.75-10,000 μg/L. Calibration solutions are measured in triplicate. Calibration curve are re-measured each time there is a significant change in instrument parameters, MS tune, or preventative maintenance done.

CALIBRATION ACCEPTANCE CRITERIA: The RSD of the response factors for all analytes must be ≤20% or the linear or non-linear calibration curve must have r2 ≥ 0.99 for each analyte.

SECOND SOURCE CALIBRATION VERIFICATION: A second standard will be prepared from a primary weighed sample or documented vendor provided solution. Vendors include Sigma-Aldrich, Wellington, and Absolute Standards.

CALIBRATION VERIFICATION: A continuing calibration which is a triplicate injection of a standard which is compared to a working calibration curve. Verification is done with each set of 20 samples. Analyte concentrations must be within ±30%. Retention times must be ±0.4 minutes of their expected times.

BLANKS AND CONTROLS: A laboratory reagent blank is run before each set of samples and several times during each daily worklist. Blanks must have responses ≤0.5 the LOQ. A laboratory control is run with each sample sub-set or experimental method (one control per 5 samples).

LOQ VERIFICATION: Prior to every set of samples, standards at the LOQ will be measured and must be within ±30% of their true value.

SURROGATES AND INTERNAL STANDARDS. Since a direct injection is performed, surrogates are not used. Internal standards are used when loss due to adsorption to the sample container or other forms of bias is possible. The following internal standards will be used, at least two per sample. They are chosen so as to have a wide range of HPLC retention times.

Internal Standard	**Acronym**
Perfluoro-1-[2,3,4-$^{13}C_3$]butanesulfonate	M3PFBS
Perfluoro-n-[3,4,5-$^{13}C_3$]pentanoic acid	M3PFPeA
Perfluoro-n-[1,2,3,4-$^{13}C_4$]heptanoic acid	M4PFHpA
Perfluoro-n-[1,2-$^{13}C_2$]octanoic acid	M2PFOA
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	MPFOS

QUANTITATION CRITERIA: Ion transitions must be consistent throughout the entire experimental process and be in accordance with Table 3 (selected to be in accordance with QSM Table B-15). For quantitation, S/N ≥ 10:1 is required of each analyte in each sample.

MINIMUM REPORTING LEVELS (MRL) & DETECTION LIMITS (DL). MRLs and DLs are determined as described in EPA Method 537 v1.1. Initial values are reported in Table 4.

Table 4. MRLs and DLs for direct injection analysis by HPLC-MS/MS

Analyte	MRL (µg/L)	DL (µg/L)	Precision at MRL
PFDA	0.65	0.35	<2%
PFNA	0.65	0.35	<2%
PFOA	1.25	0.35	<2%
PFHpA	1.25	0.35	<3%
PFHxA	3.5	0.65	<3%
PFPeA	3.5	0.65	<3%
PFBA	6.5	1.25	<3%
PFOS	0.65	0.35	<3%
PFHxS	1.15	0.35	<3%
PFBS	1.25	0.35	<2%
PFOSA	3.5	0.65	<3%
PFOSaAm	3.5	0.65	<3%

ANALYTICAL METHOD 2. Measurement of PFAS Mixtures by Direct Injection.
Used to measure samples from adsorption isotherms, column experiments, or regeneration studies when the expected concentration is > 2μg/L.

MOBILE PHASE COMPOSITIONS AND MS/MS PARAMETERS. For environmental samples and multi-component mixtures, a gradient elution and dynamic MRM is used using the same transitions noted in Table 3. The mobile phase gradient is given in Table 5. A chromatogram of 100 ppb of all the 10 perfluoroalkyl carboxylates / perfluoroalkyl sulfonates is shown in Appendix II.

Table 5: Gradient HPLC Method for separation of PFAS Mixtures

time (min)	**Mobile Phase Composition (%)**	
	5mM ammonium acetate in H_2O	5mM ammonium acetate in 95% MeOH%
0	70	30
3	70	30
5	40	60
21	20	80
23	0	100
25	0	100

CALIBRATION. Calibration curves are measured for each compound using standard solutions as described in METHOD 1.

SURROGATES AND INTERNAL STANDARDS. Since a direct injection is performed, surrogates are not used. Internal standards will be used as listed in Method 1. The full complement of five internal standards listed in METHOD 1 will used.

CALIBRATION ACCEPTANCE CRITERIA: The RSD of the response factors for all analytes must be ≤20% or the linear or non-linear calibration curve must have $r^2 \geq 0.99$ for each analyte.

SECOND SOURCE CALIBRATION VERIFICATION: A second standard will be prepared from a primary weighed sample or documented vendor provided solution. Vendors include Sigma-Aldrich, Wellington, and Absolute Standards.

CALIBRATION VERIFICATION: A continuing calibration which is a triplicate injection of a standard which is compared to a working calibration curve. Verification is done with each set of 20 samples. Analyte concentrations must be within ±30%. Retention times must be ±0.4 minutes of their expected times.

BLANKS AND CONTROLS: A laboratory reagent blank is run before each set of samples and several times during each daily worklist. Blanks must have responses ≤0.5 the LOQ. A laboratory control is run with each sample sub-set or experimental method (one control per 5 samples).

LOQ VERIFICATION: Prior to every set of samples, standards at the LOQ will be measured and must be within ±30% of their true value.

MINIMUM REPORTING LEVELS (MRL) & DETECTION LIMITS (DL). MRLs and DLs are determined as described in EPA Method 537 v1.1. Initial values are reported in Table 4.

ANALYTICAL METHOD 3. Measurement of Single Component PFOA and PFOS, <2 ppb
Some column experiments are performed at lower concentrations to evaluate effectiveness to treat dilute solutions of PFAS. Solid phase extraction is used to pre-concentrate the samples prior to analysis by LC/MS/MS. Compounds tested by this method are exclusively PFOA and PFOS in lab made water.

SOLID-PHASE EXTRACTION. 6 mL 0.3 g Oasis HLB cartridges are used in conjunction with a Supleco vacuum manifold and polyethylene tube delivery system. Columns are conditioned with 6.0 mL of methanol followed by 10 mL of deionized water. 1.0 L of sample is applied. After a 6.0 mL rinse with deionized water, the analytes are eluted with 6.0 mL of methanol. The eluent is evaporated to dryness under nitrogen (60°C) and the samples reconstituted in methanol with 1% ammonium formate. Surrogates is added at this stage.

SAMPLE BOTTLE AND CARTRIDGE RINSE. After the sample has been applied to the SPE cartridge, two 10 mL aliquots of reagent water will be added to the bottles and drawn through the sample lines and onto the cartridge.

MOBILE PHASE COMPOSITIONS AND MS/MS PARAMETERS. PFOA and PFOS are measured using the same instrument setting as described in ANALYTICAL METHOD 1 using isocratic elution (Table 3).

SURROGATES AND INTERNAL STANDARDS. The following surrogates and internal standards are used. Surrogates are added prior to solid-phase extraction. Internal standards are added when the sample is reconstituted prior analysis by LC-MS. Note: moving forward, if additional analytes are present, a compound specific surrogate will be used for each analyte.

Surrogate	**Acronym**
Sodium perfluoro-[$^{13}C_8$]octanesulfonate	M8PFOS
Perfluoro-n-[$^{13}C_8$]octanoic acid	M8PFOA
N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	d_3-N-MeFOSAA

Internal Standard	**Acronym**
Perfluoro-n-[1,2-$^{13}C_2$]octanoic acid	M2PFOA
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	MPFOS

MINIMUM REPORTING LEVELS (MRL) & DETECTION LIMITS (DL). MRLs and DLs are still being fully determined but initial MRLs for PFOA and PFOS are likely to be 2 ng/L with 1L extractions based on the analytical results obtained with direct injection. Method development is in progress.

CALIBRATION. Calibration curves are measured for each compound using standard solutions as described in METHOD 1.

CALIBRATION ACCEPTANCE CRITERIA: The RSD of the response factors for all analytes must be ≤20% or the linear or non-linear calibration curve must have r2 ≥ 0.99 for each analyte.

SECOND SOURCE CALIBRATION VERIFICATION: A second standard will be prepared from a primary weighed sample or documented vendor provided solution. Vendors include Sigma-Aldrich, Wellington, and Absolute Standards.

CALIBRATION VERIFICATION: A continuing calibration which is a triplicate injection of a standard which is compared to a working calibration curve. Verification is done with each set of 20 samples. Analyte concentrations must be within ±30%. Retention times must be ±0.4 minutes of their expected times.

BLANKS AND CONTROLS: A laboratory reagent blank is run before each set of samples and several times during each daily worklist. Blanks must have responses ≤0.5 the LOQ. A laboratory control is run with each sample sub-set or experimental method (one control per 5 samples).

LOQ VERIFICATION: Prior to every set of samples, standards at the LOQ will be measured and must be within ±30% of their true value.

ANALYTICAL METHOD 4. Measurement of PFASs in Site Water and Treated Water
Treatment performance using batch equilibrium tests and lab-scale column experiments will be performed to determine the effectiveness of adsorbents developed in this study to treat water from provided by a SERDP identified DoD installation. EPA Method 537 – "Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)" – will be used to conduct these determinations with additional guidance from QSM Table B-15.

SOLID-PHASE EXTRACTION. Cartridges with 0.5 g, 6-mL containing styrenedivinyl-benzene (SDVB) sorbent phase will be used in conjunction with a Supleco vacuum manifold and polyethylene tube delivery system. Columns are conditioned with 15 mL of methanol followed by 18 mL of deionized water. A water samples is applied at a flow rate of 10-15 mL/min. After a 6.0 mL rinse with deionized water, the analytes are eluted with 6.0 mL of methanol. The eluent is evaporated to dryness under nitrogen (60°C) and the samples reconstituted in 96% methanol/4% water. Surrogates are added prior to solid-phase extraction.

MOBILE PHASE COMPOSITIONS AND MS/MS PARAMETERS. PFOA and PFOS are measured using the same instrument setting as described in ANALYTICAL METHOD 2 using gradient elution (Table 4) to separate individual PFAS compounds.

SURROGATES AND INTERNAL STANDARDS. The surrogates and internal standards used in METHOD 3 will be used.

PRECISION, ACCURACY, AND MINIMUM REPORTING LEVELS. To be determined, but anticipated to be 2 ng/L for 1L extractions.

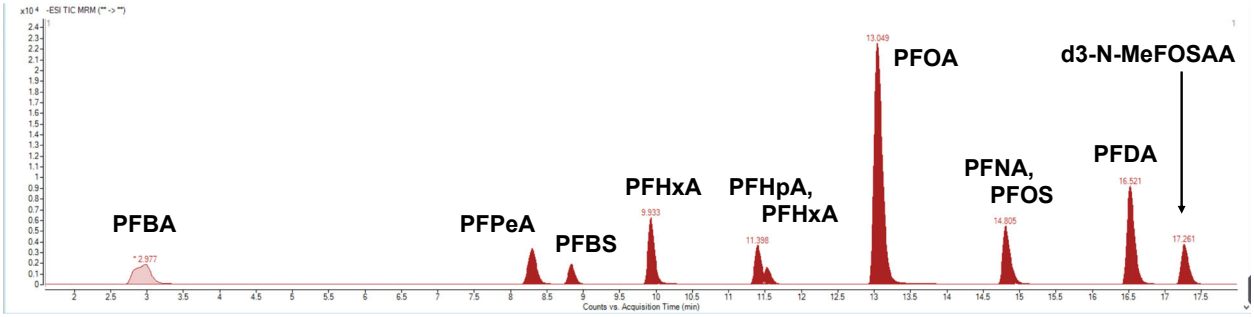
ANALYTICAL METHOD 5. Measurement of PFASs in Site Water and Treated Water
The TOP assay is an alternative method for examining site water. We will be using site water from Former Joint Reserve Base (JRB) Naval Air Station (NAS) Willow Grove which is well characterized. Thus, we do not envision need for the TOP assay at this time.

Appendix A1: Removal of PFASs by Syringe Filters

PFAS	Percent Removal After Filtration		
	PTFE	Cellulose	Nylon
PFOS-DI	24	10	99
PFOS-NaCl	97	15	99
PFOA-DI	81	61	99
PFOA-NaCl	77	30	95
PFNA-DI	50	0	99
PFNA-NaCl	99	43	98
PFOSaAm-DI	96	99	85
PFOSaAm-NaCl	97	99	96
PFBA-DI	-19	0	75
PFBA-NaCl	-3	0	14
PFOSA-DI	100	99	100
PFOSA-NaCl	100	99	100
PFDA	43	25	99
PFDA-NaCl	84	25	99
PFHxS-DI	10	6	49
PFHxS-NaCl	12	29	78
PFHxA-DI	-2	23	93
PFHxA-NaCl	-7	23	32
PFPeA-DI	11	19	82
PFPeA-NaCl	-2	8.5	40
PFHpA-DI	-17	19	99
PFHpA-NaCl	-44	21	59

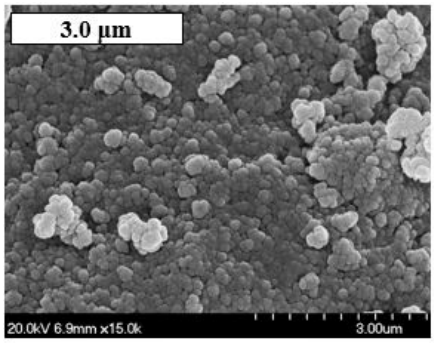
Notes: DI, solvent DI water; NaCl, solvemt 50 mM NaCl.
All filters of 0.44 um
Initial PFAS concentration: 2,000 ppb

Appendix AII: Separation of 10 Perfluoroalkyl Carboxylates and Perfluoroalkyl Sulfonates in the analyte mix.



