

**An Investigation of Factors Affecting the Adsorption
of Per- and Polyfluoroalkyl Substances (PFAS)
on Colloidal Activated Carbon (CAC):
Implications for In-situ Immobilization of PFAS**

by
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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

The research presented in this thesis was conducted at the University of Waterloo by myself under the supervision of Dr. Anh Pham. I wrote Chapters 1, 2, and 6 under the supervision of Dr. Anh Pham. The comments and suggested changes provided by the Examining Committee members helped improve the quality of the thesis.

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Chapter 4 was prepared in the form of a manuscript that will be submitted for journal publication. I contributed to developing the research idea, designed and conducted the adsorption experiments, analyzed and interpreted data, and wrote this chapter. Dr. Hak-Hyeon Kim helped me conduct experiments. The research reported in this manuscript was conducted under the supervision of Dr. Anh Pham.

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Abstract

The immobilization of per- and polyfluoroalkyl substances (PFAS) by colloidal activated carbon (CAC) barriers has been proposed as a potential in-situ method to mitigate the transport of plumes of PFAS in the subsurface. However, if PFAS are continuously released from a source zone, adsorptive sites on CAC will eventually become saturated, upon which point breakthrough of PFAS from a barrier will occur. To predict the long-term effectiveness of CAC barriers, it is important to investigate the factors that may affect the adsorption of PFAS on CAC. The objective of this research is to investigate some of these factors by answering the following questions: (1) How do co-contaminants, aquifer materials, and typical groundwater constituents affect the adsorption of PFAS by CAC?; and (2) How does reducing the particle size of activated carbons (ACs) affect their physico-chemical properties and ability to adsorb PFAS?

To address the first research question, the adsorption of seven anionic PFAS on a polymer-stabilized CAC (i.e., PlumeStop[®]) and a polymer-free CAC was investigated using batch experiments (Chapter 3). The research employed synthetic solutions consisting of one PFAS, 1 mM of sodium bicarbonate (NaHCO_3), and inorganic and organic solutes, including Na^+ , Cl^- , Ca^{2+} , dissolved organic carbon (DOC), diethylene glycol butyl ether (DGBE), trichloroethylene (TCE), benzene, 1,4-dioxane, and ethanol. It was observed that the affinity of PFAS to CACs was in the following order: PFOS > 6:2 FTS > PFHxS > PFOA > PFBS > PFPeA > PFBA. This result indicates that hydrophobic interaction was the predominant adsorption mechanism and that hydrophilic compounds such as PFBA and PFPeA will breakthrough CAC barriers first. The partition coefficient K_d for the adsorption of PFAS on the polymer-stabilized CAC was 1.3–3.5 times smaller than the K_d for the adsorption of PFAS on the polymer-free CAC, suggesting that the polymers decreased the adsorption, presumably due to competition. Thus, the PFAS adsorption

capacity of PlumeStop CAC barriers could increase once the polymers are biodegraded and/or desorbed. The affinity of PFOS and PFOA to CAC increased when the ionic strength of the solution increased from 1 to 100 mM, or when the concentration of Ca^{2+} increased from 0 to 2 mM. In contrast, less mass of PFOS and PFOA was adsorbed in the presence of 1–20 mgC/L Suwannee River fulvic acid, which represented dissolved organic carbon, or in the presence of 10–100 mg/L diethylene glycol butyl ether (DGBE), which is a major component in some aqueous film-forming foam (AFFF) formulations. Therefore, information on the occurrence of DGBE and other glycol ethers in AFFF-impacted groundwater is needed to assess if the effect of these species on CAC barrier performance is appreciable. The presence of 0.5–4.8 mg/L benzene or 0.5–8 mg/L TCE, the co-contaminants that may come along with PFAS at AFFF-impacted sites, diminished PFOS adsorption but had no effect or slightly enhanced PFOA adsorption. When the initial concentration of TCE was 8 mg/L, the K_d (514 ± 240 L/g) for the adsorption of PFOS was approximately 20 times lower than that in the TCE-free system ($K_d = 9,579 \pm 829$ L/g). Therefore, the effect of TCE and benzene may depend on the type of PFAS.

To gain insight into the effect of aquifer materials and water chemistry, the adsorption of PFOS, PFOA, and PFBS on CAC was investigated in the presence of six aquifer materials. Further, the removal of five PFAS (PFOS, PFOA, PFHxA, PFHxS, and 6:2 FTS) from six actual groundwater samples was studied (Chapter 4). Under the experimental conditions employed, the mass of PFBS, PFOA, and PFOS removed from the solution in the presence of CAC and aquifer materials was 2 to 4 orders of magnitude greater than the mass removed when only aquifer materials were present. It was also observed that the presence of aquifer materials did not appreciably affect the adsorption of PFBS, PFOA, and PFOS on CAC. In the experiments with six actual groundwater samples, the affinity of the studied PFAS to CAC was in the following order: PFOS > 6:2 FTS > PFOA ~

PFHxS > PFHxA, except for two instances of 6:2 FTS being the compound removed to the greatest extent. The adsorption affinity trend among the studied PFAS is consistent with the adsorption being driven by the hydrophobic effect. Principal component analyses (PCA) of the results obtained from the experiments with aquifer materials demonstrated that the correlation between the partition coefficient K_d for each PFAS and Ca^{2+} and DOC was the opposite of the correlations observed in Chapter 3. In the groundwater experiments, the correlation between K_d for each PFAS and ionic strength and Ca^{2+} was also the opposite of the correlations observed in Chapter 3. These opposite effects were hypothesized to be due to a complex interplay among various parameters affecting the adsorption of PFAS on CAC, which may confound the effect of each parameter. The results of this study indicate that laboratory experiments designed to evaluate the retention of PFAS in a CAC barrier should employ site-specific groundwater and aquifer materials.

To address the second research question, four commercial ACs (three granular and one powdered) were pulverized by grinding and micromilling to create powdered activated carbons (PACs) and CACs, and the adsorption of PFBS, PFOA, and PFOS on these adsorbents (11 in total) was investigated (Chapter 5). All three PFAS were adsorbed less by CACs ($d_{50} = 1.2\text{--}2.5\ \mu\text{m}$) than by their parents PACs ($d_{50} = 12\text{--}107\ \mu\text{m}$). A detailed characterization of the properties (surface area, micropore, and mesopore volumes, pH_{pzc} , and surface elemental composition) of these adsorbents suggests that the reduced adsorption capacity of CACs was likely the result of AC oxidation during milling, which decreased surface hydrophobicity. Granular activated carbons (GACs, $425\text{--}1,700\ \mu\text{m}$) adsorbed PFAS less than PACs and CACs, partly due to the slow rate of adsorption. Of all ACs, the materials made from wood possessed the greatest surface area and porosity but adsorbed PFAS the least. The repulsion between the negatively charged surface of these wood-based ACs ($\text{pH}_{\text{pzc}} = 5.1$) and the negatively charged headgroup of PFBS, PFOA, and

PFOS molecules was identified to be the dominant factor that inhibited adsorption. The results of this study suggest that the adsorption kinetic advantage of CACs may be achieved at the expense of reduced adsorption affinity and that the role of electrostatic interaction between PFAS and AC should be considered when selecting AC for PFAS treatment applications.

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Contents

List of Figures	v
List of Tables.....	x
List of Abbreviations.....	xii
List of Symbols	xv
Chapter 1: Introduction	1
1.1. Motivation	1
1.2. Thesis objective and organization	7
Chapter 2: Background	9
2.1. Per- and polyfluoroalkyl substances.....	9
2.2. PFAS treatment	13
2.3. Current knowledge about factors impacting the adsorption of PFAS on AC	14
2.4 Research Focus	29
Chapter 3: Factors Affecting the Adsorption of Per- and Polyfluoroalkyl Substances (PFAS) by Colloidal Activated Carbon	30
3.1. Introduction	31
3.2. Materials and Method.....	37
3.3. Results and Discussion	43
3.3.1 Adsorption kinetics	43
3.3.2 Adsorption trend	44
3.3.3 The effect of organics	51

3.3.4 The effect of ionic strength and Ca^{2+}	63
3.4. Conclusions	67
Chapter 4: An Investigation of the Effects of Aquifer Materials and Solution Chemistry on the Adsorption of PFAS by Colloidal Activated Carbon	70
4.1. Introduction	71
4.2. Materials and Method.....	74
4.2.1. Materials	74
4.2.2. Adsorption experiments.....	76
4.3. Results and Discussion.....	80
4.3.1. Adsorption in the presence of aquifer materials	80
4.3.2. Adsorption of a mixture of 5 PFAS in groundwater samples.....	91
4.4. Conclusion.....	98
Chapter 5: The Effect of Particle Size on the Adsorption of PFOS, PFOA, and PFBS by Granular, Powdered, and Colloidal Activated Carbons.....	100
5.1. Introduction	101
5.2. Materials and Methods	103
5.3. Results and Discussion.....	106
5.3.1 Adsorbent properties.....	106
5.3.2 Affinity of PFAS to wood-based, coconut shell-based, and coal-based ACs	109
5.3.3 Effect of particle size reduction on PFAS adsorption	113
5.4. Conclusion.....	120
Chapter 6: Implications and Recommendations	122

6.1 Implications	122
6.2 Recommendations	124
References	127
Appendix	143

List of Figures

Figure 3-1. Adsorption kinetics of PFAS on the polymer-containing CAC and the polymer-free CAC. Reaction solutions contained 0.2 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), and one of the following PFAS: [PFBA]₀ = 424 µg/L, [PFOA]₀ = 530 µg/L, [PFBS]₀ = 350 µg/L, [PFOS]₀ = 650 µg/L..... 43

Figure 3-2. Isotherms for the adsorption of PFAS on the polymer-containing CAC and the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), and one of the following PFAS: [PFBA]₀ = 424 µg/L, [PFPeA]₀ = 392 µg/L, [PFOA]₀ = 530 µg/L, [6:2 FTS]₀ = 1,100 µg/L, [PFBS]₀ = 350 µg/L, [PFHxS]₀ = 560 µg/L, [PFOS]₀ = 650 µg/L. The dashed lines represent the fitting of the experimental data to the Freundlich model. The fitting parameters are presented in Table 3-2. With the two lowest polymer-free CAC dosages, only less than 5 % PFBA was removed from the reaction solution. Thus, the PFBA/Polymer-free CAC result (in the panel on the right) was not fitted. 45

Figure 3-3. Isotherms for the adsorption of PFAS on the polymer-containing CAC (red circles) and the polymer-free CAC (blue circles). Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), and one of the following PFAS: [PFBA]₀ = 424 µg/L, [PFPeA]₀ = 392 µg/L, [PFOA]₀ = 530 µg/L, [6:2 FTS]₀ = 1,100 µg/L, [PFBS]₀ = 350 µg/L, [PFHxS]₀ = 560 µg/L, [PFOS]₀ = 650 µg/L. The dashed lines represent the fitting of the experimental data to the Freundlich model. With the two lowest polymer-free CAC dosages, only less than 5 % PFBA was removed from the reaction solution. Thus, the PFBA/polymer-free CAC result was not fitted. . 47

Figure 3-4. The effect of 1,4-dioxane (left panels) and ethanol (right panels) on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), either [PFOS]₀ = 650 µg/L or [PFOA]₀ = 530 µg/L, and either 1,4-dioxane or ethanol. The isotherm fitting parameters can be found in Table 3-3. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig S1 in the Appendix..... 52

Figure 3-5. The effect of DGBE on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), DGBE, and either

[PFOS]₀ = 650 µg/L or [PFOA]₀ = 530 µg/L. The dashed lines represent the fitting of the experimental data to the Freundlich model. The fitting parameters are presented in Table 3-3. . 54

Figure 3-6. Mass of diethylene glycol butyl ether (DGBE) removed. Reaction solutions contained either 0.1 or 0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5 - 8.5), [DGBE]₀ = 100 mg/L, and either [PFOS]₀ = 650 µg/L or [PFOA]₀ = 530 µg/L. 55

Figure 3-7. The effect of Suwannee River Fulvic Acid on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), SRFA, and either [PFOS]₀ = 650 µg/L or [PFOA]₀ = 530 µg/L. The isotherm fitting parameters can be found in Table 3-4. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig. S2 in the Appendix. 58

Figure 3-8. The effect of TCE and benzene on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), either TCE or benzene, and either [PFOS]₀ = 650 µg/L or [PFOA]₀ = 530 µg/L. The isotherm fitting parameters can be found in Table 3-5. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig. S3 in the Appendix. 61

Figure 3-9. The effect of Ca²⁺ and ionic strength on the adsorption of PFOS and PFOA by the polymer-free CAC. Reactions solution contained 0.1–0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5–8.5), and either [PFOS]₀ = 1100 µg/L (top left panel) or [PFOS]₀ = 650 µg/L (top right panel) or [PFOA]₀ = 530 µg/L. To eliminate the effect of ionic strength in Ca²⁺ experiments, between 0 and 5.7 mM of NaCl was added so that the ionic strength was 7 mM in all Ca²⁺ experiments. The isotherm fitting parameters can be found in Table 3-6. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig. S4 in the Appendix. 65

Figure 4-1. Schematic diagram illustrating the experimental approach employed to investigate the effect of aquifer materials on the adsorption of PFBS, PFOA, or PFOS. Each experimental set was conducted in triplicate. 77

Figure 4-2. Comparison of *K_d* values for the adsorption of PFBS, PFOA, and PFOS in Experimental Set 1 (i.e., suspensions containing only aquifer materials) and Experimental Set 2 (i.e., suspensions containing aquifer materials and CAC). Suspension composition: 1 mM

NaHCO₃, 500 g/L of aquifer material, 0.33 g/L CAC (in Experimental Set 2), and either [PFBS]₀ = 900 µg/L (~ 3.0 µM), [PFOA]₀ = 1,200 µg/L (~ 2.9 µM), or [PFOS]₀ = 1,390 µg/L (~ 2.8 µM). In the CAC/Borden, CAC/DNTS, and CAC/NFF systems, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for these systems. In the plot, the red circles representing these systems are positioned using the K_d value obtained from Experimental Set 3 for the x-axis and a K_d of $> 10^8$ for the y-axis. Experiments were conducted in triplicate, and average values along with one standard deviation (i.e., error bar) are presented. . 81

Figure 4-3. Aqueous phase concentration profiles of PFBS, PFOA, and PFOS. Reaction solutions contained 0.33 g/L CAC, 1 mM NaHCO₃, 500 g/L of either LSU or NFF, and one of the following PFAS: [PFBS]₀ = 900 µg/L, [PFOA]₀ = 1,200 µg/L, or [PFOS]₀ = 1,390 µg/L. The solution pH was 7.4 (in the system containing LSU) and 3.4 (in the system containing NFF). Experiments were conducted in duplicate and average values are presented. The error bars represent the min/max range of aqueous concentrations. 84

Figure 4-4. Comparison of K_d values for the adsorption of PFBS, PFOA, and PFOS on CAC in Experimental Set 3 (i.e., suspensions containing solutions that were previously in contact with aquifer materials, but the materials were removed prior to CAC addition) and in the buffer solution (i.e., solutions containing 1 mM NaHCO₃ and CAC). Suspension composition: 0.3 g/L CAC (in Experimental Set 2), and either [PFBS]₀ = 900 µg/L (~ 3.0 µM), [PFOA]₀ = 1,200 µg/L (~ 2.9 µM), or [PFOS]₀ = 1,390 µg/L (~ 2.8 µM). In the system that was in contact with NFF, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for this system. In the plot, the red circle representing this system is positioned using the K_d value obtained from the experiment with the buffer solution for the x-axis and a K_d of $> 10^8$ for the y-axis. Experiments were conducted in triplicate, and average values are presented along with one standard deviation (i.e., error bar). 86

Figure 4-5. The correlation between K_d values of PFAS adsorption on CAC and five solution chemistry parameters. The angles between the vectors represent the correlation between the parameters. In the system that was incubated with NFF, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for this system. Therefore, in the PFOS plot, the dots representing the NFF system are positioned by using the highest K_d value

among the K_d values of all systems. The location of each observation point on the plot relative to each parameter vector represents the magnitude of the parameter for the observation point. For example, the pH of the solution increases in the direction pointed by the pH arrow, and the NFF point is located in the opposite direction because the solution incubated with NFF has the lowest pH. On the contrary, the NFF point is located in the direction pointed by the K_d arrow, as K_d is the highest in the solution incubated with NFF. 87

Figure 4-6. Comparison of K_d values for the adsorption of PFBS, PFOA, and PFOS on CAC in Experimental Set 3 (K_{d-S3}) and Experimental Set 2 (K_{d-S2}). In the system that was in contact with NFF, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$) in both experimental sets, and K_d could not be calculated. Thus, there is no data point on the plot for K_d representing the NFF systems. In the systems wherein the solution was incubated with either Borden or DNTS for 2 weeks (i.e., Experimental Set 2), all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated. In the plot, the red circles representing these systems are positioned using the K_{d-S3} value obtained from the experiment wherein Borden and DNTS were removed after 1 week (i.e., Experimental Set 3) and a K_d of $> 10^8$ for the y-axis. The region within the two dashed lines is where K_{d-S3} and K_{d-S2} are different by less than 50 %. Experiments were conducted in triplicate, and average values are presented along with one standard deviation (i.e., error bar). 90

Figure 4-7. Aqueous phase concentration profiles of the studied PFAS in GW 1 and GW 6 PFBS, PFOA, and PFOS. Reaction solutions contained: 0.34 g/L CAC, and a mixture of the following PFAS: $[\text{PFHxA}]_0 = 407 \text{ } \mu\text{g/L}$, $[\text{PFHxS}]_0 = 519 \text{ } \mu\text{g/L}$, $[\text{PFOA}]_0 = 537 \text{ } \mu\text{g/L}$, $[\text{PFOS}]_0 = 649 \text{ } \mu\text{g/L}$, $[\text{6:2 FTS}]_0 = 555 \text{ } \mu\text{g/L}$, and several other PFAS at concentrations $< 10 \text{ } \mu\text{g/L}$ (see Table 4-5 for the list of the other PFAS and their concentrations). The solution pH in the experiments with GW 1 varied between 7.1 and 7.6, while the pH in the experiments with GW 6 varied between 5.3 and 5.5. Experiments were conducted in duplicate and average values along with a range (i.e., error bar) are presented. 93

Figure 4-8. Adsorption of PFHxA, PFOA, PFHxS, 6:2 FTS, and PFOS on CAC in 6 groundwater types. For GW 1 experiment, reaction solutions contained 0.09, 0.18, 0.22, 0.34, 0.45 g/L, and 0.69 g/L CAC. Since all PFOS and 6:2 FTS mass was removed at CAC = 0.45 g/L and 0.69 g/L,

in the GW 2–6 experiments, the reaction solution contained 0.05, 0.09, 0.18, 0.22, 0.34, and 0.45 g/L CAC. All groundwaters also contained a mixture of the following PFAS: $[PFHxA]_0 = 407 \mu\text{g/L}$, $[PFHxS]_0 = 519 \mu\text{g/L}$, $[PFOA]_0 = 537 \mu\text{g/L}$, $[PFOS]_0 = 649 \mu\text{g/L}$, $[6:2 \text{ FTS}]_0 = 555 \mu\text{g/L}$, and several other PFAS at $< 10 \mu\text{g/L}$ (see Table 4-5 for the list of the other PFAS and their concentrations). Experiments were conducted in duplicate and average values along with a range (i.e., error bar) are presented. 95

Figure 4-9. The correlations between K_d of PFAS adsorption on CAC and five solution chemistry parameters in groundwater samples. K_d values were calculated using the data points which represented systems containing 0.22 g/L CAC in the isotherms shown in Fig. 4-8. 96

Figure 5-1. Aqueous phase concentrations of PFBS, PFOA, and PFOS as a function of time. Reaction solutions contained 1 mM NaHCO_3 ($\text{pH} = 7.9\text{--}8.5$) and one of the following PFAS: $[PFBS]_0 = 900 \mu\text{g/L}$, $[PFOA]_0 = 1,200 \mu\text{g/L}$, or $[PFOS]_0 = 1,390 \mu\text{g/L}$. The concentration of AC was either 0.08 g/L in the experiments with GACs, ActiC PAC, and ActiC CAC, or 0.04 g/L (in all other PAC and CAC experiments). The error bars represent the min/max of aqueous phase data from duplicate bottles. 110

Figure 5-2. The relationship between adsorption density (C_s) and aqueous phase concentration (C_w). Note that for the systems wherein adsorption equilibrium had not been established at the end of the experiment (12 out of 33 systems), the $C_s\text{--}C_w$ relationship does not represent an adsorption isotherm. The lines connecting the data points are only meant to enhance the visual comparison of $C_s - C_w$ relationships. Reaction solutions contained 1 mM NaHCO_3 ($\text{pH} = 7.9\text{--}8.5$), 0.02, 0.03, 0.04, 0.08, 0.15, and 0.2 g/L AC, and one of the following PFAS: $[PFBS]_0 = 900 \mu\text{g/L}$, $[PFOA]_0 = 1,200 \mu\text{g/L}$, or $[PFOS]_0 = 1,390 \mu\text{g/L}$. The contact time between the solution and AC was 72 h. The error bars represent the min/max of aqueous phase data from duplicate bottles. 114

List of Tables

Table 2-1. Major PFAS classes.	9
Table 2-2. Examples of guidelines and screening values of PFAS in drinking water and groundwater	12
Table 2-3. Studies on PFAS adsorption by CAC and PAC	15
Table 3-1. The quantitative method for PFAS analysis.	41
Table 3-2. The linear and Freundlich isotherm parameters for the adsorption of PFAS on PlumeStop® and polymer-free CAC (Fig. 3-2). The +/- values represent the 95 % confidence interval for each isotherm parameter.	48
Table 3-3. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of 1,4-dioxane, ethanol, and DGBE (Figures 3-4 and 3-5). The +/- values represent the 95 % confidence interval for each isotherm parameter.	53
Table 3-4. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of SRFA (Figure 3-7). The +/- values represent the 95 % confidence interval for each isotherm parameter.	59
Table 3-5. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of TCE and benzene (Fig. 3-8). The +/- values represent the 95 % confidence interval for each isotherm parameter.....	62
Table 3-6. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of NaCl and Ca ²⁺ (Fig. 3-9). The +/- values represent the 95 % confidence interval for each isotherm parameter.	66
Table 4-1. Properties of aquifer materials (from Xu and Thomson, 2009).....	75
Table 4-3. Chemistry of the solution that was in contact with aquifer material after 1 week (Experimental Set 3) and 2 weeks (Experimental Set 1)	83

Table 4-4. Water chemistry parameters of groundwater samples.	92
Table 4-5. PFAS originally presented in the groundwater samples (unit: $\mu\text{g/L}$).	92
Table 5-1. Physical and chemical characteristics of ACs: particle size, surface area, and pore volume.....	108
Table 5-2. 72-hour six-point average K_d values (L/Kg) for the adsorption of PFAS on ACs. ..	115

List of Abbreviations

4:2FTS	Sodium 1H,1H,2H,2H-Perfluoro-1-hexane sulfonic acid
6:2FTS	Sodium 1H,1H,2H,2H-Perfluoro-1-octane sulfonic acid
8:2FTS	Sodium 1H,1H,2H,2H-Perfluoro-1-decane sulfonic acid
AC	Activated carbon
ActiC	ActiCarbone
AFFF	Aqueous film-forming foams
AOPs	Advanced oxidation processes
ARPs	Advanced reduction processes
CAC	Colloidal activated carbon
CMC	Critical micelle concentration
DFT	Density functional theory
DGBE	Diethylene glycol butyl ether
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EPA	Environmental Protection Agency
F400	Filtersorb400
FOSA	Perfluorooctane sulfonamide
GAC	Granular activated carbon
GenX	Hexafluoropropylene oxide-dimer acid
GW	Groundwater
HDPE	High-density polyethylene
IC	Inorganic carbon
ITRC	Interstate Technology and Regulatory Council
IX	Ion exchange resins
LC/MS/MS	Liquid chromatography tandem mass spectrometry
LHA	Lifetime health advisory
LOD	Limit of detection
LOQ	Limit of quantitation
M2-4:2FTS	Sodium 1H,1H,2H,2H-Perfluoro-1-[¹³ C ₂]-hexane sulfonic acid
M2-6:2FTS	Sodium 1H,1H,2H,2H-Perfluoro-1-[¹³ C ₂]-octane sulfonic acid