Appendix B

SEM Images of fluoroalkyl modified organosilica adsorbents versions 1-8.



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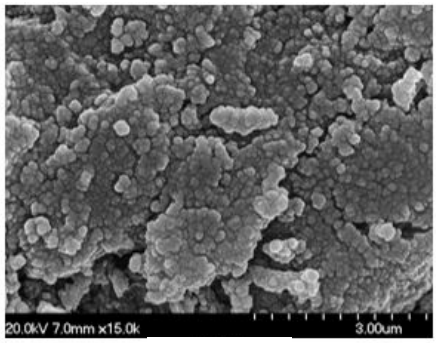

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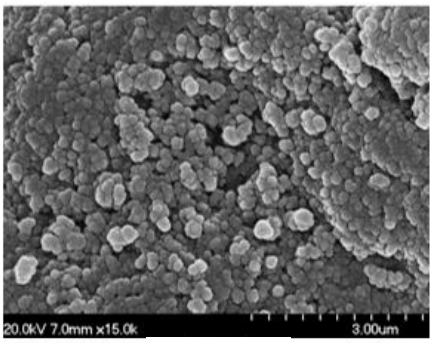

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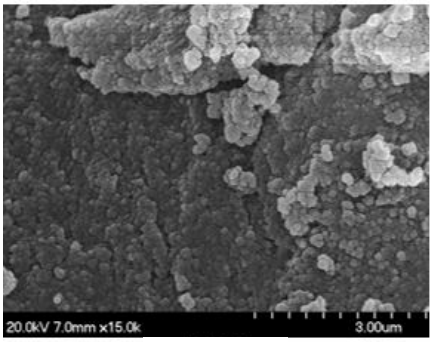

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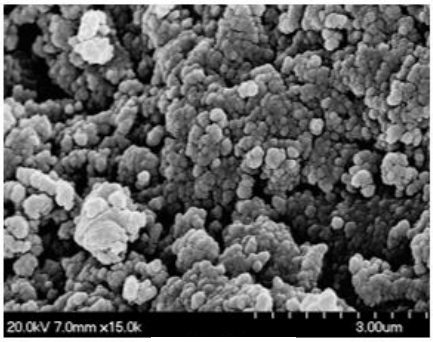

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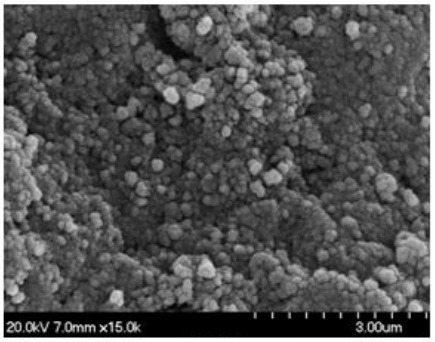

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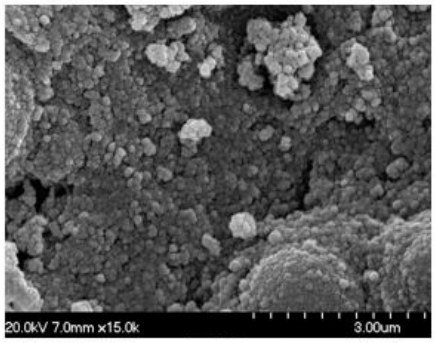

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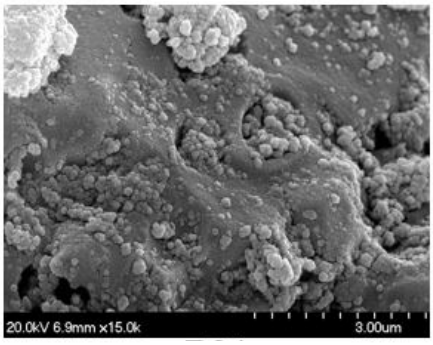
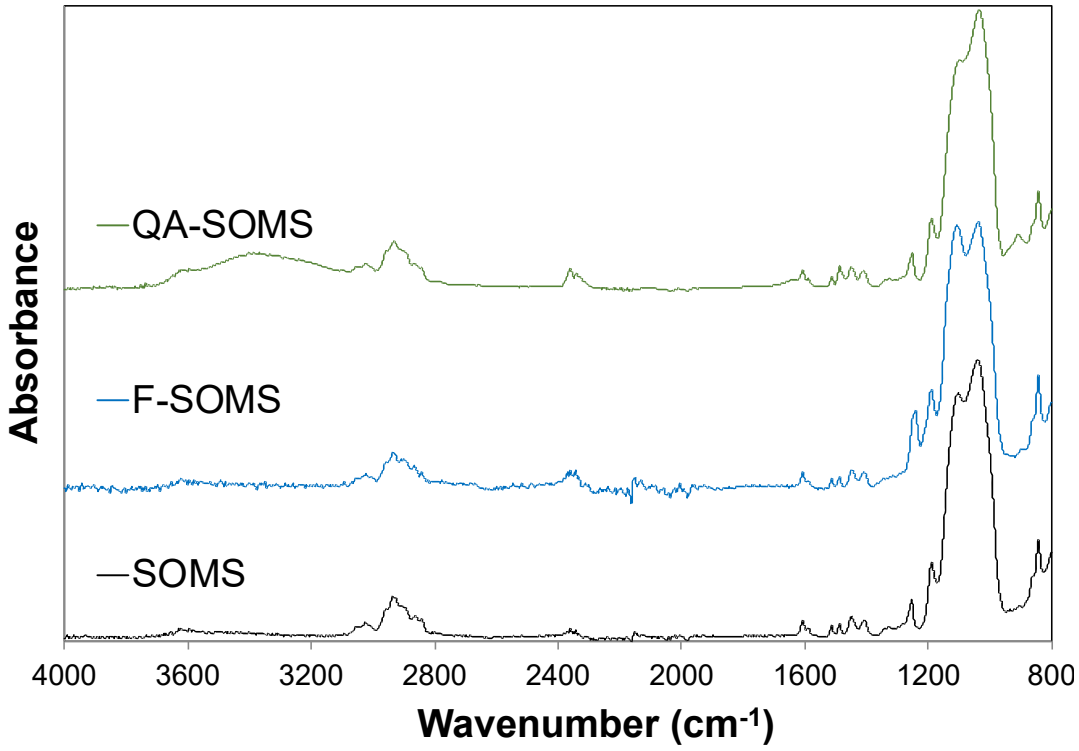


8

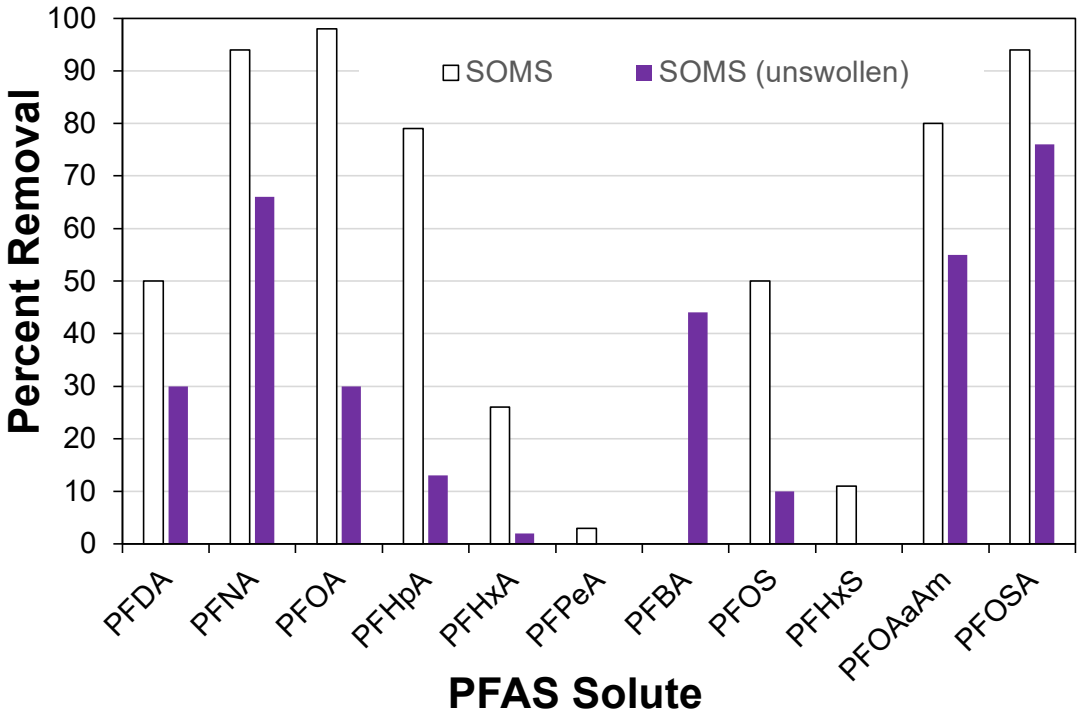
Appendix C

FT-IR spectra of SOMS adsorbents



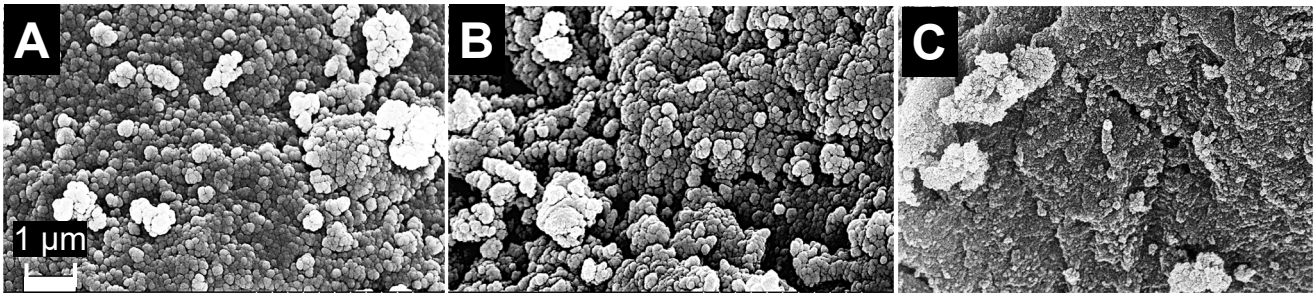
Appendix D

Percent removal of PFAS substance as a function of SOMS swollen state. PFBA is strongly removed by non-swollen SOMS. Swollen SOMS show no adsorption for PFBA.



Appendix E

SEM micrographs of A, SOMS; B, F-SOMS; and C, poly-SOMS in the unswollen state.



Appendix F

Table F1. Second order rate constants for PFAS adsorption and the associated error.

	k_2 (g adsorbent/mgPFAS•hr)									
	ionic strength = 0 mM					ionic strength = 50 mM				
PFAS	**SOMS**	**F-SOMS**	**QA-SOMS**	**poly-SOMS**	**GAC**	**SOMS**	**F-SOMS**	**QA-SOMS**	**poly-SOMS**	**GAC**
PFDA	5.6±3.1	1.9±0.4	0.7±0.2	1.1±0.2	0.8±0.2	>20	19.0±1.2	5.3±0.2	1.2±0.3	1.4±0.5
PFNA	1.0±0.3	0.7±0.3	4.9±0.7	1.2±0.6	0.9±0.2	8.2±1.7	4.0±0.9	10.5±6.1	1.4±0.3	1.4±0.4
PFOA	10.4±3.8	6.9±1.8	2.5±1.0	1.1±0.3	1.6±0.7	6.5±1.8	>20	1.9±0.6	0.6±0.1	0.7±0.3
PFHpA	6.3±0.8	3.2±0.5	0.4±0.1	1.0±0.2	0.2±0.1	3.2±0.8	8.8±2.6	2.4±0.3	0.7±0.1	0.4±0.2
PFHxA	1.7±0.4	2.4±0.5	0.3±0.2	0.7±0.1	1.0±0.5	3.1±2.3	3.6±1.8	2.1±0.7	0.2±0.2	0.4±0.3
PFPeA	5.0±3.8	*no ads*	1.1±0.5	0.9±0.1	0.4±0.1	>20	*no ads*	0.8±0.1	1.3±0.2	0.6±0.2
PFBA	*no ads*	*no ads*	1.0±0.5	1.0±0.1	0.7±0.1	*no ads*	*no ads*	0.7±0.3	2.2±0.2	0.8±0.3
PFOS	7.8±6.5	5.9±0.6	>20	1.9±0.1	0.2±0.1	14±0.8	26.3±3.5	20	3.1±0.7	22±7.6
PFHxS	4.0±2.2	2.4±0.7	>20	0.7±0.1	0.1±0.01	>20	8.7±1.0	16±3	0.9±0.3	10±0.1
PFBS	11±30	*no ads*	*n/m*	0.1±0.1	0.1±0.04	>20	*no ads*	*n/m*	0.7±0.2	0.6±0.2
PFOSA	5.2±1.3	2.6±1.3	>20	5.6±1.8	0.6±0.3	3.9±1.3	6.3±2.6	20	2.3±0.4	0.4±0.2
PFOSaAm	1.9±1.0	0.2±0.3	>20	1.1±0.6	0.3±0.06	20±0.3	0.3±0.1	12±3	1.6±0.2	1.4±0.4

Table F2. Equilibrium adsorption capacities (q_e) calculated from second order kinetics and the associated error.