M2-8:2FTS	Sodium 1H,1H,2H,2H-Perfluoro-1-[¹³ C ₂]-decane sulfonic acid
M2PFTeDA	Perfluoro[1,2- ¹³ C ₂]tetradecanoic acid
M3PFBS	perfluoro[2,3,4- ¹³ C ₃]butane sulfonic acid
M3PFHxS	Perfluoro[1,2,3- ¹³ C ₃]hexane sulfonic acid
M4PFH _p A	Perfluoro[1,2,3,4- ¹³ C ₄]heptanoic acid
M5PFH _x A	Perfluoro[1,2,3,4,6- ¹³ C ₅]hexanoic acid
M5PFPeA	Perfluoro[¹³ C ₅]pentanoic acid
M6PFDA	Perfluoro[1,2,3,4,5,6- ¹³ C ₆]decanoic acid
M7PFUdA	Perfluoro[1,2,3, 4,5,6,7- ¹³ C ₇]undecanoic acid
M8FOSA	Perfluoro-1-[¹³ C ₈]octanesulfonamide
M8PFOA	Perfluoro[¹³ C ₈]octanoic acid
M8PFOS	Perfluoro[¹³ C ₈]octane sulfonic acid
M9PFNA	Perfluoro[¹³ C ₉]nonanoic acid
MCL	Maximum contaminant levels
MPFBA	Perfluoro[¹³ C ₄]butanoic acid
MPFDoA	Perfluoro[1,2- ¹³ C ₂]dodecanoic acid
NAPL	Non-aqueous phase liquid
N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid
N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
PBP _e S	Perfluoropentane sulfonic acid
PCA	Principal component analysis
PCBs	Polychlorinated biphenyls
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCAs	Perfluoroalkyl carboxylic acids
PFDA	Perfluorodecanoic acid
PFDoA	Perfluorododecanoic acid
PFDS	Perfluorodecane sulfonic acid
PFH _p A	Perfluoroheptanoic acid
PFH _p S	Perfluoroheptane sulfonic acid

PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid
PFNS	Perfluorononane sulfonic acid
PFOA	Perfluorooctanoic acid
PFPeA	Perfluoropentanoic acid
PFSAs	Perfluoroalkyl sulfonic acids
PFTeDA	Perfluorotetradecanoic acid
PFTTrDA	Perfluorotridecanoic acid
PFUdA	Perfluoroundecanoic acid
pH _{pzc}	The point of zero charge
polyDADMAC	Polydiallyldimethyl ammonium chloride
PP	Polypropylene
PSD	Particle size distribution
PV	Pore volume
SDS	Sodium decyl sulfate
SSA	Specific surface area
TCE	Trichloroethylene
TOC	Total organic carbon
XPS	X-ray photoelectron spectroscopy

List of Symbols

C_0	The initial concentration of adsorbate (mg/L)
C_{AC}	The concentration of activated carbon (g/L)
C_{CAC}	The concentration of colloidal activated carbon (g/L)
C_s	The concentration of adsorbate in the solid phase (mg/g)
C_w	The concentration of adsorbate in the aqueous phase (mg/L)
K_d	Partition coefficient (L/Kg)
K_{d-72h}	72-hour partition coefficient (L/Kg)
$K_{d-72h-av}$	Averaged 72-hour Partition coefficient (L/Kg)
K_{d-S2}	Partition coefficient in systems in which aquifer materials were not removed (L/Kg)
K_{d-S3}	Partition coefficient in systems in which aquifer materials were removed (L/Kg)
K_f	Freundlich constant (mg/g)(mg/L) ⁻ⁿ
n	Freundlich exponential term
R	Retardation factor
ρ_b	Dry bulk density (g/cm ³)
θ	Effective porosity (cm ³ /cm ³)

Chapter 1: Introduction

1.1. Motivation

Per- and polyfluoroalkyl substances (PFAS) are a family of chemicals that possess extremely high thermal and chemical stability (Kissa, 2001). Owing to these unique properties, PFAS have been used in various commercial and industrial products, notably in aqueous film-forming foams (AFFFs) used to extinguish hydrocarbon fires (Moody and Field, 2000). Due to the historical use of AFFFs at fire-fighting training/fire response sites, PFAS have been detected in groundwater passing beneath these sites at concentrations ranging from < 1 –1000 $\mu\text{g/L}$ (Xia et al., 2017; Houtz et al., 2013; Bräunig et al., 2017). As a result, communities can be exposed to PFAS through various pathways, including consuming drinking water impacted by PFAS-containing groundwater (Andrews and Naidenko, 2020). The presence of PFAS in drinking water has been documented around the world. Recent studies estimated that 18–80 million people in the United States (US) consume water containing PFAS, while 3.6 million people in Sweden reside near PFAS-impacted sites (Andrews and Naidenko, 2020; Banzhaf et al., 2017). While no similar statistics have been reported for Canada, incidents of PFAS contaminating water resources and the environment have been documented in several places, including in North Bay (ON) (North Bay Parry Sound District Health Unit, 2017), Mississippi Mills (ON) (Kristy Nease, 2016), Hamilton (ON) (De Solla et al., 2012) and Lac-Mégantic (QC) (Mejia-Avendaño et al., 2017). Notably, a study estimated that more than 150 military and civilian airports in Canada are likely contaminated with PFAS as a result of AFFF released in firefighting training (Milley et al., 2018). While the toxicity of PFAS is not well understood, exposure to PFAS has been linked to health issues such

as increased blood cholesterol (Nelson et al., 2009), liver damage (Costello et al., 2022), kidney and testicular cancer (Barry et al., 2013), and thyroid disorders (Ballesteros et al., 2017). Considering that humans and ecosystems can be exposed to PFAS in groundwater and that future regulations may enforce remediation of PFAS-contaminated sites, it is crucial to develop technologies that can effectively remove PFAS from impacted groundwater.

Contaminated groundwater can be remediated ex situ or in situ. Ex-situ remediation, also known as pump and treat, involves extracting groundwater to the surface and treating it, followed by discharging the treated water to a publicly owned treatment system. Contrary to ex-situ remediation, in-situ remediation may involve injecting chemical and/or biological amendments into the subsurface to initiate reactions that can destroy contaminants in place. Compared to ex-situ remediation, in-situ remediation could be less energy intensive and potentially has a shorter operational timeframe and smaller carbon footprint. As such, in-situ remediation is a preferable method whenever possible (Suthersan and Payne, 2005). To date, however, PFAS-contaminated groundwater has been primarily treated by ex-situ approaches. This is because PFAS are extremely resistant to chemical and biological degradation and, therefore, cannot be destroyed in situ under typical subsurface conditions (Ross et al., 2018).

Recently, several studies have proposed the immobilization of PFAS in situ by adsorption barriers, which can be created by injecting particulate or chemical amendments into the subsurface. For example, Aly et al. demonstrated that the breakthrough of PFOA and PFOS in a one-dimensional column was delayed by 8–20 pore volumes (PV) when the column was amended with cationic polymers polyamine (PA) and polydiallyldimethyl ammonium chloride (polyDADMAC) (Aly et al., 2019). Subsequent to this study, the same research group demonstrated that by injecting a mixture of powdered activated carbon (PAC) and polyDADMAC into an Ottawa sand-packed

column, the breakthrough of PFOS and PFOA was delayed by three orders of magnitude (equivalent to 4,000–6,000 PVs) (Liu et al., 2020). They also demonstrated that injecting Amberlite IRA910 ion-exchanged resins stabilized by Pluronic F-127 polymer into an Ottawa sand-packed column resulted in a uniform adsorption zone that delayed the breakthrough of PFOS and PFOA by more than five orders of magnitude (equivalent to 5,900–9,240 PVs) (Liu et al., 2022). In parallel with bench-scale studies, there have been efforts to demonstrate in-situ immobilization of PFAS in the field (McGregor, 2018; Carey et al., 2019; McGregor, 2020a; McGregor and Benevenuto, 2021; McGregor and Zhao, 2021; Niarchos et al., 2023a). In what appears to have been the first field study on the in-situ immobilization of PFAS, McGregor demonstrated that an adsorption barrier, created by injecting PlumeStop[®] (a colloidal activated carbon (CAC) suspension trademarked by Regenesis, San Clemente, CA, US) into the subsurface, successfully contained PFOS and PFOA at a site located in a shallow silty sand aquifer in Central Canada (McGregor, 2018). At this location, following the injection of CAC into the source zone, the concentration of PFOS (3,260 ng/L) and PFOA (1,450 ng/L) decreased to below detectable levels (20 ng/L) (McGregor, 2018; Carey et al., 2019). In a separate study, McGregor conducted pilot-scale tests to evaluate the in-situ immobilization of PFAS by PlumeStop CAC, Calgon WPC[®] powdered activated carbon (PAC), Purolite Purofine PFA694E[®] ion-exchange (IX) resin, and biochar (McGregor, 2020). In each test cell, the concentration of all PFAS dropped from 140–24,000 ng/L to below detectable levels (10 ng/L) following injection. PlumeStop CAC was also used in the study by Niarchos et al. to immobilize PFAS in the groundwater at a historical firefighting training area in Sweden (Niarchos et al., 2023a). Following CAC injection at this site, the total concentration of 11 PFAS in a monitoring well downgradient of the CAC barrier decreased by as much as 76 % (Niarchos et al., 2023a).

Although the bench-scale and field-scale studies mentioned above indicate that in-situ adsorption barriers could potentially be an effective means of containing plumes of PFAS, it is important to recognize that, as with any sorption-based technology, the breakthrough of PFAS will take place once the adsorptive sites in a barrier are exhausted if PFAS is continuously released from a source zone upstream. In the pilot-scale tests conducted by McGregor, it was observed that the concentrations of all PFAS in the cells injected with CAC have been below detectable levels after over a year (McGregor, 2020a). However, partial or full concentration rebounds were observed in the cells where biochar, Purofine PFA694E, and PAC were injected (McGregor, 2020a). At the site in Central Canada, the concentrations of PFOS and PFOA have remained undetected after more than six years in all monitoring wells downgradient of the CAC barrier (Personal communication with Rick McGregor). While more field studies and longer-term PFAS monitoring will be required to further evaluate the longevity of in-situ adsorption barriers, it is reasonable to expect that the retention and breakthrough of PFAS in a barrier will be dependent upon several factors, including the mass flux of PFAS entering the barrier, the mass of adsorbent injected and its distribution in the barrier, the competition for adsorptive sites among PFAS as well as between PFAS and co-contaminants, the presence of aquifer materials, and the groundwater water chemistry. **At the time when this research commenced (i.e., September 2017), to the best of the author's knowledge, there was no study on the impact of co-contaminants, aquifer materials, and typical groundwater constituents on the adsorption of PFAS on AC. As of August 2024, there has been only one study that investigated the effect of co-contaminants on PFAS adsorption by granular activated carbon (GAC) (Siriwardena et al., 2019), and one study on the effect of groundwater chemistry on the adsorption of PFAS on CAC (Molé et al. 2024).**

As mentioned earlier, various adsorbent types have been proposed for the in-situ immobilization of PFAS, including PAC, CAC, IX, and biochar. Among these materials, PAC and CAC are the most widely used adsorbents. GAC is pulverized to produce PAC and CAC. Pulverizing GAC into PAC (diameter between 10 to 150 μm) and CAC (diameter between 0.1 to 5 μm) reduces their particle size, which enables their injection into the subsurface under low (< 400 KPa for CAC) to medium pressures (~ 2500 KPa for PAC) ((McGregor and Benevenuto, 2021; McGregor 2020b). In addition, studies have shown that particle size reduction also enhances the rate of contaminant adsorption as it decreases the intraparticle diffusion distance (i.e., the distance between the external surface of the adsorbent and the adsorptive sites inside the adsorbent pores) (Matsui et al., 2009). For example, in a study by Yu et al., the rate of adsorption of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) on a coal-based GAC (900–1,000 μm) was shown to be slower than the rate of adsorption on PAC (< 100 μm) (Yu et al., 2009). In another study, Wu et al. pulverized three types of AC into four particle size ranges. Wu et al. observed that during the first six hours of the adsorption experiment, only 25 % of PFAS mass was removed by ACs with the largest particle size range (1,000–1,700 μm), but more than 75 % of PFAS mass was removed by ACs of the smallest particle size range (10–75 μm) (Wu et al., 2020).

Grinding GAC into PAC and CAC also affects the adsorption capacity of AC by affecting the specific surface area and porosity of AC (Matsui et al., 2004; Bonvin et al., 2016; Pan et al., 2017). To date, there appears to be no consensus on how reducing AC particle size affects the adsorption capacity of PAC compared to CAC. Bakkaloglu et al. compared the adsorption data from their study and 11 studies by others and showed that for hydrophobic adsorbates ($\log K_{ow} > 3$), the adsorption capacity of CACs was similar or greater than that of PACs, but for hydrophilic

compounds ($\log K_{ow} < 3$) the adsorption capacity of CACs was lower than that of PACs (Bakkaloglu et al., 2021).

Two the best of the author's knowledge, only two studies by Yu et al. and Hansen et al. directly compared the adsorption capacity of GAC versus PAC for PFAS (Yu et al., 2009; Hansen et al., 2010), and no published study has directly compared PFAS adsorption rate and affinity on PAC and CAC. In addition to these two studies, there has been a myriad of other studies that investigated the adsorption of PFAS on GAC, PAC, or CAC (e.g., Hansen et al., 2010; Zhi and Liu, 2015; Senevirathna et al., 2010; Ochoa-Herrera and Sierra-Alvarez, 2008; Siriwardena et al., 2019; Inyang and Dickenson, 2017; Zhang et al., 2016; Yu et al., 2012; Qu et al., 2009; Yu and Hu, 2011; Chularueangaksorn et al., 2014; Liang et al., 2011; Rattanaoudom et al., 2012; Senevirathna et al., 2010; Yao et al., 2014; Qian et al., 2017; Söregård et al., 2020; Deng et al., 2015; Du et al., 2015; Murray et al., 2019; Park et al., 2020; Qu et al., 2009; Umeh et al., 2023). Unfortunately, the findings of these studies cannot be readily compared because the experimental conditions employed varied widely. **Thus, additional research is needed to investigate how reducing the particle size of ACs affects their physico-chemical properties and ability to adsorb PFAS.**

1.2. Thesis objective and organization

The overarching goal of this research was to investigate some of the factors affecting the adsorption of PFAS on CAC, as developing a better understanding of these factors is important for predicting the performance of in-situ PFAS adsorption barriers. The remaining sections of this thesis are organized into five Chapters. Chapter 2 provides background on PFAS characteristics, applications, and treatment technologies, with a special emphasis placed on reviewing the current knowledge about PFAS adsorption on AC. Chapter 3 reports the results of a series of experiments designed to investigate the adsorption of seven PFAS on two commercial CACs, (i.e., a polymer-containing CAC and a polymer-free CAC), as well as the effects of five co-contaminants and three water chemistry parameters on the adsorption of PFOS and PFOA on the polymer-free CAC. These experiments were performed with synthetic water and in the absence of aquifer materials. The objective of the research reported in Chapter 4 was to expand the Chapter 3 research scope, by investigating the effect of six types of aquifer materials on the adsorption of PFOS, PFOA, and PFBS on the polymer-free CAC, as well as the adsorption of a mixture of five PFAS on this CAC in six actual groundwater samples. In Chapter 4, the correlation between the concentration of major groundwater constituents (i.e., ionic strength, dissolved organic carbon, Ca^{2+} , Mg^{2+} , and pH) and the affinity of these PFAS to the polymer-free CAC was assessed using principal component analysis (PCA). In Chapter 5, the adsorption of PFOS, PFOA, and PFBS on four types of CAC were investigated. These CACs were prepared by pulverizing GACs and PACs of different sources, including wood, coal, and coconut shells. The adsorption of PFAS on the parent GACs and PACs was also investigated. To gain insight into how pulverization affects the physico-chemical properties and adsorption performance of ACs, a detailed characterization of GACs,

PACs, and CACs was performed. Lastly, Chapter 6 summarizes key findings and their implications, and identifies future research needs.

Chapter 2: Background

2.1. Per- and polyfluoroalkyl substances

PFAS are a group of synthetic organic compounds whose chemical structure contains at least one fully fluorinated carbon atom and a functional group, such as carboxylic acid (-COOH), sulfonic acid (-SO₃H), alcohol (-OH), sulfonamides (-SO₂NR₂) and others (Organisation for Economic Co-operation and Development, 2018). PFAS are divided into two main groups of compounds, namely the *perfluoro* compounds, which are those that contain only fully fluorinated carbons in the chain, and the *polyfluoro* compounds, which are those that, in addition to the fully fluorinated carbons, also contain one or several hydrogenated carbons (Buck et al., 2011). Major classes of PFAS are listed in Table 2-1.

Table 2-1. Major PFAS classes.

Family	Class	Group	General chemical structure	Examples
Perfluoroalkyl substances	Perfluoroalkyl acids (PFAAs)	Perfluorocarboxylic acids (PFCAs)	$C_nF_{2n+1}-COOH$	Perfluorooctanoic acid (PFOA): $C_7F_{15}COOH$
		Perfluorosulfonic acids (PFSAs)	$C_nF_{2n+1}-SO_3H$	Perfluorooctane sulfonic acid (PFOS): $C_8F_{17}SO_3H$
	Perfluoroalkane sulfonamides (FASAs)	-	$C_nF_{2n+1}-SO_2NRR'$ where $R = C_mH_{2m+1}$ $R' = C_nH_{2n+1}$ $(m, n = 0, 1, 2, 4)$	Perfluorooctane sulfonamide (PFOSA): $C_8F_{17}SO_2NH_2$
				N-Ethyl perfluorooctane sulfonamide (EtFOSA): $C_8F_{17}SO_2N(C_2H_5)H$
				N-Methyl perfluorooctane sulfonamide (MeFOSA): $C_8F_{17}SO_2N(CH_3)H$

Table 2-1. Major PFAS classes (continued)

Family	Class	Group	General chemical structure	Examples
Polyfluoroalkyl substances	Fluorotelomer substances	n:2 Fluorotelomer sulfonic acids (n:2 FTSA)s	$C_nF_{2n+1}-CH_2CH_2SO_3H$	8:2 Fluorotelomer sulfonic acid (8:2 FTS): $C_8F_{17}CH_2CH_2SO_3H$
		n:2 Fluorotelomer alcohols (n:2 FTOH)s	$C_nF_{2n+1}-CH_2CH_2OH$	10:2 Fluorotelomer alcohol (10:2 FTOH): $C_{10}F_{21}CH_2CH_2OH$

Owing to the high electronegativity of the fluorine atoms and the low polarizability of the C-F bonds, together with the tendency of the functional groups to bear a charge, PFAS possess unique properties such as high chemical and thermal stability, hydrophobicity, and oleophobicity (Kissa, 2001). As a result, they have been used in a wide variety of products, including textiles, leathers, papers, industrial surfactants, resins, moulds, plastics, and others (Interstate Technology and Regulatory Council (ITRC), 2024). Notably, PFAS are an important component of AFFFs, which were historically used to extinguish hydrocarbon fires at places such as military bases, airports, petroleum refineries, and chemical plants (Sunderland, 2019). At these places, the release of large volumes of AFFF during firefighting training activities resulted in contaminated sites where the concentration of PFAS in groundwater can range from below one to a few thousand $\mu\text{g/L}$ (Houtz et al., 2013; Xiao et al., 2017; Bräunig et al., 2017). PFAS-contaminated groundwater at these sites poses serious risks to nearby residential areas that rely on groundwater as a source of drinking water (Andrews and Naidenko, 2020). In addition, the discharge of PFAS-containing groundwater to surface water can contaminate surface water resources and the ecosystem. While the toxicity of PFAS has not been fully understood, health issues such as cancer, increased blood cholesterol, liver damage, and effects on immune, metabolic, and neurodevelopmental systems have been

shown to be associated with exposure to PFAS (Sunderland, 2019). Because of these harmful effects on human health, several countries have developed guidelines for PFAS in drinking water. For example, US EPA has developed enforceable maximum contaminant levels (MCL) of 4.0 ng/L for PFOA and PFOS, and 10 ng/L for PFHxS, PFNA, and hexafluoropropylene oxide-dimer acid (GenX). In addition, US EPA has developed a hazard index of 1 for the mixture of PFBS, PFHxS, and PFNA (US EPA, 2024). In Canada, Health Canada has established drinking water quality guidelines for PFOS (600 ng/L) (Health Canada, 2018a) and PFOA (200 ng/L) (Health Canada, 2018b), and drinking water screening values for PFBA (30,000 ng/L), PFBS (15,000 ng/L), and 9 other PFAS (Health Canada, 2019). Recently, an objective of 30 ng/L for all PFAS that can be analyzed in drinking water has also been proposed by Health Canada (Health Canada, 2023). As our understanding of PFAS toxicity continues to improve, it can be expected that guidelines for more compounds in drinking water and for other environmental compartments (e.g., surface water, groundwater, soil and sediment, wastewater effluent) will be established (The European Union, 2020; US EPA, 2023). In fact, Denmark (Larsen and Giovalle, 2015), Germany (von der Trenck et al., 2018), and the US (US EPA, 2023) have already established guidance values for PFAS in groundwater, and there are several groundwater clean-up action levels across the US that are expected to become effective in the near future (ITRC, 2024). Table 2-2 summarizes some of the aforementioned regulations and guidelines.

Considering these anticipated regulations, as well as the role of PFAS-impacted groundwater in PFAS exposure to humans, a cost-effective technology must be developed to clean up PFAS-impacted groundwater.

Table 2-2. Examples of guidelines and screening values of PFAS in drinking water and groundwater

Location	Canada		The U.S.	The U.K.	Denmark
Source	Health Canada		Environmental Protection Agency	Drinking Water Inspectorate	Environmental Protection Agency
Media	Drinking water		Drinking water	Drinking water	Drinking water/Groundwater
Standard	Maximum acceptable concentration ^a (µg/L)	Screening value ^a (µg/L)	Enforceable maximum contaminant level ^b (µg/L)	The threshold for frequent sampling and monitoring ^c (µg/L)	Health-based value ^d (µg/L)
Compound	-		-	0.01 = any PFAS from a list of 47 PFAS including all PFAS listed in Table 2-2	0.1 = sum of PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUnS, PFDoS, PFTTrS, PFOSA, 6:2 FTS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA
PFBA	-	30	-		
PFPeA	-	0.2	-		
PFHxA	-	0.2	-		
PFHpA	-	0.2	-		
PFOA	0.2	0.2	0.040		
PFNA	-	0.02	0.010		
PFBS	-	15	-		
PFHxS	-	0.6	0.010		
PFOS	0.6	0.6	0.040		
6:2 FTS	-	0.2	-		
8:2 FTS	-	0.2	-		
					0.002 = sum of PFOA, PFOS, PFNA, PFHxS

^a (Health Canada, 2019)^b (US EPA, 2024)^c (Drinking Water Inspectorate, 2022)^d (Danish EPA, 2021)

2.2. PFAS treatment

A wide variety of PFAS treatment methods have been studied, including biological, chemical, and physical methods. Studies in the past decade have shown that biological treatments can only transform polyfluoroalkyl compounds into shorter-chain perfluoroalkyl compounds, which are highly resistant to further transformation (Arvaniti and Stasinakis, 2015). Chemical degradation methods that have been studied to destroy PFAS include incineration, advanced oxidation processes (AOPs), and advanced reduction processes (ARPs). Incineration involves thermal degradation of target contaminant by combustion at high temperatures (Loganathan et al., 2007). AOPs involve generating reactive species such as hydroxyl and sulfate radicals to oxidize contaminants. AOPs that have been studied for the degradation of PFAS include electrochemical oxidation (Schaefer et al., 2018), heat-activated persulfate (Bruten et al., 2018), photolytic/photochemical oxidation (Jin and Zhang, 2015), sonolysis (Moriwaki et al., 2005), sub- or supercritical oxidation (Hori et al., 2006; Chen et al., 2012), microwave-hydrothermal treatment (Lee et al., 2009), and high-voltage electric discharge (Stratton et al., 2017). ARPs employ reducing agents such as dithionite, sulfite, and sulfide (Vellanki et al., 2013). To activate these reducing agents, methods such as UV light, electron-beam irradiation, microwave irradiation, and ultrasonic irradiation have been used (Vellanki et al., 2013). Since incineration, AOPs, and ARPs require external energy and/or harsh operating conditions, they can only be implemented *ex-situ*, i.e., the contaminated groundwater has to be extracted to the surface prior to treatment. A study proposed heat-activated persulfate for in-situ PFAS remediation. However, this approach can only destroy PFCAs and not PFSAAs (Bruten et al., 2018).