PFAS	q_e (mg/g)									
	ionic strength = 0 mM					ionic strength = 50 mM				
	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC
PFDA	5.0±0.4	5.8±0.1	6.0±0.4	10.0±0.3	7.5±0.3	9.9±0.1	10.0±0.1	6.2±0.1	9.9±0.3	9.9±0.4
PFNA	9.2±0.5	8.9±1.0	8.3±0.1	9.1±0.7	6.5±0.3	9.9±0.3	9.9±0.1	6.3±0.1	9.9±0.2	9.5±0.3
PFOA	9.9±0.6	9.8±0.1	4.5±0.1	10.0±0.4	9.9±0.5	10.0±0.4	10.0±0.9	8.9±0.3	7.0±0.1	9.5±0.8
PFHpA	8.0±0.2	7.6±0.1	8.7±0.8	10.0±0.4	10.0±0.7	3.0±0.1	3.1±0.1	2.9±0.1	7.1±0.2	9.9±0.9
PFHxA	2.9±0.1	2.6±0.1	7.3±2.1	10.0±0.1	3.0±0.2	4.9±0.6	4.9±0.1	2.9±0.1	7.5±0.3	1.9±0.7
PFPeA	2.0±0.2	*no ads*	3.9±4.4	10.0±0.1	9.9±0.9	1.5±0.1	*no ads*	5.6±0.4	5.8±0.2	7.2±0.4
PFBA	*no ads*	*no ads*	3.8±2.5	8.9±0.1	6.8±0.3	*no ads*	*no ads*	2.5±0.9	6.8±0.1	6.0±0.4
PFOS	4.5±0.6	7.8±0.1	9.9±0.1	10.0±0.1	9.8±0.1	9.9±0.9	9.9±0.9	9.9±0.1	9.9±0.3	9.9±0.1
PFHxS	1.1±0.1	2.1±0.1	9.9±0.1	10.0±0.3	10.0±0.9	3.9±0.9	9.7±0.1	9.0±2.5	7.9±0.4	9.2±0.7
PFBS	0.4±0.1	*no ads*	*n/m*	8.4±2.1	6.7±0.3	1.2±0.9	*no ads*	*n/m*	2.1±0.1	3.4±0.3
PFOSA	9.4±0.4	9.0±0.3	*n/m*	9.4±0.5	8.8±1.3	8.0±0.4	8.3±0.1	*n/m*	6.7±0.3	8.4±1.0
PFOSaAm	8.8±0.8	9.9±0.1	9.9±0.1	6.7±0.6	9.3±1.0	9.9±0.2	10.0±0.4	9.3±0.1	5.9±0.1	8.0±0.3

Table F3. r^2 values (coefficient of determination) for second order kinetics linear regression fits,

PFAS	r^2									
	ionic strength = 0 mM					ionic strength = 50 mM				
	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC	SOMS	F-SOMS	QA-SOMS	poly-SOMS	GAC
PFDA	0.999	0.999	0.989	0.998	0.994	0.999	0.995	0.999	0.997	0.995
PFNA	0.989	0.965	0.999	0.986	0.994	0.999	0.999	0.999	0.998	0.997
PFOA	0.999	0.999	0.997	0.995	0.993	0.999	0.999	0.997	0.999	0.980
PFHpA	0.999	0.999	0.975	0.996	0.991	0.999	0.999	0.999	0.997	0.976
PFHxA	0.998	0.999	0.804	0.999	0.982	0.994	0.998	0.998	0.993	0.963
PFPeA	0.998	*no ads*	0.203	0.998	0.979	0.999	*no ads*	0.975	0.996	0.988
PFBA	*no ads*	*no ads*	0.999	0.999	0.995	*no ads*	*no ads*	0.999	0.999	0.987
PFOS	0.999	0.999	0.999	0.999	0.986	0.999	fast	0.999	0.999	0.999
PFHxS	0.999	0.999	0.999	0.995	0.989	0.999	0.999	0.999	0.991	0.981
PFBS	0.996	*no ads*	*n/m*	0.134	0.809	0.999	*no ads*	*n/m*	0.987	0.976
PFOSA	0.999	0.997	*n/m*	0.999	0.942	0.999	0.999	0.999	0.995	0.960
PFOSaAm	0.994	0.996	fast	0.977	0.968	0.999	0.993	0.999	0.999	0.996

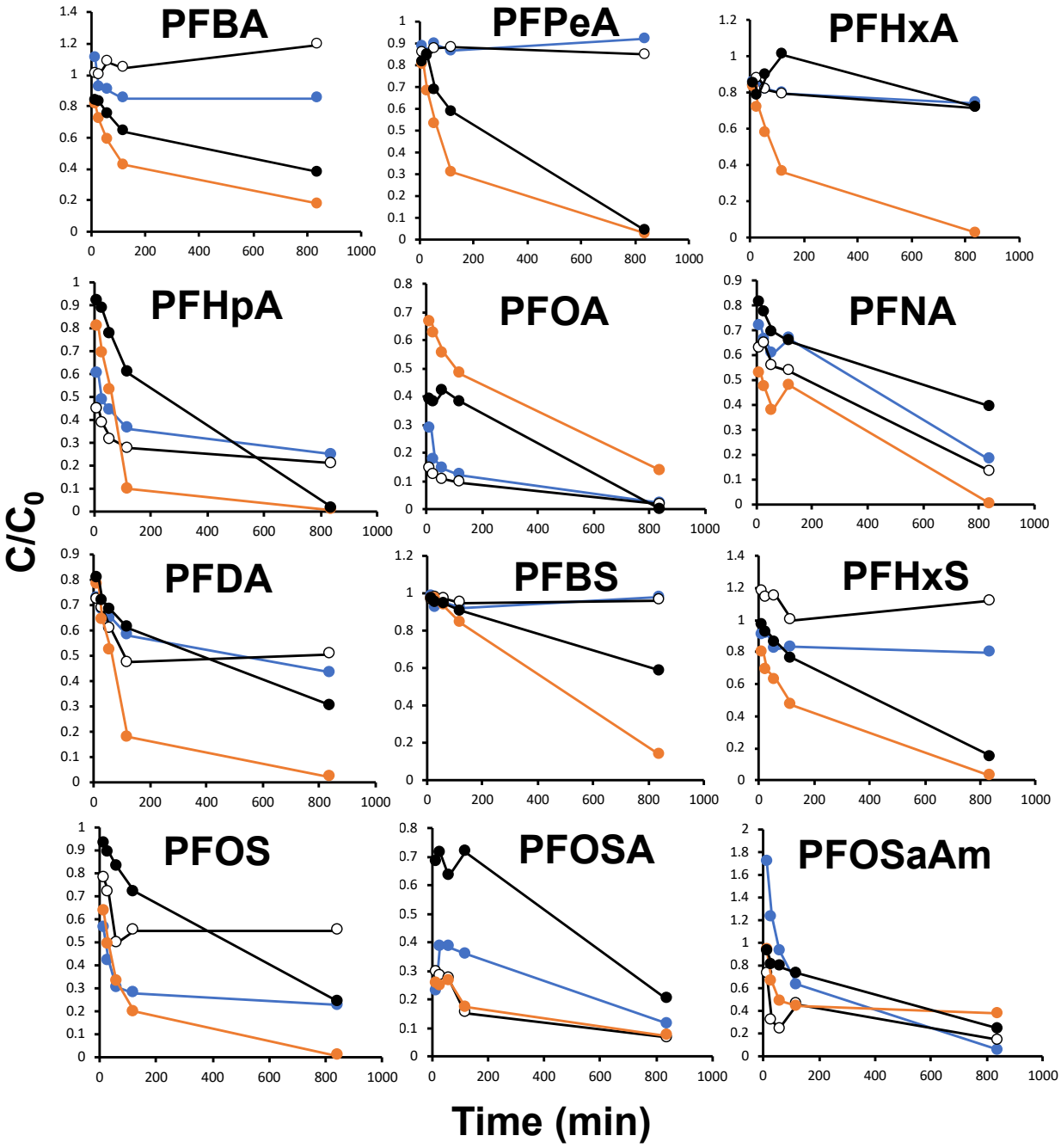


Figure F1: Adsorption kinetics for SOMS (○); F-SOMS (●); poly-SOMS (●); and GAC (●). Dosage 200 mg/L, temperature 25°C, constant agitation, DI water.

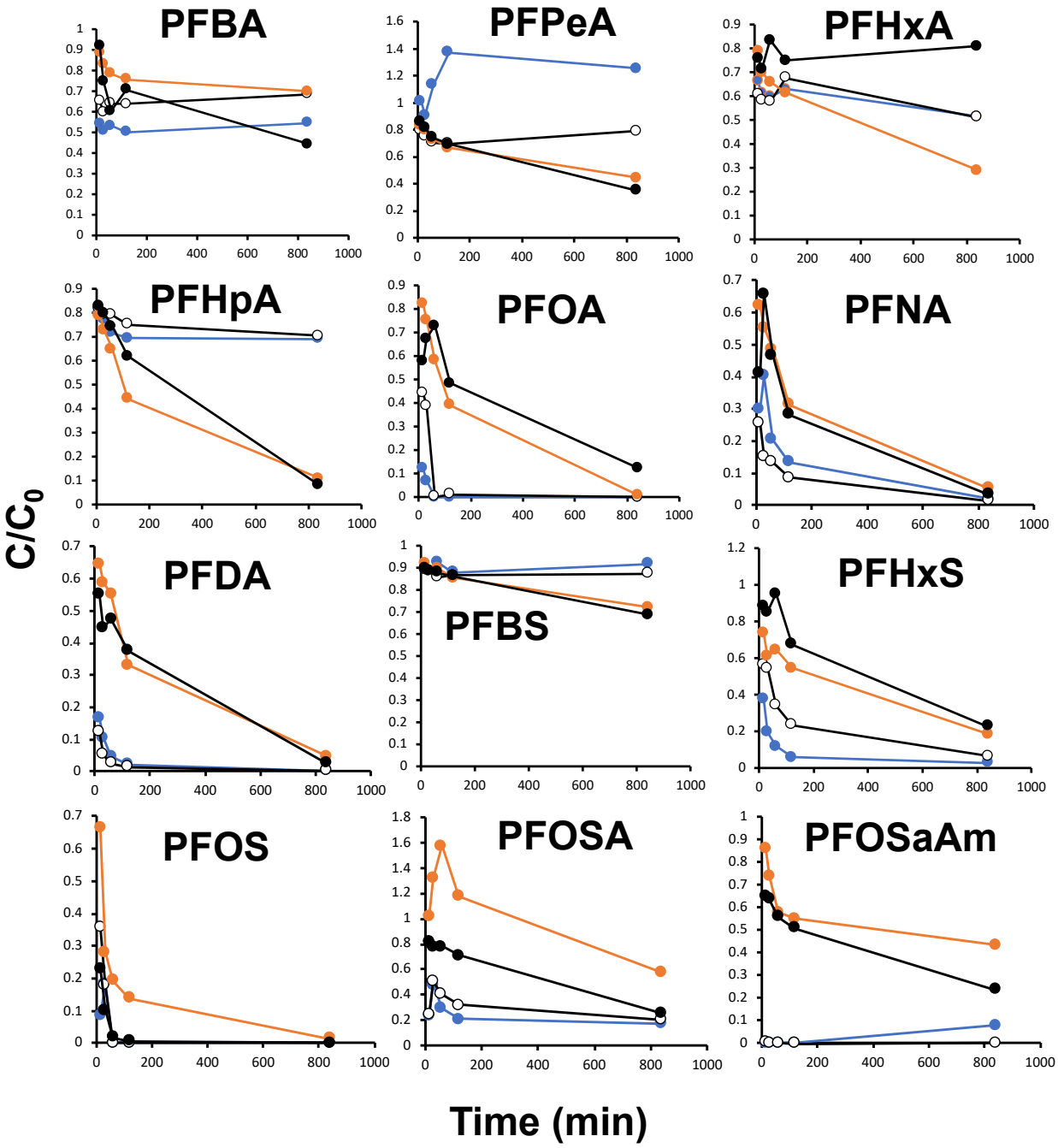


Figure F2: Adsorption kinetics for SOMS (○); F-SOMS (●); poly-SOMS (●); and GAC (●). Dosage 200 mg/L, temperature 25°C, constant agitation, 50 mM NaCl.