Contrary to biological and chemical treatments, which aim to destroy PFAS, physical methods, such as adsorption (Murray et al., 2021; Zeng et al., 2020; McCleaf et al., 2017), membrane

filtration (Liu et al., 2021; Lee et al., 2022), and foam fractionation (Burns et al., 2021), remove PFAS from water by separation. While these technologies are relatively effective at removing PFAS from surface water and groundwater, they have only been applied ex situ. Recently, several studies have proposed that PFAS in groundwater can be immobilized in situ by stationary adsorption barriers, which can be created by injecting particulate or chemical amendments into the subsurface. Bench-scale and field-scale studies have demonstrated that in-situ adsorption barriers could potentially be an effective means of containing plumes of PFAS (McGregor, 2018; Carey et al., 2019; McGregor, 2020; McGregor and Benevenuto, 2021; McGregor and Zhao, 2021; Liu et al., 2020; Liu et al., 2022; Niarchos et al., 2023a). Subsequent sections of this chapter review existing studies concerning the adsorption of PFAS on AC to identify factors that may control the adsorption of PFAS on CAC in AFFF-impacted groundwater.

2.3. Current knowledge about factors impacting the adsorption of PFAS on AC

Over the past decade, researchers have investigated the adsorption of PFAS onto a wide variety of adsorbents, including GAC (Xiao et al., 2017), aluminosilicates (Wang et al., 2012), polymeric resins, and iron (hydr)oxides (Tang et al., 2010). GAC appears to be one of the most promising adsorbents (and thus the most studied one), owing to its low cost and ability to adsorb a wide range of PFAS. GAC is a popular adsorbent for the remediation of PFAS-contaminated groundwater ex situ (Gagliano et al., 2023). GAC is also being used by drinking water treatment plants to remove PFAS (McCleaf et al., 2017). There also have been several studies on the removal of PFAS by PAC and CAC, which are summarized in Table 2-3.

Table 2-3. Studies on PFAS adsorption by CAC and PAC

Sorbent type	Sorbent commercial name	Sorbent properties	Experimental conditions	Compound	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²	Ref.
PAC	Silcarbon TH90 extra	Iodine number = 1,000 mg/g Particle size = 80 % < 45 μm	Matrix = Well water T = 20 °C Sorbent mass = 20 mg Volume = 800 mL Initial concentration = 2–1400 ng/L Duration = 4 weeks	PFOS	2,512	0.9	0.53	Hansen et al, 2010
				PFHxS	0.8	0.32	0.99	
				PFOA	26.3	0.6	0.81	
PAC	BPL	Surface area = 1387 m ² /g Pore volume = 0.72 mL/g Particle size = 44 μm	Matrix = DI water T = 25 °C Sorbent mass = 10 mg Volume = 100 mL Initial concentration = 5–5,000 μg/L	PFOS	90	1	0.96	Zhi and Liu, 2015
	AquaNuchar	Surface area = 1860 m ² /g Pore volume = 3.79 mL/g Particle size = 45–150 μm		PFOA	966	1.29	0.97	
				PFOS	159	0.6	0.98	
				PFOA	69	0.66	0.97	
PAC	NA	Surface area = 812 m ² /g Particle size < 0.1 mm	Matrix = 2 mM NaH ₂ PO ₄ in DI water T = 25 °C pH = 5 Volume = 100 mL Initial concentration = 20–250 mg/L Duration = 12 h	PFOS	207.13	0.18	0.96	Yu et al., 2009
PAC	-	Surface area = 1000 m ² /g Particle size ≥ 100 mesh	Matrix = DI water Temperature = 25 °C Sorbent mass = 0.25 g Volume = 100 mL Initial concentration = 5–40 mg/L Duration = 2 h	PFOA	24.24	0.45	0.96	Qu et al., 2009

Table 2-3. Studies on PFAS adsorption by CAC and PAC (continued)

Sorbent type	Sorbent commercial name	Sorbent properties	Experimental conditions	Compound	$K_f(\text{mg/g})(\text{mg/L})^{-n}$	n	R^2	Ref.
PAC	-	Surface area = 763.8 m^2/g Particle size (nominal) $\leq 40 \mu\text{m}$	Matrix = 1 mM phosphate in DI water Temperature = 25 °C Sorbent mass = 2–20 mg/L Volume = 1 L pH = 7.2 Initial concentration = 10–300 $\mu\text{g/L}$ Duration = 7 days	PFOS	17.48	0.48	0.99	Yu et al., 2012
				PFOA	9.93	0.51	0.98	
			Matrix = The fresh PAC was first preloaded with EfOM ^a solution for 7 days, then the solution spiked with PFAS and was agitated for another 7 days Temperature = 25 °C Sorbent mass = 2–20 mg/L Volume = 1 L pH = 7.2 Initial concentration = 100 $\mu\text{g/L}$ Duration = 7 days	PFOS	1.06	0.67	0.92	
				PFOA	0.49	0.74	0.93	
			Matrix = EfOM ^a solution Temperature = 25 °C Sorbent mass = 2–20 mg/L Volume = 1 L pH = 7.2 Initial concentration = 100 $\mu\text{g/L}$ Duration = 7 days	PFOS	2.25	0.62	0.96	
				PFOA	1.16	0.64	0.95	

^a EfOM: effluent organic matter

Table 2-3. Studies on PFAS adsorption by CAC and PAC (continued)

Sorbent type	Sorbent commercial name	Sorbent properties	Experimental conditions	Compound	$K_f(\text{mg/g})(\text{mg/L})^{-n}$	n	R^2	Ref.
PAC	-	Surface area = 763.8 m ² /g Particle size (nominal) ≤ 40 μm	Matrix = 1 mM phosphate buffer Volume = 1 L Temperature = 25 °C Sorbent mass = NA Initial concentration = 0.1–500 μg/L Duration = 5 days	PFOS	17.48	0.48	> 0.98	Yu and Hu, 2011
				PFOA	10.03	0.54	> 0.98	
			Matrix = Effluent organic matter solution Volume = 1 L Temperature = 25 °C Sorbent mass = NA Initial concentration = 0.1–500 μg/L Duration = 5 days	PFOS	0.66	0.93	> 0.98	
				PFOA	0.20	1.11	> 0.98	
PAC	-	Surface area = 1521.85 m ² /g	Concentration = 30–200 mg/L Other conditions were not mentioned	PFOS	141.96	0.19	0.92	Liang et al., 2011
Magnetic PAC	-	Surface area = 947.9814 m ² /g			155.25	0.20	0.78	

Table 2-3. Studies on PFAS adsorption by CAC and PAC (continued)

Sorbent type	Sorbent commercial name	Sorbent properties	Experimental conditions	Compound	$K_f(\text{mg/g})(\text{mg/L})^{-n}$	n	R^2	Ref.
PAC	-	Not mentioned	Matrix = DI water Volume = 100 mL Temperature = 25 °C Sorbent mass = 1 g/L Initial concentration = 1–1000 mg/L Duration = 48 h	PFOS	32.57	0.47	0.91	Ratanaoudom et al., 2012
				PFOA	31.67	0.48	0.96	
PAC	-	Surface area = 980 m ² /g Particle size = 36 µm	Matrix = 0.1 M phosphate buffer in DI water Volume = 200 mL Temperature = 25 °C Sorbent mass = 0.067 g pH = 7 Initial concentration = 25–300 mg/L Duration = NA	PFOS	24.65	0.67	0.94	Punyapalakul et al., 2013
				PFOA	76.81	0.4	0.98	
PAC	-	Surface area = 1000 m ² /g Particle size ≥ 200 mesh	Matrix = 0.1 M phosphate buffer in DI water Volume = 100 mL Temperature = 25 °C Sorbent mass = 0.5 g Initial concentration = 0.5–25 mg/L Duration = 2.5 h	PFOS	0.55	0.68	0.90	Qian et al., 2017
Magnetic CAC	-	Particle size < 2 µm	Matrix = DI water Volume = 35 mL Temperature = 40 °C Sorbent mass = 5 mg Initial concentration = 0.05–0.72 mmol/L Duration = 24 h	PFBS	6.73	0.4	0.93	Meng et al., 2019
				PFHxS	19.90	0.33	0.97	
				PFOS	52.86	0.44	0.99	
				PFOA	46.65	0.35	0.94	
CAC	-	Particle size = 0.88 µm	CAC was coupled with ceramic microfiltration in a continuous flow system. Two sources of water were used: 1- Contaminated groundwater 2- Diluted firefighting containment tank water	5 PFCAs (C5 - C9) and 7 PFSAAs (C3 - C8)	-	-	-	Murray et al., 2019

Studies have shown that the adsorption of PFAS by AC is driven by hydrophobic, electrostatic, and van der Waals interactions, with the van der Waals interaction being insignificant because of the low polarizability of PFAS (Deng et al., 2012). Between the hydrophobic and electrostatic interactions, the hydrophobic interaction is usually more important, especially for longer-chain compounds such as PFOS and PFOA. The electrostatic interaction between the surface and the head group of PFAS molecules could also be important because PFCAs and PFSA are strong acids, and as such, they are negatively charged under environmental pH. Overall, the contributions of the hydrophobic and electrostatic interactions to the adsorption of PFAS on AC are impacted by various factors, including PFAS chain length and functional group, AC properties, solution chemistry, competitive sorption among PFAS compounds, and competitive sorption between PFAS and non-fluorinated co-contaminants (Gagliano et al., 2019). The effect of each of these factors on the adsorption of PFAS is summarized below.

PFAS chain length and functional group. Previous studies have shown that the affinity of PFAS to AC increased with chain length. In particular, it has been shown that PFOS and PFOA are better removed by GAC than PFBS and PFBA (Xiao et al., 2017). It has also been reported that among the compounds with the same number of carbons, PFSA have a greater affinity to AC than PFCAs (Xiao et al., 2017). This was attributed to the larger size of the sulfonate functional group in PFSA compared to the carboxylate group in PFCAs (Higgins and Luthy, 2007). It is important to note that the head group of PFCAs and PFSA carries a negative charge. As such, in addition to being driven by the hydrophobic interaction, PFAS sorption is also driven by the electrostatic interaction (attraction or repulsion) between the head group and the surface, the pre-sorbed PFAS molecule, or the sorbed organic matter and cations (Du et al., 2014) (The effect of organic matter and cations will be discussed in more detail later). In addition to the hydrophobic and electrostatic interactions

between PFAS and the surface, it has been proposed that the hydrophobic carbon chain of PFAS molecules can aggregate to form hemi-micelles/micelles or become an adsorption site for subsequent PFAS molecules to form bilayers (Du et al., 2014). The critical micelle concentrations (CMC) of PFAS (> 5 mg/L) are higher than the typical PFAS concentrations in AFFF-impacted groundwaters. However, it has been argued that the concentration of PFAS near the surface and inside the pores of adsorbents could exceed the CMC. If so, this could lead to the aggregation of PFAS, resulting in a multilayer sorption (Chen et al., 2017). However, the formation of micelle and/or multilayers of PFAS could also hinder adsorption by blocking adsorptive pores (Park et al., 2020). Therefore, it is unclear whether micelle formation on adsorbent surfaces would enhance or hinder PFAS removal.

It is noted that previous studies mostly investigated the adsorption of PFCAs and PFSAAs, but AFFF-impacted groundwaters often contain other types of PFAS such as fluorotelomer sulfonic acids (e.g., 6:2 FTS, 8:2 FTS). To date, there have been only two studies that investigated the removal of polyfluorinated compounds (4:2 FTS, 6:2 FTS, and 8:2 FTS, as well as several perfluoroalkyl sulfonamides) by GAC columns (Xiao et al., 2017; Rodowa et al., 2020). However, these studies employed solutions containing a mixture of PFAS with different initial concentrations. Due to the effect of initial concentration on competitive sorption among PFAS, it is difficult to evaluate the affinity of each fluorotelomer to AC based on the data reported in these studies. In a recent study, Hamid et al. conducted single-point adsorption of 6:2 FTS, 8:2 FTS, and 3 other fluorotelomer compounds by a biosolid-based activated carbon. However, Hamid et al. did not provide any quantitative parameters (e.g., partition coefficients, K_d) to evaluate the adsorption affinity of fluorotelomers to AC (Hamid et al., 2024). Moreover, these studies only used GAC and PAC, and there has been no study on the adsorption of fluorotelomer sulfonic acids on CAC.

AC properties. PAC and CAC can be produced by pulverizing granular activated carbon (GAC) made from various source materials (e.g., lignite or bituminous coal, coconut shells, wood). The adsorption of contaminants on GAC, PAC, and CAC can generally be described by an intraparticle diffusion model where diffusion of contaminants from the external surface into meso- and micropores is considered the rate-limiting step (Matsui et al., 2009). Consistent with this conceptual model, it has been demonstrated that the rate of adsorption is inversely proportional to the AC size (i.e., the adsorption rate follows $CAC > PAC > GAC$) (Yu et al., 2009; Matsui et al., 2009; Hansen et al., 2010; Bonvin et al., 2016). For example, Yu et al. reported that the adsorption of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) on a coal-based GAC (900–1,000 μm) and PAC ($< 100 \mu\text{m}$), created by grinding GAC) reached equilibrium within 168 hrs and 4 hrs, respectively (Yu et al., 2009). Shen et al. observed that the adsorption of 11 polychlorinated biphenyls took at least twice as long to reach equilibrium on GAC ($D_{50} = 1,100 \mu\text{m}$) than on PAC ($D_{50} = 24 \mu\text{m}$) (Shen et al., 2023). In the study by Wu et al., three types of AC were ground into four particle size ranges and were used to adsorb 20 PFAS. It was observed that more than 75 % of the PFAS mass initially presented in the solution was removed by ACs of the smallest particle size range (10–75 μm), while only 25 % of PFAS mass was removed by ACs with the largest particle size range (1,000–1,700 μm) (Wu et al., 2020). Nevertheless, the effect of reducing AC particle size on the adsorption capacity, particularly the adsorption capacity of PAC compared to CAC, has been shown to depend on the type of adsorbate. Pan et al. reported that decreasing AC particle size from 30 μm to less than a few μm resulted in a decrease in the adsorption of lower molecular weight adsorbates (e.g., phenol, geosmin, salicylic acid, 2-methylisoborneol) but increased the adsorption of higher molecular weight adsorbates (e.g., Suwannee River natural organic matter (SRNOM)) (Pan et al., 2017). In another study, Bakkaloglu

et al. demonstrated that pulverizing a bituminous coal PAC ($\sim 21 \mu\text{m}$) resulted in a CAC ($\sim 0.42 \mu\text{m}$) with a lower adsorption capacity for carbamazepine, and attributed this behavior to a lower Brunauer-Emmett-Teller (BET) surface area and smaller micropore volume compared to the parent PAC. In the same study, the authors compared PAC versus CAC by synthesizing data from their study and 11 studies by others and concluded that CACs have a similar or greater adsorption capacity for hydrophobic compounds ($\log K_{ow} > 3$) compared to PACs, but lower adsorption capacity for hydrophilic compounds ($\log K_{ow} < 3$) (see Fig. 5 in Bakkaloglu et al., 2021).

There has been no study that directly compares the rate and capacity of PAC and CAC to adsorb PFAS. Only a few studies have directly compared the adsorption capacity of GAC versus PAC for PFAS. In the study by Yu et al., which was mentioned above, the adsorption capacity of PAC was greater than that of GAC (Yu et al., 2009). Hansen et al. investigated the adsorption of a mixture of PFAS on a coal-based GAC ($180\text{--}400 \mu\text{m}$) and PAC ($80\% < 45 \mu\text{m}$) and observed that the adsorption capacity of PAC was greater (Hansen et al., 2010). In addition to these two studies, many other studies investigated the adsorption of PFAS on GAC, PAC, or CAC (Table 2-3) (Hansen et al., 2010; Zhi and Liu, 2015; Senevirathna et al., 2010; Ochoa-Herrera and Sierra-Alvarez, 2008; Siriwardena et al., 2019; Inyang and Dickenson, 2017; Zhang et al., 2016; Yu et al., 2012; Qu et al., 2009; Yu and Hu, 2011; Chularueangaksorn et al., 2014; Liang et al., 2011; Rattanaoudom et al., 2012; Yao et al., 2014; Qian et al., 2017; Söregård et al., 2020; Deng et al., 2015; Du et al., 2015; Murray et al., 2019; Park et al., 2020; Qu et al., 2009; Umeh et al., 2023). However, PFAS adsorption data of these studies cannot be readily compared because these studies were not conducted under identical experimental conditions (e.g., solution chemistry, type of PFAS and initial concentrations, type and dosage of AC), as can be seen in Table 2-3.

Effect of water chemistry. Solutes such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and dissolved organic matter (DOM) can affect PFAS adsorption on AC. To date, there has been only one study on the effect of inorganic ions on PFAS adsorption by GAC, which showed that the adsorption of PFHxA, PFHpA, and PFOA increased in the presence of NaNO_3 (0.04 mM), KCl (0.10 mM), NaCl (0.59), Na_2SO_4 (0.61 mM), NaF (1.31 mM), MgCl_2 (0.96 mM), and CaCl_2 (0.70 mM) (Du et al., 2015). This increase was attributable to the salting-out effect. However, the role of inorganic ions in adsorption can go beyond the salting-out effect since inorganic ions can influence the electrostatic interaction between PFAS and adsorbent surface through various mechanisms, including electrical double-layer compression, surface charge neutralization, and surface bridging (Du et al., 2014). These different mechanisms could result in a complex role of inorganic ions in the adsorption of PFAS on inorganic minerals. A previous study reported that as the concentration of NaCl increased, the adsorption of PFOS on goethite decreased at $\text{pH} = 3$ but increased at $\text{pH} = 7$ and 9 (Tang et al., 2010). In this study, it was suggested that the adsorption of PFOS was driven by intermolecular interactions between PFOS and the goethite surface, as well as between PFOS molecules. At $\text{pH} = 3$, the surface of goethite was positively charged (because the point of zero charge (pH_{pzc}) of goethite is 9.4 and will attract the negatively charged PFOS molecule. Therefore, increasing NaCl concentration would compress the electrical double layer and hinder the PFOS-surface attraction, leading to a decreased PFOS adsorption (Tang et al., 2010). When the solution pH was 7 or pH 9, the electrostatic attraction between PFOS and the goethite surface became weaker because the goethite surface was less positively charged. At these pH values, the adsorption of PFOS was speculated to be more affected by the repulsion among PFOS molecules rather than by the attraction between PFOS molecules and the surface. An increase in NaCl concentration, in this case, would decrease the PFOS-PFOS repulsion, leading to an increased PFOS adsorption (Tang

et al., 2010). In the same study, when CaCl_2 was added into the solution, the adsorption of PFOS on goethite did not change appreciably when the concentration of CaCl_2 ranged between 0 and 1 mM but dramatically increased when the concentration of CaCl_2 increased to 3 mM. This was attributed to the ability of Ca^{2+} to bind to the goethite surface, thus increasing the surface charge (Tang et al., 2010). In a separate study, an increase in the concentration of Ca^{2+} was also observed to enhance the adsorption of PFOS on sediments and an oil-derived black carbon. The authors speculated that the enhanced PFOS adsorption was due to the Ca^{2+} ions neutralizing the negative charges on the surface (Chen et al., 2009). An increase in the concentration of Ca^{2+} was also observed to enhance the adsorption of PFOS and PFNA on polymeric membranes (Kwon et al., 2012), PFOS on biochars (Fabregat-Palau et al., 2022), and PFOA on a magnetic GAC (Xu et al., 2020). These enhanced adsorptions were attributed to Ca^{2+} acting as a bridge between the negatively charged surface of the adsorbent and PFAS anions. In addition to influencing electrostatic interaction between PFAS and the surface, inorganic anions can compete with PFAS for adsorptive sites. As a result, the adsorption of PFOS and PFOA on boehmite (Wang et al., 2012), ion exchange resins (Deng et al., 2010), and chitosan (Zhang et al., 2011) decreased in the presence of Cl^- and SO_4^{2-} . In a recent study by Molé et al., the adsorption of PFOA and GenX on CAC was unaffected but the adsorption of PFBA decreased in the presence of NaCl , which was suggested to be due to the competition between chloride anions and PFBA (Molé et al., 2024). This explanation is consistent with the observation made by Umeh et al., who investigated the adsorption-desorption of a mixture of 9 PFAS on an organoclay, carbonaceous organic amendments, and PAC in the presence of several inorganic ions. Umeh et al. showed that 20–80 % of the adsorbed mass of PFBS, PFPeA, and PFHxA desorbed in the presence of NO_3^- , Cl^- and SO_4^{2-} (Umeh et al., 2023). Saeidi et al. investigated the effect of Na_2SO_4 on the adsorption of PFOS

and PFOA on four types of activated carbon felts (ACFs). When the concentration of Na_2SO_4 increased from 10 to 200 mM, a decreased adsorption was observed on ACFs (which had a positively charged surface) due to the competition between SO_4^{2-} and PFOS and PFOA anions. In contrast, the adsorption of PFOS/PFOA was enhanced on negatively charged ACFs due to electrical double layer compression, which decreased the electrostatic repulsion between PFOS/PFOA and ACFs (Saeidi et al., 2020).

DOM, an important solute in natural waters, can influence PFAS adsorption in different ways. Firstly, if DOM is more hydrophobic, it can compete with PFAS for adsorption sites (Du et al., 2014). Secondly, the pre-sorbed DOM can form a hydrophobic region on the surface, which subsequently acts as a secondary adsorptive site for PFAS (Du et al., 2014; Kothawala et al., 2017). Thirdly, since DOM consists of negatively charged functional groups (e.g., hydroquinones, phenols, carboxylic acids), the repulsion between DOM and PFAS will prevent PFAS adsorption (Du et al., 2014). Lastly, DOMs are macromolecules and can block AC pores, making the inner adsorption sites inaccessible to PFAS (Yu et al., 2012). Owing to these different mechanisms, DOM can either decrease or enhance PFAS adsorption. For example, several studies reported a decreased PFAS adsorption in the presence of various types of DOM such as wastewater treatment plant effluent (Yu et al., 2012), humic acid (Pramanik et al., 2015), and landfill groundwater (Zhao et al., 2011). However, PFAS adsorption on GAC was observed to be enhanced by a hydrophobic lake water DOM. The effect of DOM in this study was attributable to the formation and co-adsorption of the PFAS-DOM complex (Kothawala et al., 2017). Saeidi et al. reported that SRNOM did not affect the adsorption of PFOA and PFOS by ACFs. This was attributed to the large size of SRNOM, which prevented SRNOM from diffusing into the ACFs pores due to the size exclusion effect (Saeidi et al., 2020). Molé et al. studied the effect of DOMs of different

molecular weights on the adsorption of PFBS, PFPeA, and PFOA by CAC. They observed that lower molecular weight DOMs decreased PFAS adsorption by CAC to a larger extent compared to higher molecular weight DOMs. This was attributed to the lower molecular weight DOMs diffusing into micropores and competing with PFAS for sorptive sites (Molé et al., 2024).