Appendix G: Adsorption Isotherms

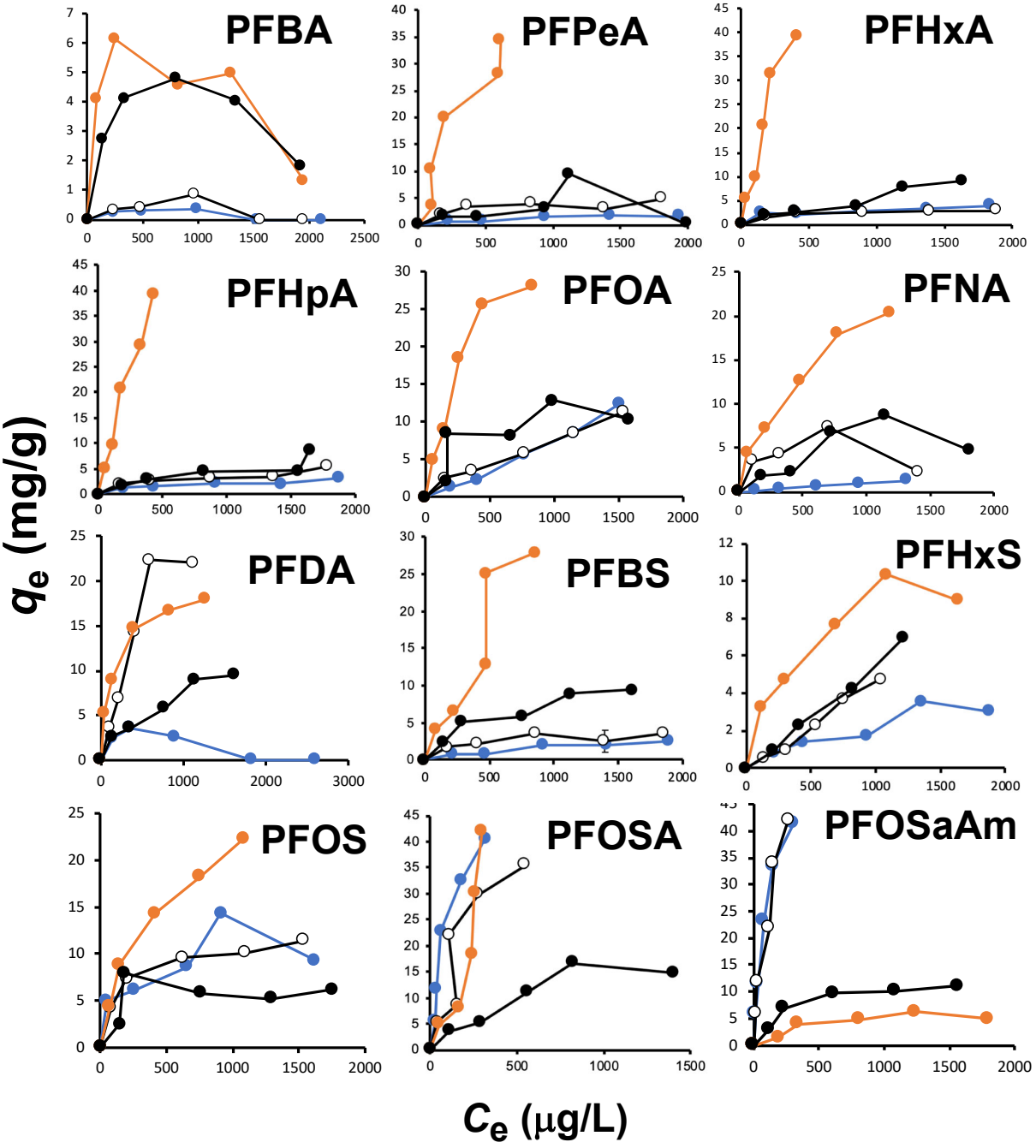


Figure G2. Adsorption isotherms for SOMS (○); F-SOMS (●); poly-SOMS (●); and GAC (●). Dosage 40 mg/L, temperature 25°C, constant agitation, DI water.

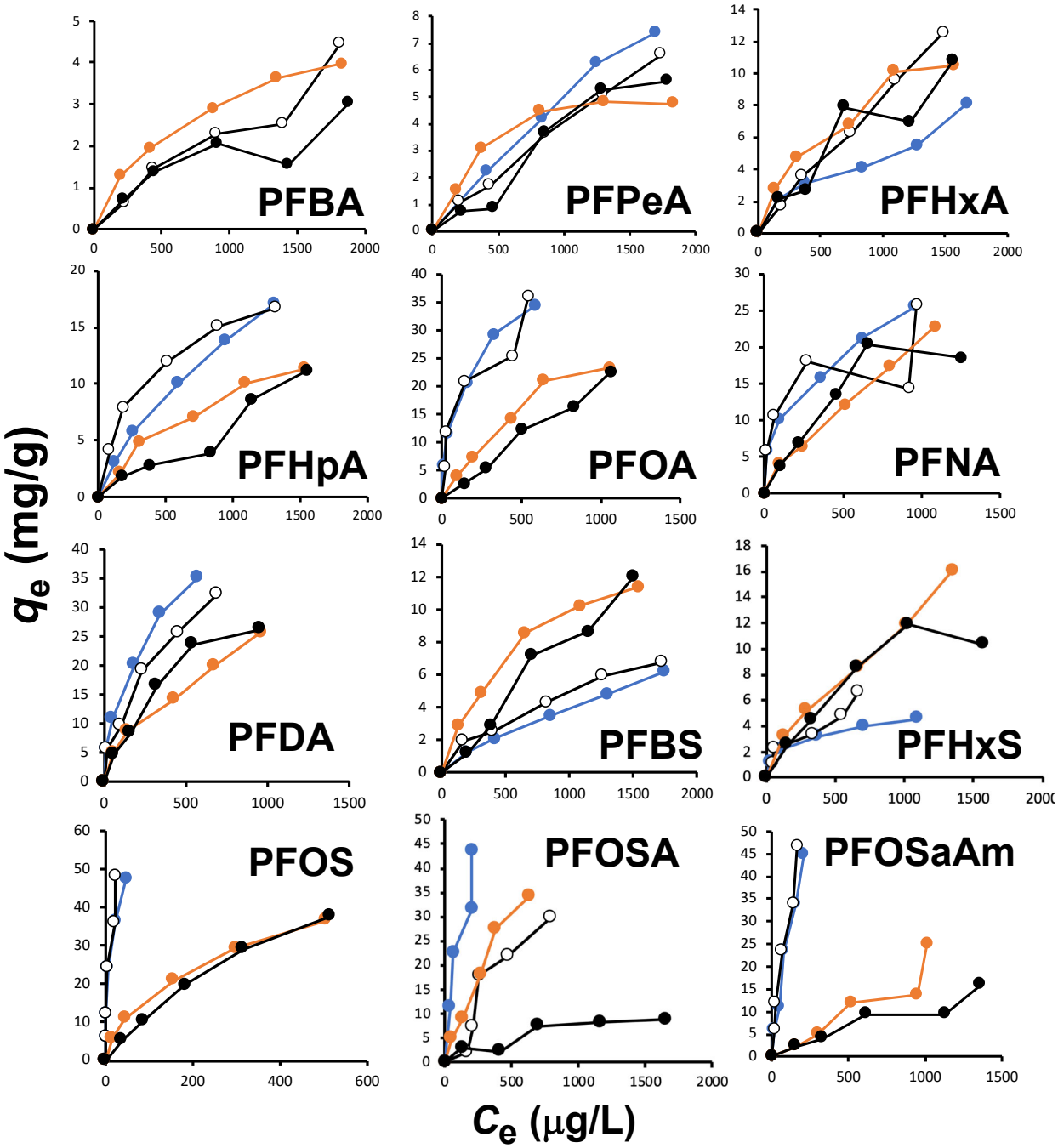


Figure G2: Adsorption isotherms for SOMS (○); F-SOMS (●); poly-SOMS (●); and GAC (●). Dosage 40 mg/L, temperature 25°C, constant agitation, 50 mM NaCl.

Table G1: Freundlich constants and capacity for PFAS solutes in DI water.

PFAS Solute	Adsorbent	1/*n*	K_F (mg/g)(L/μg)$^{1/n}$	r^2	Capacity q_e (mg/g) at C_e = 200 μg/L
PFDA	SOMS	0.84±0.13	80±60	0.929	**6.8±0.8**
	F-SOMS	nominal adsorption			**0.1±0.1**
	poly-SOMS	0.37±0.04	1400±300	0.971	**10.0±0.2**
	GAC	0.56±0.07	150±60	0.961	**2.9±0.4**
PFNA	SOMS	does not fit Freundlich model*			**3.6±0.6**
	F-SOMS	nominal adsorption			**0.1±0.1**
	poly-SOMS	0.56±0.03	400±90	0.986	**7.7±0.2**
	GAC	0.60±0.26	79±35	0.640	**2.0±1.3**
PFOA	SOMS	0.65±0.07	85±40	0.966	**2.7±0.5**
	F-SOMS	1.12±0.06	3±1	0.991	**1.2±0.5**
	poly-SOMS	0.69±0.09	325±170	0.949	**12.7±0.5**
	GAC	0.84±0.08	30±16	0.971	**2.7±0.6**
PFHpA	SOMS	0.36±0.08	300±150	0.874	**2.0±0.6**
	F-SOMS	0.35±0.08	190±105	0.856	**1.2±0.7**
	poly-SOMS	0.92±0.08	145±40	0.976	**19.5±0.4**
	GAC	0.74±0.05	34±10	0.992	**1.7±0.3**
PFHxA	SOMS	0.23±0.04	540±150	0.900	**1.8±0.3**
	F-SOMS	0.19±0.09	820±480	0.605	**2.3±0.6**
	poly-SOMS	0.8±0.1	270±180	0.876	**22.8±0.6**
	GAC	0.7±0.1	45±40	0.890	**1.8±1.0**
PFPeA	SOMS	0.35±0.08	370±200	0.889	**2.3±0.6**
	F-SOMS	0.46±0.13	50±45	0.803	**0.6±1.4**
	poly-SOMS	0.55±0.10	960±550	0.937	**17.5±0.6**
	GAC	does not fit Freundlich model*			**1.3±0.9**
PFBA	SOMS	nominal adsorption			**0**
	F-SOMS	nominal adsorption			**0**
	poly-SOMS	does not fit Freundlich model**			**5.7±0.7**
	GAC	does not fit Freundlich model**			**3.2±0.5**
PFOS	SOMS	0.31±0.05	1180±370	0.927	**6.3±0.3**
	F-SOMS	0.19±0.02	2300±360	0.996	**6.4±0.2**
	poly-SOMS	0.57±0.06	430±160	0.972	**8.9±0.4**
	GAC	0.36±0.07	430±190	0.900	**2.9±0.5**
PFHxS	SOMS	1.13±0.10	2±1	0.979	**0.7±0.9**
	F-SOMS	0.64±0.12	25±20	0.902	**0.8±1.1**
	poly-SOMS	0.43±0.07	420±180	0.935	**4.2±0.4**
	GAC	1.11±0.07	3±1	0.999	**2.9±0.5**
PFBS	SOMS	0.28±0.11	425±300	0.691	**1.8±0.8**
	F-SOMS	0.62±0.15	25±20	0.847	**0.6±1.6**
	poly-SOMS	0.87±0.19	95±00	0.879	**7.7±1.1**
	GAC	0.53±0.10	210±130	0.905	**3.3±0.6**
PFOSA	SOMS	0.69±0.25	480±620	0.713	**19.1±1.3**
	F-SOMS	0.69±0.15	895±610	0.870	**34.9±0.7**
	poly-SOMS	2.86±0.38	<1	0.965	**13.1±2.1**
	GAC	0.64±0.12	160±120	0.905	**5.1±0.8**
PFOSaAm	SOMS	0.68±0.07	960±310	0.966	**35.5±0.3**
	F-SOMS	0.64±0.06	1260±320	0.974	**36.7±0.2**
	poly-SOMS	0.53±0.18	120±150	0.726	**2.0±1.3**
	GAC	0.45±0.12	440±330	0.831	**4.9±0.8**

Initial concentrations: 250, 500, 1000, 1500, 2000 ppb *q_e when C_e at 200 ppb calculated from isotherm. ** $q_e$when C_e at 200 ppb calculated from Freundlich fit of first three data points.

Table S7b: Freundlich constants and capacity for PFAS solutes in 50 mM NaCl.

PFAS Solute	Adsorbent	1/*n*	K_F (mg/g)(L/μg)$^{1/n}$	r^2	Capacity q_e (mg/g) at C_e = 200 μg/L
PFDA	SOMS	0.49±0.05	1260±350	0.957	**16.8±0.3**
	F-SOMS	0.51±0.01	1440±80	0.998	**21.2±0.1**
	poly-SOMS	0.56±0.03	510±80	0.992	**10.1±0.2**
	GAC	0.67±0.07	300±110	0.971	**10.6±0.4**
PFNA	SOMS	0.28±0.08	3060±1300	0.813	**13.6±0.4**
	F-SOMS	0.36±0.02	1930±180	0.994	**13.7±0.1**
	poly-SOMS	0.71±0.05	150±50	0.983	**6.4±0.3**
	GAC	0.70±0.10	165±120	0.913	**6.7±0.7**
PFOA	SOMS	0.44±0.10	2020±980	0.871	**21.2±0.1**
	F-SOMS	0.44±0.03	2190±290	0.989	**22.6±0.1**
	poly-SOMS	0.77±0.06	130±50	0.980	**7.4±0.4**
	GAC	1.06±0.06	15±5	0.989	**3.9±0.4**
PFHpA	SOMS	0.49±0.05	520±160	0.970	**7.1±0.3**
	F-SOMS	0.72±0.02	100±10	0.997	**4.5±0.1**
	poly-SOMS	0.70±0.09	70±37	0.956	**2.9±0.6**
	GAC	0.82±0.15	22±20	0.905	**1.7±1.1**
PFHxA	SOMS	0.93±0.03	14±3	0.999	**1.9±0.2**
	F-SOMS	0.52±0.07	150±70	0.942	**2.3±0.5**
	poly-SOMS	0.55±0.05	185±50	0.979	**3.5±0.3**
	GAC	0.72±0.20	50±55	0.863	**2.3±1.1**
PFPeA	SOMS	0.87±0.05	10±3	0.999	**1.0±0.4**
	F-SOMS	0.91±0.03	9±2	0.996	**1.1±0.3**
	poly-SOMS	0.49±0.10	140±100	0.877	**1.9±0.7**
	GAC	1.12±0.20	2±2	0.892	**0.5±2.5**
PFBA	SOMS	nominal adsorption			**0**
	F-SOMS	nominal adsorption			**0**
	poly-SOMS	0.51±0.02	85±10	0.996	**1.3±0.2**
	GAC	0.54±0.15	45±40	0.804	**0.8±1.4**
PFOS	SOMS*	0.44±0.07	11000±9700	0.991	**>56.0±0.2**
	F-SOMS**	0.47±0.07	8600±1340	0.943	**>68.0±0.2**
	poly-SOMS	0.52±0.01	1450±90	0.998	**23.4±0.1**
	GAC	0.76±0.03	355±50	0.995	**19.7±0.2**
PFHxS	SOMS	0.52±0.12	190±130	0.855	**3.0±0.7**
	F-SOMS	0.35±0.02	400±50	0.988	**2.7±0.1**
	poly-SOMS	0.66±0.04	130±30	0.991	**4.2±0.2**
	GAC	0.66±0.11	100±60	0.988	**3.3±0.7**
PFBS	SOMS	0.57±0.05	95±35	0.973	**2.0±0.4**
	F-SOMS	0.74±0.01	25±2	0.999	**1.2±0.1**
	poly-SOMS	0.58±0.05	170±50	0.980	**3.8±0.3**
	GAC	1.12±0.11	3±2	0.973	**1.3±0.8**
PFOSA	SOMS	1.42±0.50	3±9	0.721	**5.8±2.9**
	F-SOMS	0.63±0.17	1310±1000	0.875	**38.0±0.8**
	poly-SOMS	0.79±0.06	294±70	0.952	**14.3±0.3**
	GAC	0.51±0.22	200±280	0.643	**3.0±1.5**
PFOSaAm	SOMS	0.83±0.11	640±280	0.954	**52.6±0.4**
	F-SOMS	0.75±0.08	780±270	0.966	**41.9±0.4**
	poly-SOMS	1.09±0.16	11±8	0.943	**3.6±1.0**
	GAC	0.82±0.12	40±30	0.935	**2.9±0.8**

Initial concentrations: 250, 500, 1000, 1500, 2000 ppb *q_e at 200 ppb is outside the isotherm, extrapolation leads to q_e = 115.8 mg/g for PFOS to SOMS. **q_e at 200 ppb is outside the isotherm, extrapolation leads to q_e = 102.0 mg/g for PFOS to F-SOMS.

Appendix H

Draft Guidelines for Cross-Comparison Studies
Testing Adsorbents for Removing PFAS Compounds from Water Using Bench-Scale Column Testing

Introduction. This document provides guidance into evaluating adsorbents for *ex situ* remediation of PFAS compounds from groundwater. The goal is to provide a general set of experimental conditions that can be used to compare the capacity of different adsorbents.

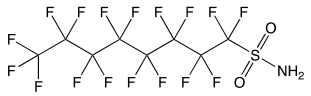
Preparation of adsorbents. Adsorbents will be in granular form to be used in large scale packed columns for ex situ remediation. Thus, adsorbents should first be demonstrated to be granular prior to testing. Adsorbents that are water soluble, emulsions, or fine powders should be engineered as granular material to be as large as at least 80 mesh (diameter = 0.18 mm). Ideally, adsorbents should be 40-80 mesh for testing.

Note: Rapid small-scale column testing as reported by Schaefer et al.[1] has reported that finer materials can be used bench-scale tests. Data from rapid testing can then be extrapolated to predict the performance of larger diameter particles using modeling. It should be noted that this approach can be used for homogeneous porous adsorbents that are milled in the laboratory and used in testing. Rapid small-scale column testing is not appropriate for small particles, powders, or polymers that would be scaffolded to granular material to create a heterogenous final product.

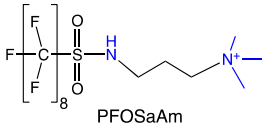
PFAS Analytes. Analytes are used to evaluate performance as a function of chain length and polar group. C4-C10 carboxylates and C4-C6 sulfonates are recommended in addition to a neutral PFAS compound. A cationic compound can optionally be included. A potential selection of analytes is provided in Table 1.

Table 1: Example Analyte List

Analyte Name	Acronym	CAS
perfluorodecananoic acid, C_{10}	PFDA	375-95-1
perfluorononanoic acid, C_9	PFNA	335-67-1
perfluorooctanoic acid, C_8	PFOA	375-85-9
perfluoroheptanoic acid, C_7	PFHpA	307-24-4
perfluorohexanoic acid, C_6	PFHxA	2706-90-3
perfluorpentanoic acid, C_5	PFPeA	375-22-4
perfluorobutanoic acid, C_4	PFBA	375-95-1
perfluorooctanesulfonic acid, C_8	PFOS	1763-23-1
perfluorohexanesulfonic acid, C_6	PFHxS	355-46-4
Perfluorbuatanesulfonic acid, C_4	PFBS	375-73-5
perfluorooctanesulfonamide, C_8	PFOSA	754-91-6
perfluorooctane sulfonamide quaternary ammonium, C_8	PFOSaAm	13417-01-1



PFOSA



PFOSaAm

Initial Evaluations (Isotherms and Kinetics). Adsorbents can be evaluated using adsorption isotherms and measuring adsorption kinetics. Such data can provide relative fast initial comparisons and predictions. For these tests it is recommended that PFAS concentrations do not exceed 2.0 ppm to be well under the critical micelle concentration. Isotherm experiments can be used to evaluate effects of pH, ionic strength, etc. Ideally granular material similar to finished product should be used for testing. Column tests are recommended for direct comparisons.

Column Testing Design

Option 1. High Concentration (200 µg/L), Rapid Scale Testing. High concentration PFAS solutions can be used to more quickly assess capacity. Concentrations of 200 µg/L allow for direct injection LC-MS measurements eliminating the need for solid-phase extraction. Generally, 200 µg/L can be used to linearly extrapolate performance at lower concentrations.

Adsorbent:	granular 40-80 mesh
Bed Size	1-5 mL
Contact Time:	4 min
PFAS:	mixture, 200 µg/L each
Analysis:	LC-MS, direct injection

Aliquots (250 µL) of influent and effluent are taken at time intervals and diluted with (750 µL) of methanol with isotopically labeled internal standards. Breakthrough is measured. Capacity is measured in terms of mass of PFAS bound per mass of dry adsorbent.

Option 2. Low Concentration (1 µg/L) Simulated Groundwater. Lower concentrations of PFAS can be using simulated groundwater as the optimal evaluation of comparative performance. Simulated groundwater is based on published reports[2] and includes the solutes listed in Table 2. Humic acid (1 mg/L) is added to provide natural organic matter. Due to the low concentrations, solid-phase extraction is used to pre-concentrate analytes.

Adsorbent:	granular 40-80 mesh
Bed Size	1-5 mL
Contact Time:	4 min
PFAS:	mixture, 1 µg/L each
Analysis:	LC-MS, pre-concentration using solid-phase extraction

Samples of influent and effluent (250 mL or greater) are collected and concentrated using solid phase extraction. Isotopically labeled surrogates and internal standards are used per DoD QSM 5.2 Table B-15. Oasis WAX or similar solid-phase extraction cartridges can be used. Breakthrough is measured for all compounds. Capacity is measured in terms of mass of PFAS bound per mass of dry adsorbent.

A control is performed using and empty column (no adsorbent) to ensure pump and columns system does not remove PFAS compounds.

Table 2. Simulated Groundwater Composition

Solute	Concentration (mg/L)
Cations	
Ca^{2+}	10
Mg^{2+}	1.5
Na^{+}	14
Anions	
HCO_3^{-}	25
Cl^{-}	22
SO_4^{2-}	10
Natural Organic Matter	
Humic acid	1.0
pH	7.7
conductivity	128 µS

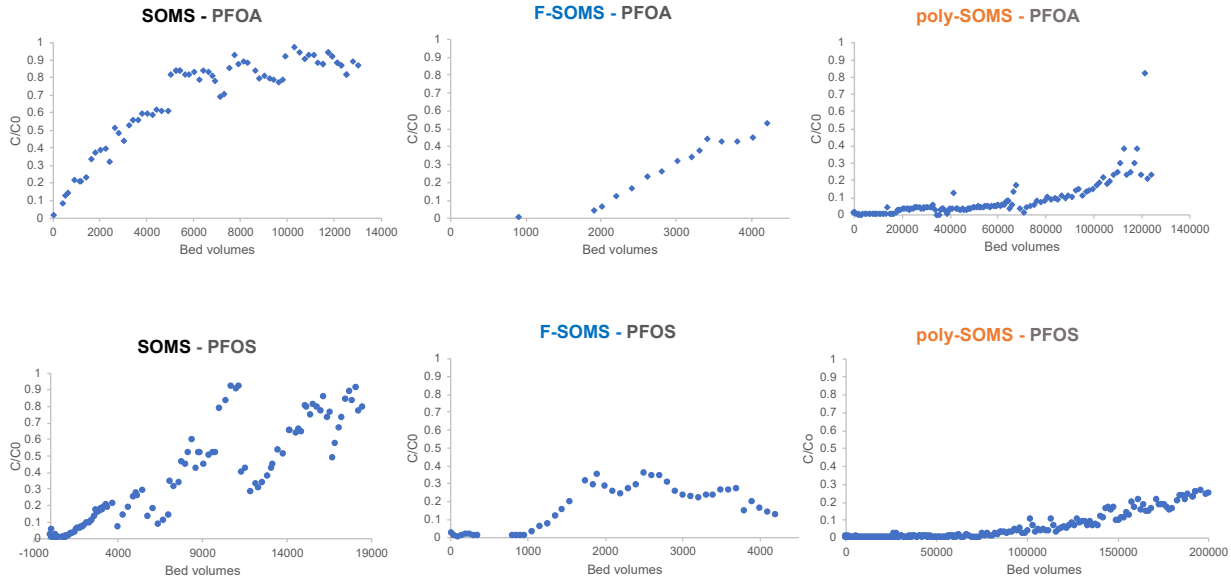
References

[1] Charles E. Schaefer, Dung Nguyen, Paul Ho, Jihyon Im, and Alan LeBlanc Assessing Rapid Small-Scale Column Tests for Treatment of Perfluoroalkyl Acids by Anion Exchange Resin. *Industrial & Engineering Chemistry Research* 2019 58 (22), 9701-9706.

[2] Shand, Paul, W. M. Edmunds, A. R. Lawrence, Pauline Smedley, and Sean Burke. The natural (baseline) quality of groundwater in England and Wales. Environment Agency, 2007.

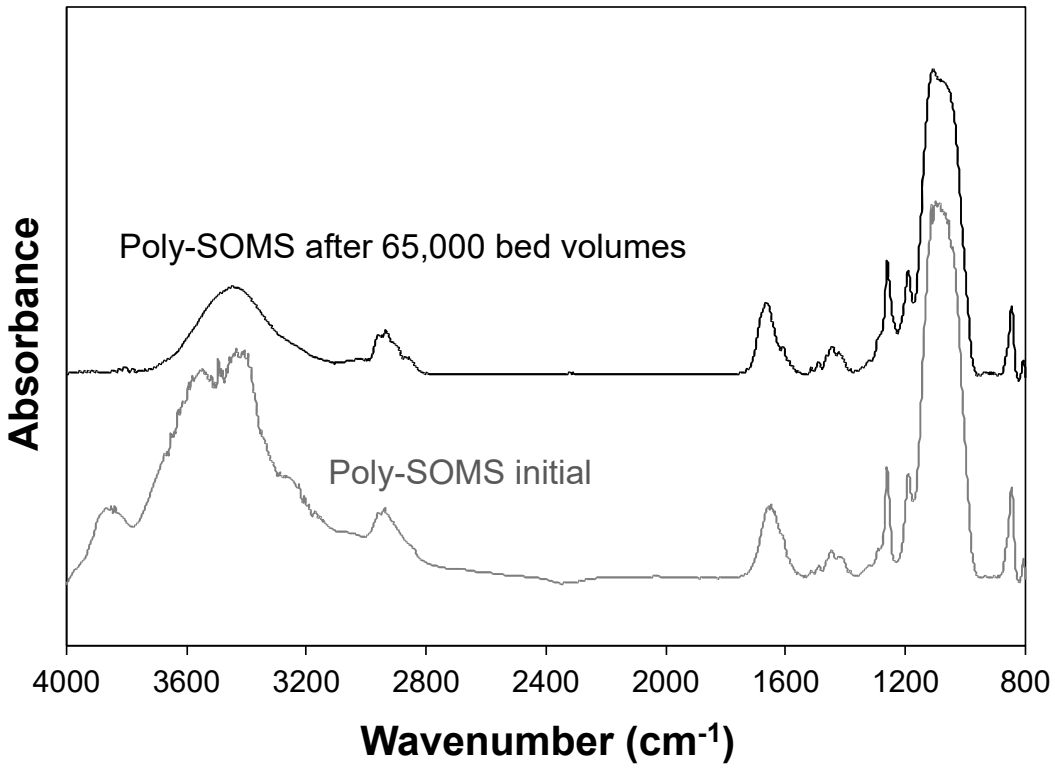
Appendix I

Single PFAS component breakthrough curves



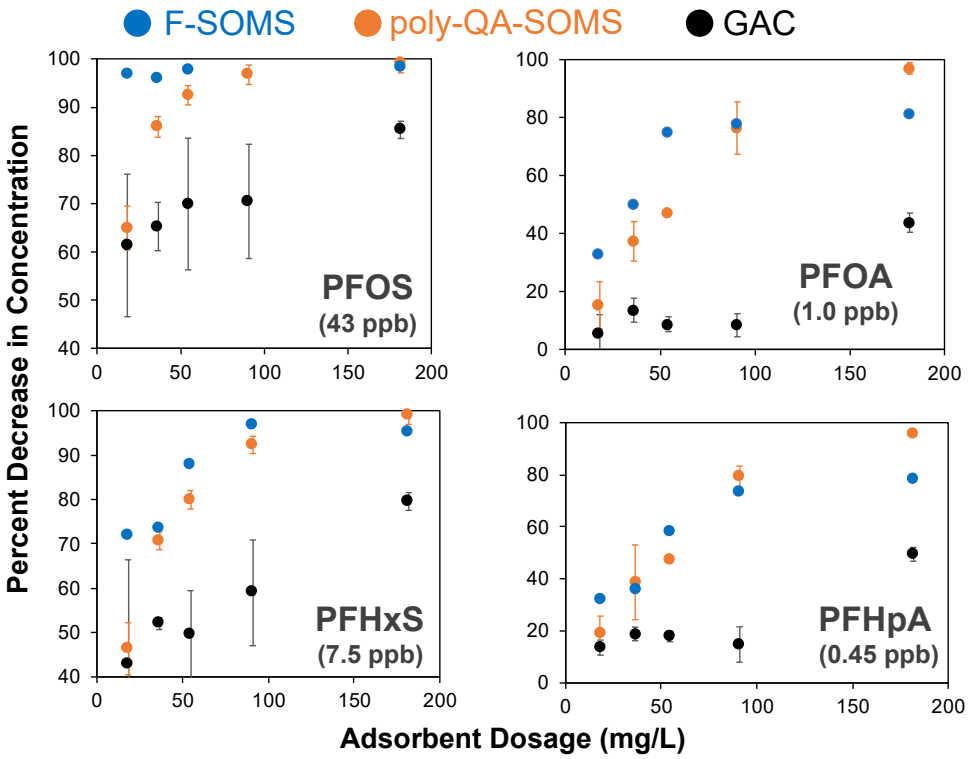
Appendix J: FT-IR Data

FT-IR spectra (KBr pellet) of poly-SOMS before and after use in column experiment with 12 component mixture of 200 µg/L PFAS compounds in DI water. 65,000 bed volumes of the PFAS solution had been passed through the poly-SOMS bed after which the material was dried at 25°C and measured by FT-IR. The amide band at 1650 cm^{-1} was used for quantitation.