Since groundwater contains a wide variety of inorganic ions and different levels of DOM concentration, the roles of these solutes on the adsorption of PFAS in AC barriers need to be investigated. The effect of Ca^{2+} and Mg^{2+} could be particularly important since these cations are major solutes in groundwater. Whether DOM has a significant influence on the performance of AC barriers is uncertain since AFFF-impacted groundwater often has other non-fluorinated organic co-contaminants whose presence might have a greater influence on PFAS adsorption than DOM. This point is discussed further below.

Competitive adsorption among PFAS as well as between PFAS and other co-contaminants.

AFFF-impacted groundwater usually contains other constituents since AFFF formulation is composed of PFAS, non-PFAS surfactants, and organic solvents (Moody et al., 2000). Moreover, since AFFF is used to extinguish hydrocarbon- and chlorinated solvent-based fires, these compounds can also infiltrate into the subsurface and come in contact with PFAS at contaminated sites (Moody and Field, 2000). Therefore, AFFF-impacted groundwater usually contains a complex mixture of various PFAS and non-PFAS co-contaminants, resulting in competition among compounds for adsorptive sites on AC. For example, studies have shown that the affinity of each compound in a PFAS mixture to GAC was lower compared to the affinity measured in single-compound solutions, owing to competitive adsorption among PFAS (Xiao et al., 2017). It has also been shown that competitive adsorption decreased the adsorption of short-chain PFAS to a larger extent compared to long-chain PFAS (Kancharla et al., 2022; Zhang et al., 2023). Niarchos et al.

studied the competitive adsorption among 7 PFAS on CAC and showed that the adsorption of short-chain PFAS, including PFBS and PFPeA, decreased to the greatest extent (Niarchos et al., 2023b). Since competitive sorption is controlled not only by the hydrophobic nature of each compound but also by the compound's diffusivity and the adsorbent's pore structure, research is still needed to evaluate the effect of competitive sorption on the removal of PFAS by CAC.

Non-fluorinated co-contaminants such as surfactants, chlorinated solvents, and petroleum hydrocarbons (PHCs) can have a complex influence on PFAS adsorption (Guelfo and Higgins, 2013). On the one hand, co-contaminants can decrease PFAS adsorption if they compete for the same adsorptive sites and/or if they enhance PFAS solubility (Guelfo and Higgins, 2013). On the other hand, co-contaminants can enhance PFAS adsorption if they form a non-aqueous phase liquid (NAPL), which can absorb PFAS (Guelfo and Higgins, 2013). Non-fluorinated surfactants can also form mixed hemimicelles with PFAS, thereby enhancing the removal of the latter (Guelfo and Higgins, 2013; Ji et al., 2021). Additionally, PHCs, which are hydrophobic, can adsorb and enhance PFAS removal (Guelfo and Higgins, 2013). Guelfo and Higgins observed that TCE influenced PFAS adsorption to soils via two of the processes explained above. In the first process, NAPL TCE served as an adsorption site for PFAS and increased PFAS adsorption. In the second process, NAPL TCE competed with PFAS for the hydrophobic adsorption sites on soils, thus decreasing PFAS adsorption. As such, whether TCE enhances or diminishes the adsorption of PFAS is dependent on the TCE concentration, the type of soil (i.e., soil containing low organic carbon versus soil containing high organic carbon), and the PFAS chain length (Guelfo and Higgins, 2013). Ji et al. also observed that the retardation factor (R) of PFOA in a sand column increased from 2.4 to 3.6 when sodium dodecyl benzene (a non-fluorinated surfactant) was present in water (Ji et al., 2021). In a study by Van Glubt and Brusseau, the presence of NAPLs, including

TCE and decane, increased the retardation factor of PFOS in a sand column up to 3 times (Van Glubt and Brusseau, 2021). Liao et al. observed that in the presence of tetrachloroethene (PCE) NAPL, the breakthrough of PFNA and PFOS in a sand column increased from 1 pore volume to 1.2 and 2 pore volumes for PFNA and PFOS, respectively (Liao et al., 2022). This observation suggests that the adsorption of PFOS and PFNA was enhanced in the presence of PCE NAPL. However, Liao et al. did not observe an appreciable effect of PCE NAPL on the adsorption of PFBS, PFHpA, PFHxS, and PFOA (Liao et al., 2022). In the only study on the effect of co-contaminants on PFAS adsorption by AC, it was observed that the presence of TCE, kerosene, and ethanol in the non-NAPL phase enhanced the adsorption of PFOS and PFOA on GAC (Siriwardena et al., 2019). Overall, past studies indicate that non-fluorinated co-contaminants could either enhance or reduce the adsorption of PFAS, depending on the concentration of the co-contaminant, the type of PFAS, and the type of adsorbent. Therefore, research is needed to investigate the effect of co-contaminants on PFAS adsorption by CAC. If non-fluorinated co-contaminants also enhance PFAS sorption by CAC, it can be expected that PFAS retention by in-situ CAC barriers can be improved by the presence of co-contaminants in AFFF-contaminated groundwater.

2.4 Research Focus

It has been suggested that CAC barriers could be used to contain plumes of PFAS at AFFF-impacted sites. Since CAC barriers immobilize plumes of PFAS through adsorption, the breakthrough of PFAS in a CAC barrier is expected to occur once the adsorptive sites in the barrier are saturated. The retention and breakthrough of PFAS in a CAC barrier is controlled, in part, by the ability of CAC to adsorb PFAS. This research investigated some of the factors that affect the adsorption of PFAS on CAC, focusing on:

- Assessing the adsorption of seven PFAS (6:2 FTS, three PFCAs, and three PFSAAs) on two CACs, including a polymer-containing CAC (i.e., PlumeStop) and a polymer-free CAC (Chapter 3).
- Evaluating the effect of five co-contaminants (benzene, TCE, ethanol, 1,4-dioxane, butyl carbitol) on the adsorption of PFOA and PFOS on CAC (Chapter 3).
- Evaluating the effect of groundwater chemistry, including ionic strength, Ca^{2+} , DOM, pH, and Mg^{2+} on the adsorption of several PFAS (Chapter 3 and Chapter 4).
- Evaluating the adsorption of PFBS, PFOA, and PFOS on CAC in the presence of aquifer materials (Chapter 4).
- Investigating the linkage between the physical and chemical properties of CAC, PAC, and GAC and the ability of these materials to adsorb PFBS, PFOA, and PFOS (Chapter 5).

Chapter 3: Factors Affecting the Adsorption of Per- and Polyfluoroalkyl Substances (PFAS) by Colloidal Activated Carbon

This chapter was published in Water Research in 2023 (Hakimabadi, S.G., Taylor, A. and Pham, A.L.T., 2023. Factors affecting the adsorption of per- and polyfluoroalkyl substances (PFAS) by colloidal activated carbon. Water Research, 242, 120212). Reproduced with permission from Elsevier. Minor editorial changes were made to the published version to improve clarity. These changes do not affect the overall conclusion of the research.

3.1. Introduction

Owing to their extremely high thermal and chemical stability, as well as oil repellency, per- and polyfluoroalkyl substances (PFAS) have been used in a wide variety of commercial and industrial products, including aqueous film-forming foams (AFFF), adhesives, cosmetics, cleaning products, as well as coatings for fabrics, paper, and furniture (Buck et al., 2011; Glüge et al., 2020). Among these applications of PFAS, the use of AFFF to extinguish fires at military sites, airports, petroleum refineries, and firefighter training facilities has created sites contaminated with PFAS (Salvatore et al., 2022). A recent study identified 3,493 military sites and 519 airports in the US as presumptive PFAS contamination locations (Salvatore et al., 2022). In Canada, of the 2,071 airports surveyed, 152 airports were identified as likely being contaminated with PFAS (Milley et al., 2018). Many of these sites are located near residential areas and pose direct threats to the drinking water resources of nearby residents (Dickman and Aga, 2022). Because exposure to PFAS has been linked to various health issues (Dickman and Aga, 2022; Sunderland et al., 2019; Sims et al., 2022), guidelines for PFAS are beginning to emerge. Recently, the US Environmental Protection Agency (EPA) has issued interim updated drinking water lifetime health advisory (LHA) levels of 0.004 ng/L for perfluorooctanoic acid (PFOA) and 0.020 ng/L for perfluorooctane sulfonic acid (PFOS), and final LHA levels of 2,000 ng/L for perfluorobutane sulfonic acid (PFBS) and 10 ng/L for hexafluoropropylene oxide-dimer acid (GenX) (US EPA, 2022). Considering that humans and ecosystems can be exposed to PFAS in groundwater and that future regulations may enforce remediation of PFAS-contaminated sites, there is an urgent need to develop technologies that can effectively remove PFAS from groundwater at AFFF-impacted sites.

Contaminated groundwater can be remediated ex situ or in situ. Ex-situ remediation, also known as pump and treat, involves extracting groundwater to the surface and treating it, followed

by discharging the treated water to a publicly owned treatment system. Contrary to *ex-situ* remediation, *in-situ* remediation involves injecting chemical and/or biological amendments into the subsurface to initiate reactions that can destroy contaminants in place. Compared to *ex-situ* remediation, *in-situ* remediation is less energy intensive and potentially has a shorter operational timeframe and smaller carbon footprint. As such, *in-situ* remediation is a preferable method whenever possible (Suthersan and Payne, 2005). To date, however, PFAS-contaminated groundwater has been primarily treated by *ex-situ* approaches. This is because PFAS are extremely resistant to chemical and biological degradation and, therefore, cannot be destroyed *in situ* under conditions typical of the subsurface (Ross et al., 2018).

Recently, several studies have proposed that PFAS in groundwater can be immobilized *in situ* by stationary adsorption barriers, which can be created by injecting particulate or chemical amendments into the subsurface. For example, Aly et al. demonstrated that the breakthrough of PFOA and PFOS in a one-dimensional soil column was delayed by 8–20 pore volumes (PV) when the soil column was amended with cationic polymers polyamine (PA) and polydiallyldimethyl ammonium chloride (polyDADMAC) (Aly et al., 2019). Subsequent to this study, the same research group demonstrated that by injecting a mixture of powdered activated carbon (PAC) and polyDADMAC into an Ottawa sand column, the breakthrough of PFOS and PFOA in the column was delayed by three orders of magnitude (equivalent to 4,000–6,000 PVs) (Liu et al., 2020). They also demonstrated that injecting Amberlite IRA910 ion exchange resins stabilized by Pluronic F-127 polymer into an Ottawa sand column resulted in a uniform adsorption zone that delayed the breakthrough of PFOS and PFOA by more than five orders of magnitude (equivalent to 5,900–9,240 PVs) (Liu et al., 2022). In parallel with bench-scale studies, there have been efforts to demonstrate the *in-situ* immobilization of PFAS in the field (McGregor, 2018; Carey et al., 2019;

McGregor, 2020a; McGregor and Benevenuto, 2021; McGregor and Zhao, 2021; Niarchos et al., 2023). In what appears to have been the first field study on the in-situ immobilization of PFAS, McGregor demonstrated that an adsorption barrier, created by injecting PlumeStop® (a colloidal activated carbon (CAC) suspension trademarked by Regenesis, San Clemente, CA, US) into the subsurface, successfully contained PFOS and PFOA at a contaminated site located in a shallow silty sand aquifer in Central Canada (McGregor, 2018). At this location, following the injection of CAC into the source zone, the concentration of PFOS (3,260 ng/L) and PFOA (1,450 ng/L) decreased to below detectable levels (20 ng/L) (McGregor, 2018; Carey et al., 2019). In a separate study, McGregor conducted pilot-scale tests to evaluate the in-situ immobilization of PFAS by PlumeStop CAC, Calgon WPC® powdered activated carbon (PAC), Purolite Purofine PFA694E® ion-exchange (IX) resin, and biochar (McGregor, 2020a). In each test cell, the concentration of all PFAS dropped from 140–24,000 ng/L to below detectable levels (10 ng/L) following adsorbent injection. PlumeStop CAC was also used in the study by Niarchos et al. to immobilize PFAS in the groundwater at a historical firefighting training area in Sweden (Niarchos et al., 2023a). Following CAC injection at this site, the total concentration of 11 PFAS in the monitoring well downgradient of the CAC barrier decreased by as much as 76 % (Niarchos et al., 2023a).