Appendix K

Adsorption Isotherms Using Willow Grove Water. Adsorption isotherms for F-SOMS, poly-QA-SOMS, and Norit® GAC on site water. Measurement was made by varying dosage and measuring percent decrease in concentration. (Initial PFAS concentration) are given in parenthesis.



Appendix L: Site Water Lab Testing

Data for Table 12: Bench Scale Testing Using Willow Grove Site Water						
Sample	**Concentration (ppb)**					
	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFOS
Site Water Untreated Replicate 1	1.02	1.30	0.31	7.81	0.88	40.50
Site Water Untreated Replicate 2	0.99	1.32	0.32	8.06	0.87	44.60
Column: F-SOMS						
Initial treatment (@1800 bed vol)	0.37	0.51	0.04	0.28	0.05	0.54
Column: Poly-SOMS (2 BV/min)						
Applied Vol: 500 Bed Volumes	0.02	0.10	0.02	0.14	0.05	0.28
Applied Vol: 3500 Bed Volumes	0.07	0.26	0.04	0.35	0.06	0.23
Applied Vol: 7000 Bed Volumes	0.22	1.92	0.69	0.44	0.25	2.51
Applied Vol: 11000 Bed Volumes	0.35	2.06	0.73	0.68	0.35	1.49
Column: Poly-SOMS (0.4 BV/min)						
Initial Treatemnt @1800 bed vol)	0.002	0.003	0.002	0.001	0.004	0.010

Appendix M: Simulated Groundwater Lab Columns

Poly-SOMS Simulated Groundwater Column

Sample Type	Applied Vol (mL)	Concentration (ppt)									
		PBFA	PFBS	PFDA	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFPeA
influent		635.0	563.7	7.3	659.7	660.2	816.7	983.5	847.1	911.5	540.5
effluent	10440	24.5	0.4	0.9	2.6	8.2	0.9	8.9	9.0	4.1	6.6
influent		805.0	769.5	76.2	991.0	968.1	989.4	1230.5	1210.3	1326.1	704.6
effluent	30600	21.2	0.5	9.6	7.1	16.1	1.2	9.4	9.8	10.6	15.9
influent		828.9	816.4	22.3	907.3	876.7	1127.3	1251.8	1057.7	1294.8	681.6
effluent	48960	428.4	0.3	63.5	7.4	12.3	1.1	6.0	7.5	5.0	8.9
influent		822.6	791.3	19.4	886.3	844.7	1096.1	1046.4	1011.5	1397.1	679.8
effluent	63360	503.4	0.8	3.1	0.2	7.1	1.7	1.9	8.8	7756.1	5.9
influent		731.1	739.6	14.7	778.2	734.0	931.7	2599.4	1132.3	1257.7	602.2
effluent	86400	879.7	0.5	8.1	4.5	9.5	1.0	5.8	7.0	2216.6	26.7
influent		632.6	563.7	7.3	659.7	660.2	816.7	983.5	847.1	911.5	540.5
effluent	103680	1014.6	0.8	41.2	2.9	10.7	1.7	7.1	193.4	7326.7	66.8
influent		809.0	790.1	203.9	870.7	819.4	992.0	1161.1	975.0	1252.8	669.3
effluent	123840	1032.4	1.2	20.2	3.9	8.0	2.1	25.8	10.9	7779.3	139.9
influent		656.5	769.0	3.5	921.7	679.7	852.2	824.7	852.3	1042.7	793.3
effluent	165240	843.9	14.9	6.1	19.2	57.3	5.8	12.0	15.3	15.4	437.5
influent		655.7	788.8	39.9	889.7	674.7	797.6	802.8	822.3	945.7	789.0
effluent	185400	872.9	76.3	12.2	66.9	153.0	18.7	29.6	8655.5	113.9	887.7
influent		311.6	883.5	123.1	5016.4	1997.5	846.1	819.0	889.1	921.2	411.5
effluent	205560	801.5	97.3	50.8	66.4	195.0	13.0	20.1	30.4	68.6	1004.0
influent	0	676.9	705.9	243.6	886.6	671.2	792.4	872.3	772.9	923.2	779.1
effluent	225720	765.3	112.7	29.1	68.6	237.0	10.6	17.6	24.9	23.6	49.9
influent	0	640.1	740.8	1.4	910.9	675.5	880.9	834.0	794.5	1024.3	741.3
effluent	257400	671.9	197.7	3.4	164.4	333.3	60.2	76.6	7.2	49.3	971.8
influent	0	678.6	796.0	1.3	1018.1	756.7	922.4	858.3	877.7	685.2	824.8
effluent	309240	685.4	341.0	1.8	247.9	517.5	6.5	77.5	110.5	34.6	1107.9
influent	0	626.7	767.3	1.8	906.5	695.2	338.0	835.5	803.3	961.2	739.0
effluent	329400	501.0	22.5	5.3	33.5	41.0	7.3	22.9	93.5	39.6	120.0
influent	0	686.1	793.9	1.6	1002.1	736.3	381.2	861.7	858.3	743.9	814.5
effluent	349560	701.3	421.9	1.1	283.1	33.2	25.5	68.6	114.5	18.2	1011.0
influent	0	681.9	841.1	1.9	993.5	751.8	381.3	939.3	865.3	913.3	828.7
effluent	369720	730.9	554.4	6.4	357.9	721.7	26.9	72.3	130.1	16.2	1171.7
influent	0	634.5	717.7	2.2	960.8	701.1	329.6	617.4	801.4	712.8	785.6
effluent	392760	608.2	444.1	0.6	288.9	632.7	22.1	51.9	104.0	15.3	955.6
influent	0	771.8	902.6	3.2	1181.1	866.5	439.1	746.9	990.3	1499.4	994.6
effluent	410040	635.4	550.5	0.6	343.6	738.5	23.3	53.2	112.6	13.7	991.5
influent	0	2490.6	1882.6	7.0	1331.0	2344.3	120.0	292.5	472.2	101.6	3129.8
	430200	295.4	303.5	0.0	264.5	198.7	105.3	256.0	225.8	113.6	222.3

Flow rate was 2 mL/min. (Time = applied volume / 2mL/min)
Bed volume was 4 mL (Applied bed volume = applied mL/ 4 mL)

Ion Exchange Resin (marathon) Simulated Groundwater

Sample Type	Applied Vol (mL)	Concentration, ppt								
		PBFA	PFPeA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFOS	PFNA
influent		2939	764	1264	1128	848	1227	1182	1231	1290
effluent	1197	24	3	4	11	20	13	8	4	3
effluent	1915	21	13	6	42	63	31	29	6	20
effluent	3112	8	9	4	23	44	12	20	6	17
effluent	3830	13	9	2	35	12	13	9	14	13
effluent	5027	9	7	2	10	12	5	6	14	10
influent		702	830	1153	857	1260	1151	1098	1901	1428
effluent	5746	97	10	3	19	17	7	11	8	15
effluent	6943	31	16	12	24	24	26	14	25	14
effluent	7661	18	11	1	20	9	7	7	5	22
effluent	8858	12	8	1	10	6	4	6	7	10
effluent	10055	16	9	1	9	13	5	7	9	6
effluent	10773	19	9	1	11	14	5	8	26	1
influent		741	878	1186	925	1262	1225	1123	1895	1422
effluent	11853	14	8	1	9	8	3	6	6	6
effluent	12571	21	10	1	13	16	5	7	7	9
effluent	13768	19	10	1	18	8	3	8	5	4
effluent	15683	25	10	0	8	13	2	5	4	4
influent		731	941	1192	938	1302	1175	1170	1936	1373
effluent	17599	39	134	1	12	7	3	5	4	11
influent		641	782	1364	807	1455	1328	1166	2065	1316
effluent	27175	165	48	18	35	47	22	42	27	65
effluent	36751	1218	736	486	680	753	645	773	572	1035
influent		573	577	955	591	981	872	811	1648	905
effluent	40581	1205	935	591	736	1002	635	754	460	882
influent		476	465	756	589	787	937	1093	1419	1814
effluent	54706	735	654	522	674	771	641	935	504	1853

Flow rate was 2 mL/min. (Time = applied volume / 2mL/min)
Bed volume was 4 mL (Applied bed volume = applied mL/ 4 mL)

Appendix N: Pilot unit photograph

Appendix O: Pilot Test Data

Pilot Test Analytical Results Wooster

Bed dimensons at start-up 3/9/20				
Total Bed Volume	3.45	L	0.91	gal
QA-Osorb (dry) mass	1	kg (0.5 kg per cartridge)		
Flow Rate	0.5	gpm	1.9	lpm
Contact Time	1.83	min		
QA-Osorb swell:	2.5	times volume		
QA-Osorb density:	0.6	kg/L		
Volume of PQ-Osorb:	1.67	L		
2.5 times swell:	4.17	L		

Bed dimensions since 3/11/20						
Total Bed Volur	1.725	L	0.06	ft^3	0.46	gal
QA-Osorb (dry)	0.5	kg	0.5	kg/cartridge		
Flow Rate	1.9	L/min	0.50	gpm		
Contact Time	0.91	min				
QA-Osorb swell	2.5	times volume				
QA-Osorb densi	0.6	kg/L				
Volume of PQ-(	0.83	L				
2.5 times swell	2.08	L				

			3/9/20 - Start Up Day 1					3/16/20 Day 7					3/23/20 Day 14					3/30/20 Day 21					4/6/20 - End of Test Day 28				
			Influent (ng/L)		Effluent Day 1 (ng/L)			Influent Day 7 (ng/L)		Effluent Day 7 (ng/L)			Influent Day 14 (ng/L)		Effluent Day 14 (ng/L)		%	Influent Day 21 (ng/L)		Effluent Day 21 (ng/L)		%	Influent Day 28 (ng/L)		Effluent Day 28 (ng/L)		%
	PFAS Analyte	Blank	Result	Error	Result	Error	% Removal	Result	Error	Result	Error	% Removal	Result	Error	Result	Error	Removal	Result	Error	Result	Error	Removal	Result	Error	Result	Error	Removal
PFBS	PFBS	0.2	570	30	0.5	0.4	99.91%	960	30	1,400	100	-45.83%	910	60	981	40	-7.80%	900	15	790	90	12.22%	900	200	715	60	20.56%
PFHxS	PFHxS	0.5	3,050	230	0.8	0.07	99.97%	4,800	130	14	3	99.71%	5,600	50	790	120	85.89%	4,800	60	5,300	550	-10.42%	6,100	480	7750	1700	-27.05%
PFOS	PFOS	0.4	10,900	380	0.4	0.07	100.00%	16,200	140	6	2	99.96%	24,000	2,900	10	2	99.96%	28,000	3000	10	2	99.96%	19,800	400	4000	2000	79.80%
PFBA	PFBA	0.3	200	7	0.6	0.1	99.70%	283	16	290	14	-2.47%	320	25	300	15	6.25%	290	25	300	10	-3.45%	330	8	315	25	4.55%
PFPeA	PFPeA	0.2	460	130	0.2	0.2	99.96%	740	35	720	60	2.70%	770	60	730	35	5.19%	690	65	730	20	-5.80%	670	22	640	50	4.48%
PFHxA	PFHxA	0.2	920	30	0.2	0.1	99.98%	1,230	10	1,740		-41.46%	1,480	100	1,450	35	2.03%	1,350	60	1,470	40	-8.89%	1,440	75	1,410	75	2.08%
PFHpA	PFHpA	0.1	285	10	0.1	0.2	99.96%	366	6	160	20	56.28%	410	30	830	100	-102.44%	375	30	530	40	-41.33%	380	50	370	30	2.63%
PFOA	PFOA	0.5	2,370	140	1.2	0.2	99.95%	2,870	160	115	20	95.99%	3,500	430	3,200	700	8.57%	3,250	350	8,300	1500	########	3,620	20	4960	280	-37.02%
PFNA	PFNA	0.06	53	4	0.2	0.2	99.62%	55	1	0.5	0.2	99.09%	62	5	3	1	95.16%	60	5	6	1	90.00%	66	2	27	4	59.09%
PFDA	PFDA	0.08	36	4	0.9	0.2	97.50%	39	3	1	0.1	97.44%	120	12	8	9	93.33%	62	40	2	0.2	96.77%	37	12	6	2	83.78%
PFUda	PFUda	<0.01	2	1	1	0.3	50.00%	4	7	0.03		99.25%	1	0	0		90.00%	2	0.1	0.2	0.1	90.00%	1	0.1	0.2	0.1	80.00%
PFDoA	PFDoA	<0.01	3	1	0.03		99.00%	0.1		0.03		70.00%	3	0	1	0.3	66.67%	0.2	0.1	0	0.1	100.00%	2	0.1	0.1	0.1	95.00%
Sum PFAS	Sum PFAS		18,849		6.13		99.97%	27,547		4,447		83.86%	37,176		8,303		77.67%	39,779		17,438		56.16%	33,346		20,193		39.44%
TOP Assay	Total PFAS (TOP Assay)		37,150		59		99.84%	32,470		6,630		79.58%	52,800		16,600		68.56%	55,200		29,500		46.56%	45,500		30,600		32.75%

Throughput Calculations

Day	Sample Description	Date/Time	Incremental Bed Volumes		Cumulative Bed Volumes		Incremental Volume Treated		umulative Volume Treate	
0	Baseline Influent Sampling [	3/9/20 10:00	Start-up							
0.04	Effluent Day 1 Sampling Dat	3/9/20 11:00	33	BVs (incremental	33	BVs (cumulative)	30	gal (incremental)	30	gal (cumulative)
2.08	Change of Conditions:	3/11/20 12:00	1,452	BVs (incremental	1,485	BVs (cumulative)	1,323	gal (incremental)	1,353	gal (cumulative)
7.02	Effluent Day 7 Sampling Dat	3/16/20 10:30	6,319	BVs (incremental	7,804	BVs (cumulative)	2,880	gal (incremental)	4,233	gal (cumulative)
13.95	Effluent Day 14 Sampling Da	3/23/20 8:45	7,881	BVs (incremental	15,685	BVs (cumulative)	3,591	gal (incremental)	7,824	gal (cumulative)
20.94	Effluent Day 21 Sample Date	3/30/20 8:30	7,952	BVs (incremental	23,637	BVs (cumulative)	3,623	gal (incremental)	11,447	gal (cumulative)
28.08	Effluent Day 28 Sample Date	4/6/20 12:00	8,130	BVs (incremental	31,766	BVs (cumulative)	3,704	gal (incremental)	15,151	gal (cumulative)

Third Party Data: Willow Grove Pilot Test

Influent	3/16/20					Effluent	3/16/20				
Constituent	Result	Units	Qualifers		Percentage Difference*	Result	Units	Qualifers		Percentage Difference*
PFBS	610	ng/L	E		44.6%	870	ng/L	E		46.7%
PFPeS	620	ng/L	E	M		72	ng/L	M		
PFHxS	2,900	ng/L	E		49.4%	17	ng/L	M		19.4%
PFHpS	770	ng/L	E			0.37	ng/L	J	M	
PFOS	15,000	ng/L	E		7.7%	20	ng/L	M		107.7%
PFNS	17	ng/L				0.89	ng/L	U		
PFDS	6.9	ng/L				1.3	ng/L	U		
PFOSA	52	ng/L				2.7	ng/L	U		
NETFOSAA	9.1	ng/L	U	M		8.9	ng/L	U		
NMeFOSAA	9.1	ng/L	U			0.89	ng/L	U		
4:2-FtS	16	ng/L	J			21	ng/L			
6:2-FtS	1,700	ng/L	E			69	ng/L			
8:2-FtS	200	ng/L				8.9	ng/L	U		
PFBA	310	ng/L	M		9.1%	310	ng/L	M		6.7%
PFPeA	670	ng/L	E	M	9.9%	660	ng/L	E	M	8.7%
PFHxA	1,200	ng/L	E		2.5%	1,300	ng/L	E		28.9%
PFHpA	350	ng/L	M		4.5%	150	ng/L	M		6.5%
PFOA	1,800	ng/L	E	M	45.8%	120	ng/L	M		4.3%
PFNA	50	ng/L	M		9.5%	1.3	ng/L	U		88.9%
PFDA	17	ng/L			78.6%	0.9	ng/L	U		11.6%
PFUda	1.8	ng/L	M		75.9%	1.3	ng/L	U		191.0%
PFDoA	1.4	ng/L	U	M	173.3%	1.3	ng/L	U		191.0%
PFTriA	2.7	ng/L	U			2.7	ng/L	U		
PFTeA	2.7	ng/L	U			2.7	ng/L	U		

*Minor differences between TA lab and Woostermay be attributed to how branched isomers where included.

Qualifier	Qualifier Description
D	The reported value is from a dilution
E	Result exceeded calibration range
J	Estimated: the analyte was positively identified, quantitation is estimated
M	Manual integrated compound
Q	One or more quality control criteria failed
U	Undetected at the limit of detection

Appendix P: Regeneration Data

Poly-SOMS Regeneration Data: 80% MeOH + 1M NaCl

	Peak Areas												Concentration (ppb)										% Absorbed										
Sample	**[M2] PFOA**	**PBFA**	**PFBS**	**PFDA**	**PFHpA**	**PFHxA**	**PFHxS**	**PFNA**	**PFOA**	**PFOS**	**PFOSA**	**PFPeA**	**PBFA**	**PFBS**	**PFDA**	**PFHpA**	**PFHxA**	**PFHxS**	**PFNA**	**PFOA**	**PFOS**	**PFOSA**	**PFPeA**	**PBFA**	**PFBS**	**PFDA**	**PFHpA**	**PFHxA**	**PFHxS**	**PFNA**	**PFOA**	**PFOS**	**PFOSA**	**PFPeA**
input	41468.92	7797.45	1953.54	8472.39	11259.43	34372.04	6070.55	11607.45	26695.62	5445.27	1806.29	16305.27	44.25	15.04	9.29	49.05	81.76	54.52	20.67	33.70	47.95	4.17	56.80	89.3	74.2	55.8	92.8	92.5	96.9	90.1	95.2	91.3	88.3	90.3
initial treat	40972.14	835.34	504.75	3744.71	806.3	2581.04	188.55	1150.26	1293.5	476.44	211.59	1582.28	4.74	3.89	4.11	3.51	6.14	1.69	2.05	1.63	4.20	0.49	5.51										
input	39605.31	6655.52	6416.96	29033.57	9026.12	9722.57	2360.24	23100.64	21881.12	1711.42	8364.78	13079.23	37.77	49.39	31.85	39.32	23.13	21.20	41.13	27.63	15.07	19.32	45.56	100.0	99.8	77.3	99.3	99.0	99.1	82.2	92.0	69.5	98.9	99.5
regen treat 1	43392.15	0	14.97	6601.11	65.07	94.28	21.49	4112.6	1745.79	521.7	93.49	65.38	0.00	0.12	7.24	0.28	0.22	0.19	7.32	2.20	4.59	0.22	0.23										
input	14971.41	6668.79	1978.4	18071.27	5709.01	26313.22	5962.14	19165.05	9567.33	1862.99	8029.76	13039.72	37.85	15.23	19.82	24.87	62.59	53.54	34.12	12.08	16.41	18.55	45.43	87.1	78.3	80.7	92.2	92.2	98.5	90.1	91.9	90.5	99.6	88.8
regen treat 2	17297.92	859.88	429.33	3490.47	446.32	2057.81	87.74	1906.19	774.83	176.18	29.62	1454.77	4.88	3.30	3.83	1.94	4.90	0.79	3.39	0.98	1.55	0.07	5.07										
Trial 2																																	
input	15334.07	6562.85	6464.88	31214.3	8386.49	20425.85	5861.74	24360.42	22542.92	5187.07	9301.91	12554.87	37.24	49.76	34.24	36.54	48.59	52.64	43.37	28.46	45.68	21.49	43.74	86.2	89.7	81.7	95.4	86.5	95.6	53.4	89.2	87.1	96.2	86.8
initial treat	14402.3	902.65	664.33	5726.62	384.2	2751.88	259.46	11344.31	2435.86	669.99	350.05	1654.93	5.12	5.11	6.28	1.67	6.55	2.33	20.20	3.08	5.90	0.81	5.77										
input	40855.41	6856.77	3122.53	28419.45	2999.03	27374.1	3087.42	9306.46	23538.02	5384.86	2375.44	13109.31	38.91	24.03	31.18	13.07	65.12	27.73	16.57	29.72	47.42	5.49	45.67	99.2	98.4	77.5	97.2	99.3	98.5	-35.6	92.4	88.5	91.8	99.5
regen treat 1	16939.94	52.19	50.25	6401.34	85.02	194.74	45.43	12615.49	1795.12	616.57	194.08	64.63	0.30	0.39	7.02	0.37	0.46	0.41	22.46	2.27	5.43	0.45	0.23										
input	41804.36	6525.95	6519.35	23660.36	8440.8	19031.84	5635.03	21109.68	23497.29	5568.26	3517.01	13177.16	37.04	50.18	25.96	36.77	45.27	50.61	37.58	29.67	49.04	8.12	45.91	93.9	95.8	12.7	96.2	93.7	98.8	46.8	89.5	89.3	97.9	94.7
regen treat 2	17380.64	400.1	271.91	20663.72	321.03	1200.72	66.82	11228.66	2466.3	594.34	73.76	693.74	2.27	2.09	22.67	1.40	2.86	0.60	19.99	3.11	5.23	0.17	2.42										
Trial 3																																	
input	37443.85	6596.17	1865.26	43635.3	9290.68	27411.55	5866.23	31856.68	27023.85	4203.03	8432.11	12444.69	37.43	14.36	47.87	40.48	65.21	52.68	56.72	34.12	37.01	19.48	43.35	89.0	73.6	61.9	91.8	90.6	96.6	66.5	80.4	84.3	97.0	90.5
initial treat	41634.12	722.86	491.74	16646.59	757.94	2583.3	198.23	10684.81	5294.5	660.72	253.28	1178.39	4.10	3.78	18.26	3.30	6.15	1.78	19.02	6.68	5.82	0.59	4.11										
input	40352.5	6374.11	2494.66	42001.39	8935.55	26073.37	5699.64	29696.47	30063.03	5280.13	2885.53	6808.62	36.17	19.20	46.08	38.93	62.02	51.19	52.87	37.96	46.50	6.67	23.72	99.3	99.0	52.4	98.5	99.7	99.4	42.8	82.8	88.2	94.5	98.1
regen treat 1	40369.15	46.66	24.62	19985.73	138.31	87.23	36.64	16980.17	5157.68	623.8	158.9	129.47	0.26	0.19	21.92	0.60	0.21	0.33	30.23	6.51	5.49	0.37	0.45										
input	16738.6	6821.61	5291.86	41835.72	9691.38	10234.24	5971.93	30250.59	12551.39	2272.31	9578.08	11303.9	38.71	40.73	45.90	42.22	24.35	53.63	53.86	15.85	20.01	22.13	39.38	97.7	99.1	87.9	99.3	97.7	99.7	69.9	84.9	79.3	99.2	97.8
regen treat 2	42909.88	156.18	45.01	5047.57	68.51	238.04	18.17	9096.39	1896.77	471.27	75.23	249.89	0.89	0.35	5.54	0.30	0.57	0.16	16.19	2.39	4.15	0.17	0.87										

SOMS Regeneration Data (Methamol)

Regen cycle	Sample Type	Peak Areas												Concentration (ppb)											% Absorbed										
		[M2] PFOA	PBFA	PFBS	PFDA	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFOSA	PFPeA	PBFA	PFBS	PFDA	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFOSA	PFPeA	PBFA	PFBS	PFDA	PFHpA	PFHxA	PFHxS	PFNA	PFOA	PFOS	PFOSA	PFPeA
0	input	41394	10286	2773	38031	11981	36479	6275	30767	32234	4696	7487	18908	58.4	21.3	41.7	52.2	86.8	56.4	54.8	40.7	41.4	17.3	65.9	68.7	64.1	97.8	90.5	96.2	93.7	98.2	93.2	95.3	99.5	79.6
	treated	43854	3223	996	831	1135	1375	395	566	2207	219	38	3865	18.3	7.7	0.9	4.9	3.3	3.5	1.0	2.8	1.9	0.1	13.5											
1	input	42873	9126	3077	16018	9421	31961	6144	27573	27279	3896	12262	7265	51.8	23.7	17.6	41.0	76.0	55.2	49.1	34.4	34.3	28.3	25.3	42.1	64.1	86.0	86.6	92.8	91.1	84.6	87.9	89.8	98.5	21.5
	treated	45690	5288	1104	2240	1263	2303	545	4246	3314	398	181	5700	30.0	8.5	2.5	5.5	5.5	4.9	7.6	4.2	3.5	0.4	19.9											
2	input	44117	8881	2367	22937	11787	11971	3382	35467	33889	4050	3714	16398	50.4	18.2	25.2	51.4	28.5	30.4	63.1	42.8	35.7	8.6	57.1	27.0	13.3	85.8	80.3	70.5	72.8	81.9	85.1	86.5	92.2	49.0
	treated	47138	6486	2053	3251	2327	3537	921	6430	5055	548	290	8358	36.8	15.8	3.6	10.1	8.4	8.3	11.4	6.4	4.8	0.7	29.1											
3	input	45034	8666	6857	16945	11630	12142	6253	33584	33108	6279	4059	16358	49.2	52.8	18.6	50.7	28.9	56.2	59.8	41.8	55.3	9.4	57.0	24.3	70.9	54.3	94.1	74.0	88.2	82.9	95.8	90.6	93.1	77.5
	treated	16941	6564	1994	7745	681	3162	736	5756	1407	588	282	3684	37.3	15.3	8.5	3.0	7.5	6.6	10.2	1.8	5.2	0.7	12.8											
4	input	41693	9135	5451	20890	11206	10870	3378	35811	35144	6326	3483	16807	51.8	42.0	22.9	48.8	25.9	30.3	63.8	44.4	55.7	8.0	58.6	21.0	76.5	31.3	71.4	58.4	54.5	75.5	77.4	81.6	83.2	34.1
	treated	42162	7217	1279	14350	3202	4526	1538	8761	7943	1164	585	11073	41.0	9.8	15.7	13.9	10.8	13.8	15.6	10.0	10.3	1.4	38.6											
5	input	37646	9085	6903	15989	3909	10828	3447	32845	31924	6238	3955	8171	51.6	53.1	17.5	17.0	25.8	31.0	58.5	40.3	54.9	9.1	28.5	21.6	58.1	83.4	29.0	58.7	64.3	84.0	83.6	88.0	89.1	-36.3
	treated	42588	7120	2890	2662	2775	4470	1230	5243	5247	748	430	11141	40.4	22.2	2.9	12.1	10.6	11.0	9.3	6.6	6.6	1.0	38.8											
6	input	41388	8775	2095	23247	10865	33243	6343	35955	33987	6106	2972	17395	49.8	16.1	25.5	47.3	79.1	57.0	64.0	42.9	53.8	6.9	60.6	22.3	-54.6	59.2	75.4	84.8	94.3	80.9	84.7	89.9	84.9	72.2
	treated	17170	6816	3239	9482	2671	5050	364	6874	5188	615	448	4829	38.7	24.9	10.4	11.6	12.0	3.3	12.2	6.5	5.4	1.0	16.8											
7	input	16388	8191	1880	24224	11365	36036	6125	30884	13447	4013	9053	15654	46.5	14.5	26.6	49.5	85.7	55.0	55.0	17.0	35.3	20.9	54.5	22.0	-68.2	80.2	70.3	55.7	79.9	86.1	61.3	90.2	97.0	73.0
	treated	19792	6385	3163	4786	3370	15970	1229	4299	5202	395	268	4222	36.2	24.3	5.3	14.7	38.0	11.0	7.7	6.6	3.5	0.6	14.7											
8	input	37229	7809	2719	42846	10783	33802	5680	31038	31610	1867	8259	7605	44.3	20.9	47.0	47.0	80.4	51.0	55.3	39.9	16.4	19.1	26.5	58.7	50.6	93.1	83.6	78.4	87.5	91.0	95.0	83.2	98.9	75.6
	treated	16884	3226	1344	2959	1766	7294	709	2802	1575	313	91	1855	18.3	10.3	3.2	7.7	17.3	6.4	5.0	2.0	2.8	0.2	6.5											
9	input	37385	7570	6956	41559	3993	25168	5661	30480	13472	3808	8060	13583	43.0	53.5	45.6	17.4	59.9	50.8	54.3	17.0	33.5	18.6	47.3	37.1	79.7	94.4	69.0	67.3	89.3	92.6	89.8	92.5	99.6	79.2
	treated	17014	4765	1409	2315	1238	8237	605	2263	1372	287	28	2828	27.0	10.8	2.5	5.4	19.6	5.4	4.0	1.7	2.5	0.1	9.9											
Trial 2																																			
0	input	43610	9760	2692	36414	12186	36779	6098	32719	33794	3983	2040	18159	55.4	20.7	39.9	53.1	87.5	54.8	58.3	42.7	35.1	4.7	63.3	76.1	70.2	96.1	90.3	95.8	92.6	94.1	92.0	90.8	96.5	92.6
	treated	46962	2334	803	1423	1181	1546	450	1936	2697	367	70	1343	13.2	6.2	1.6	5.1	3.7	4.0	3.4	3.4	3.2	0.2	4.7											
1	input	18906	9122	5123	50345	3562	30999	5846	35911	14209	2592	3689	15812	51.8	39.4	55.2	15.5	73.7	52.5	63.9	17.9	22.8	8.5	55.1	64.3	84.9	87.0	67.1	94.9	91.9	87.8	76.0	82.0	93.9	76.7
	treated	45797	3256	773	6531	1174	1586	472	4379	3414	467	226	3684	18.5	6.0	7.2	5.1	3.8	4.2	7.8	4.3	4.1	0.5	12.8											
2	input	43756	8520	1999	49892	11295	33657	3315	36461	35250	4203	3444	17349	48.4	15.4	54.7	49.2	80.1	29.8	64.9	44.5	37.0	8.0	60.4	50.1	44.0	94.6	88.6	93.4	84.1	94.3	89.9	89.3	90.4	72.4
	treated	44964	4249	1120	2702	1292	2222	528	2081	3566	450	332	4788	24.1	8.6	3.0	5.6	5.3	4.7	3.7	4.5	4.0	0.8	16.7											
3	input	44751	8615	6832	49630	11275	11887	2370	35882	32381	4273	5167	8249	48.9	52.6	54.4	49.1	28.3	21.3	63.9	40.9	37.6	11.9	28.7	32.9	76.2	94.2	84.5	76.0	69.3	84.0	88.1	86.1	94.8	58.4
	treated	42040	5780	1623	2857	1752	2848	728	5756	3854	593	268	3428	32.8	12.5	3.1	7.6	6.8	6.5	10.2	4.9	5.2	0.6	11.9											
4	input	39190	8459	2936	17217	11596	11874	6250	16170	33920	4494	3622	15079	48.0	22.6	18.9	50.5	28.2	56.1	28.8	42.8	39.6	8.4	52.5	22.2	27.9	31.3	92.8	5.9	84.5	81.3	82.2	82.2	86.4	73.8
	treated	41239	6582	2116	11826	837	11175	968	3031	6045	801	492	3947	37.4	16.3	13.0	3.6	26.6	8.7	5.4	7.6	7.1	1.1	13.7											
5	input	17637	8875	6603	50504	3400	10779	5915	37934	14788	2633	3781	16169	50.4	50.8	55.4	14.8	25.6	53.1	67.5	18.7	23.2	8.7	56.3	26.6	83.9	80.4	42.3	4.6	86.8	81.9	71.0	78.5	93.2	45.2
	treated	42789	6516	1066	9901	1960	10283	780	6871	4296	567	259	8865	37.0	8.2	10.9	8.5	24.5	7.0	12.2	5.4	5.0	0.6	30.9											
6	input	39756	8825	3559	52008	4014	31787	3159	37236	14548	2516	3537	14408	50.1	27.4	57.1	17.5	75.6	28.4	66.3	18.4	22.2	8.2	50.2	24.1	46.7	83.6	84.5	67.3	77.6	83.3	72.7	77.0	91.4	33.5
	treated	41830	6696	1898	8504	620	10399	709	6232	3974	579	305	9575	38.0	14.6	9.3	2.7	24.7	6.4	11.1	5.0	5.1	0.7	33.4											
7	input	14465	8089	5798	36333	11734	35856	6235	31435	13718	2179	9323	8485	45.9	44.6	39.9	51.1	85.3	56.0	56.0	17.3	19.2	21.5	29.6	21.2	61.2	98.3	72.1	36.6	88.0	97.9	83.7	93.2	95.9	-122.3
	treated	16087	6377	2249	611	3273	22729	747	654	2242	147	384	18864	36.2	17.3	0.7	14.3	54.1	6.7	1.2	2.8	1.3	0.9	65.7											
8	input	39704	7155	7157	42611	11064	30669	5794	31300	13304	2050	8237	16256	40.6	55.1	46.7	48.2	73.0	52.0	55.7	16.8	18.1	19.0	56.6	50.8	87.8	89.4	77.2	67.9	80.1	85.4	56.6	65.6	98.6	63.7
	treated	18939	3520	875	4517	2525	9837	1151	4569	5772	706	114	5898	20.0	6.7	5.0	11.0	23.4	10.3	8.1	7.3	6.2	0.3	20.5											
9	input	14155	7854	1924	45258	8754	35751	6177	32376	14859	5599	9099	6805	44.6	14.8	49.6	38.1	85.0	55.5	57.6	18.8	49.3	21.0	23.7	44.5	55.6	90.3	76.8	71.7	84.9	86.3	62.7	89.1	93.5	59.0
	treated	42301	4356	854	4390	2029	10110	933	4436	5537	613	588	2792	24.7	6.6	4.8	8.8	24.0	8.4	7.9	7.0	5.4	1.4	9.7											
0	input	17798	9874	2760	40410	12012	36699	6305	33597	17527	2005	8585	17343	56.0	21.2	44.3	52.3	87.3	56.6	59.8	22.1	17.7	19.8	60.4	58.9	72.1	98.5	82.7	74.6	88.4	91.1	78.1	77.7	99.6	66.8
	treated	18918	4054	770	586	2077	9315	734	2977	3834	448	33	5757	23.0	5.9	0.6	9.0	22.2	6.6	5.3	4.8	3.9	0.1	20.1											
1	input	43280	8691	6092	17713	8575	31888	6384	34876	33955	6272	4472	7698	49.3	46.9	19.4	37.4	75.9	57.3	62.1	42.9	55.2	10.3	26.8	46.9	82.5	87.8	83.8	79.5	90.6	86.5	89.5	92.4	95.0	35.0
	treated	46951	4619	1065	2167	1392	6524	601	4717	3550	479	225	5001	26.2	8.2	2.4	6.1	15.5	5.4	8.4	4.5	4.2	0.5	17.4											
2	input	42091	8205	6768	15227	4097	31586	3304	34670	33029	6104	4085	14092	46.6	52.1	16.7	17.8	75.1	29.7	61.7	41.7	53.8	9.4	49.1	32.6	76.7	50.7	46.7	91.0	75.7	94.6	94.5	93.8	94.2	50.4
	treated	19116	5527	1579	7500	2183	2852	804	1872	1816	376	238	6990	31.4	12.2	8.2	9.5	6.8	7.2	3.3	2.3	3.3	0.6	24.4											
3	input	44310	8059	6033	19234	11523	12345	2460	35129	34089	6113	3662	16127	45.7	46.4	21.1	50.2	29.4	22.1	62.5	43.0	53.8	8.5	56.2	23.1	71.3	91.0	85.1	76.4	75.7	95.2	91.0	95.0	95.4	78.0
	treated	42027	6196	1731	1736	1719	2912	599	1683	3082	309	167	3547	35.2	13.3	1.9	7.5	6.9	5.4	3.0	3.9	2.7	0.4	12.4											
4	input	14953	8585	6997	56611	10956	31841	6391	37553	12967	6008	5381	15665	48.7	53.9	62.1	47.7	75.7	57.4	66.9	16.4	52.9	12.4	54.6	22.1	56.9	95.9	76.0	88.6	93.0	87.9	59.7	88.5	92.4	70.8
	treated	42174	6683	3015	2335	2627	3628	449	4548	5231	690	412	4576	37.9	23.2	2.6	11.4	8.6	4.0	8.1	6.6	6.1	1.0	15.9											
5	input	38408	8088	7033	17306	11385	10459	2357	36176	33599	6158	12443	7140	45.9	54.1	19.0	49.6	24.9	21.2	64.4	42.4	54.2	28.7	24.9	15.4	58.2	86.7	79.6	59.0	64.4	87.4	87.3	90.9	97.0	35.0
	treated	41829	6842	2940	2301	2317	4285	839	4563	4269	562	373	4644	38.8	22.6	2.5	10.1	10.2	7.5	8.1	5.4	4.9	0.9	16.2											
6	input	40295	8386	6747	18223	11553	12803	2249	14581	32845	6171	12977	6781	47.6	51.9	20.0	50.3	30.5	20.2	26.0	41.5	54.3	30.0	23.6	18.5	58.3	86.6	77.4	59.3	57.7	85.7	87.5	91.1	97.9	34.0
	treated	40576	6833	2814	2448	2609	5209	951	2090	4117	546	271	4478	38.8	21.7	2.7	11.4	12.4	8.5	3.7	5.2	4.8	0.6	15.6											
7	input	38600	8220	2343	39553	4221	33742	3568	30154	33489	6076	3167	15681	46.6	18.0	43.4	18.4	80.3	32.0	53.7	42.3	53.5	7.3	54.6	60.4	18.8	98.9	19.7	25.4	78.0	98.2	92.9	98.3	85.8	20.5
	treated	42646	3258	1903	416	3391	25176	784	534	2394	104	448	12461	18.5	14.6	0.5	14.8	59.9	7.0	1.0	3.0	0.9	1.0	43.4											
8	input	38593	7680	1370	41427	12230	31763	2142	29942	32157	5706	2259	13031	43.6	10.5	45.4	53.3	75.6	19.2	53.3	40.6	50.2	5.2	45.4	32.3	-93.2	91.6	68.9	85.5	28.3	91.8	75.3	88.3	93.0	32.1
	treated	41587	5196	2647	3479	3800	4598	1537	2449	7957	668	158	8846	29.5	20.4	3.8	16.6	10.9	13.8	4.4	10.0	5.9	0.4	30.8											
9	input	39182	7711	5355	44712	12042	9973	3051	12680	32125	5469	9425	16138	43.8	41.2	49.1	52.5	23.7	27.4	22.6	40.6	48.2	21.8	56.2	30.8	82.8	97.4	78.1	-34.9	58.4	62.2	80.4	90.6	98.8	76.8
	treated	40179	5338	920	1155	2639	13457	1268	4797	6281	517	112	3746	30.3	7.1	1.3	11.5	32.0	11.4	8.5	7.9	4.5	0.3	13.0											