Although the bench-scale and field-scale studies mentioned above indicate that in-situ adsorption barriers could potentially be an effective means of containing plumes of PFAS, it is important to recognize that, as with any sorption-based technology, the breakthrough of PFAS will take place once the adsorptive sites in a barrier are exhausted if PFAS is continuously released from a source zone upstream. In the pilot-scale tests conducted by McGregor, it was observed that the concentrations of all PFAS in the cells injected with CAC have been below detectable levels after over a year (McGregor, 2020a). However, partial or full concentration rebounds were

observed in the cells where biochar, Purofine PFA694E, and PAC were injected (McGregor, 2020a). At the site in Central Canada, the concentrations of PFOS and PFOA have remained undetected after over six years in all monitoring wells downgradient of the CAC barrier (Personal communication with Rick McGregor). While more field studies and longer-term PFAS monitoring will be required to further evaluate the longevity of in-situ adsorption barriers, it is reasonable to expect that the retention and breakthrough of PFAS in a barrier will be dependent upon several factors, including the mass flux of PFAS entering the barrier, the mass of adsorbent injected and its distribution in the barrier, the competition for adsorptive sites among PFAS as well as between PFAS and co-contaminants, and the groundwater water chemistry. In the pilot-scale studies conducted by McGregor, the breakthrough of the shorter-chain PFAS in the barriers created by biochar, Purofine PFA694E[®] IX, and PAC could be due to the low adsorption capacity in some areas within these barriers, since the adsorbents were found to preferentially accumulate along a coarse-grained sand seam. (McGregor, 2020) Contrary to these adsorbents, PlumeStop, which consists of AC colloids stabilized with polymers, was distributed uniformly in both the coarse-grained sand seam and the fine-grained sand area (McGregor, 2020a; McGregor, 2020b). McGregor also speculated that the breakthrough of the shorter-chain PFAS could be due to competitive adsorption (McGregor, 2020a). This hypothesis is consistent with the studies showing that compounds with longer carbon chains (e.g., PFOS and PFOA) are better removed by AC and IX than those with shorter carbon chains (e.g., PFBS, perfluorobutanoic acid (PFBA), and perfluoropentanoic acid (PFPeA)) and that longer-chain compounds can desorb the shorter chain ones (Liu et al., 2022; Niarchos et al., 2022; Chow et al., 2022; Park et al., 2020). Competitive adsorption also could occur between PFAS and organic co-contaminants, such as petroleum hydrocarbons and chlorinated solvents, which could be released during firefighting training

activities, and nonfluorinated surfactants and solvents, which are present alongside PFAS in AFFF formulations (Moody et al., 1999; Place et al., 2012; Guelfo and Higgins, 2013). To date, there have been limited studies on the impact of co-contaminants on PFAS adsorption (Guelfo and Higgins, 2013; Siriwardena et al., 2019; Ji et al., 2021; Pan et al., 2009). Guelfo and Higgins observed that the nonfluorinated surfactants sodium decyl sulfate (SDS) and n,n-dimethyldodecylamine n-oxide (AO) either increased, had no effect, or decreased PFAS sorption on soils (Guelfo and Higgins, 2013). They also observed that the trichloroethylene (TCE) non-aqueous phase liquid (NAPL) had a complex influence on PFAS sorption. On the one hand, TCE could decrease PFAS sorption by competing for the same adsorptive sites. On the other hand, the NAPL phase on the soil surface could absorb PFAS, thereby enhancing PFAS partitioning to soil (Guelfo and Higgins, 2013). In another study, Siriwardena et al. observed that the presence of kerosene, ethanol, and dissolved TCE did not appreciably affect the adsorption of PFOS but slightly enhanced the adsorption of PFOA on a coal-based and a coconut-based granular activated carbon (GAC) (Siriwardena et al., 2019). These past studies suggest that it is difficult to predict how co-contaminants would affect PFAS adsorption, since their effects are dependent upon a range of factors, including the co-contaminant concentration (e.g., non-NAPL versus NAPL, the latter of which could absorb PFAS; at high concentration surfactants can form semi-micelle or micelle, thereby enhancing PFAS solubility and decreasing their affinity to surfaces), adsorbent properties (e.g., surface charge, organic carbon content), and PFAS type (e.g., short-chain versus long-chain compounds, perfluoro carboxylates versus perfluoro sulfonates). Because the concentration of organic co-contaminants at AFFF-impacted sites could be up to a few orders of magnitude greater than those of PFAS (Carey et al., 2023), their influence on the retention and breakthrough of PFAS in adsorption barriers is likely significant. Thus, additional research is needed to gain insights into

how co-contaminants may affect the adsorption of PFAS on amendments used to create in-situ adsorption barriers. Such insights are important for the design and implementation of the barriers.

The objective of this study was to investigate the adsorption of PFAS on PlumeStop CAC, focusing specifically on assessing how adsorption was influenced by the stabilizing polymers, co-contaminants, and solution chemistry. To this end, a series of batch adsorption experiments were conducted to investigate the adsorption of PFAS on two types of CAC, namely a stabilizer-free and a stabilizer-containing CAC suspension. Seven PFAS were studied, including PFBA, PFPeA, PFOA, PFBS, perfluorohexane sulfonic acid (PFHxS), PFOS, and 6:2 fluorotelomer sulfonic acid (6:2 FTS). These compounds were chosen because they are currently driving PFAS regulations (PFOS and PFOA), are pervasive at AFFF-impacted sites (all seven compounds), or are highly mobile (PFBA, PFPeA, PFBS) and thus are likely among the first to break through CAC barriers. Further, the adsorption of PFOS and PFOA was investigated in the presence of five co-contaminants, including benzene, TCE, 1,4-dioxane, ethanol, and diethylene glycol butyl ether (DGBE, also known as butyl carbitol). Benzene, TCE, and 1,4-dioxane could be present at sites where they were used as fuels in firefighting training activities, whereas DGBE and other alcohols are important components in some AFFF formulations (Kao and Prosser, 1999; Bugna et al., 2005; Titaley et al., 2022). Additionally, the effects of three key solution chemistry parameters, namely ionic strength, Ca^{2+} , and dissolved organic carbon, on the adsorption of PFOS and PFOA were investigated.

3.2. Materials and Method

Chemicals. Single PFAS were purchased from either Sigma Aldrich (PFBA, PFPeA, PFOA, PFBS, PFHxS, PFOS) or Toronto Research Chemicals (6:2 FTS), while analytical native and isotopically labeled PFAS standards were purchased from Wellington Laboratories (Guelph, Canada). See Table 3-1 for the list of native and isotopically labeled PFAS. Suwannee River Fulvic Acid (SRFA) was purchased from the International Humic Substances Society (USA). Benzene, TCE, 1,4-dioxane, DGBE, and ethanol were purchased from Sigma Aldrich. All other chemicals were purchased from Sigma Aldrich or Fisher Scientific.

Methanolic stock solutions of single-compound PFAS (350–1,100 mg/L) were prepared by dissolving each compound in LCMS-grade methanol. Stock solutions of benzene (479 mg/L), TCE (436 mg/L), 1,4-dioxane (2,700 mg/L), and ethanol (1,400 mg/L) were prepared using 18.2 M Ω ·cm MilliQ water (Millipore).

Adsorbents. Two CAC materials were used in this study, both of which were provided by Regenesis (San Clemente, California, USA). The first material was PlumeStop CAC, which will be denoted from this point forward as the polymer-containing CAC. This material was a slurry consisting of CAC, water, and organic polymers. The organic polymers served as the stabilizing agent, which aimed to minimize particle aggregation and enhance CAC mobility in in-situ applications. For this study, Regenesis also provided a material that only consisted of CAC and water (denoted as the polymer-free CAC). The adsorption of PFAS on these two materials was compared to assess how the presence of the polymers affected the adsorption of PFAS by CAC. While Regenesis indicated that the size of the CAC particles ranged between 1 and 2 μm , it was noticed in our preliminary experiments that when CAC-containing samples were filtered using a 0.2- μm filter and subsequently analyzed by liquid chromatography-tandem mass spectrometry

(LC/MS/MS), the backpressure in the LC system increased over time. This observation suggests that some CAC particles must have passed through the 0.2- μm filter and clogged the analytical column. Sörengård et al. also noticed that some PlumeStop CAC passed through a 0.45- μm filter (Sörengård et al., 2019). Their dynamic light scattering analyses revealed that the size of PlumeStop CAC ranged between 0.1 and 1.1 μm , with an average particle size being 0.6 μm (Sörengård et al., 2019). The point of zero charge (pH_{pzc}) of the two CAC materials was determined using a method described by Saeidi et al. (Saeidi et al., 2020).

Adsorption experiments. Six-point adsorption isotherms for PFAS were generated using the bottle-point approach. The initial concentration of the adsorbate was kept constant, while the adsorbent dose was varied. In brief, experiments were conducted in either polypropylene (PP) conical centrifuge tubes or glass tubes (when benzene or TCE was present in the reaction solution) that contained 50–73 mL of an aqueous solution of 1 mM NaHCO_3 , which served as the background electrolyte and as a pH buffer ($\text{pH} \approx 7.5\text{--}8.5$). A 50–73 μL aliquot of a methanolic single-PFAS stock was added to each test tube, resulting in test tubes that contained the same amount of methanol (0.1 v/v %) and a similar initial PFAS concentration. That is, each reaction solution consisted of only one of the following compounds: $[\text{PFBA}]_0 = 2.12 \mu\text{M}$, $[\text{PFPeA}]_0 = 1.18 \mu\text{M}$, $[\text{PFOA}]_0 = 1.28 \mu\text{M}$, $[\text{PFBS}]_0 = 1.17 \mu\text{M}$, $[\text{PFPHxS}]_0 = 1.4 \mu\text{M}$, $[\text{PFOS}]_0 = 1.3 \mu\text{M}$, or $[\text{6:2 FTS}]_0 = 2.57 \mu\text{M}$. These molar concentration values are equivalent to mass concentration values ranging from 350 $\mu\text{g/L}$ (PFBA) to 1,100 $\mu\text{g/L}$ (6:2 FTS). Because the concentration of PFAS in the groundwater at AFFF-impacted sites usually ranges from less than $\mu\text{g/L}$ to a few hundred $\mu\text{g/L}$ (Carey et al., 2023), the initial PFAS concentrations employed in this study represented some of the most contaminated scenarios. The initial concentrations were chosen to be high enough such that the amount of PFAS remaining in the solution after adsorption (i.e., C_w) could be measured.

Also, C_w was targeted to span over an order of magnitude so that PFAS adsorption could be compared at different C_w . Additionally, the initial molar concentrations were aimed to be within a factor of 2.5 of each other to enable the comparison (based on a molar basis) of the adsorption trend among PFAS.

Carey et al. reviewed 17 PFAS-contaminated sites in the US, UK, and Canada (Carey et al., 2023). At these sites, the total concentration of BTEX (benzene, toluene, ethyl benzene, xylene) ranged from non-detect to approximately 6 mg/L, while the total concentration of TCE and other chlorinated solvents was as high as approximately 1 mg/L. To examine how BTEX and chlorinated solvents might affect PFOS and PFOA adsorption by CAC, in some experiments, the reaction solution contained 0.5 or 4.8 mg/L benzene (i.e., 6.4 or 61.6 μM), or 0.5 or 8.5 mg/L TCE (i.e., 3.8–61.6 μM). Because 1,4-dioxane is usually present at sites contaminated with chlorinated solvents, it could be present at PFAS-contaminated sites as well. However, little is known about 1,4-dioxane concentration levels in plumes of PFAS. In this study, the effect of 5.4–54 mg/L 1,4-dioxane (i.e., 61.6–616 μM) on the adsorption of PFOS and PFOA by CAC was investigated. Also, DGBE and ethanol could be present at AFFF-impacted sites because these two compounds are part of some AFFF formulations. As in the case of 1,4-dioxane, the concentration level of DGBE and ethanol in PFAS-contaminated groundwater is not known. Herein, the concentration of DGBE and ethanol was set to range between 10–100 mg/L (i.e., 61.6–616 μM) and 2.8–28 mg/L (i.e., 61.6–616 μM), respectively. Lastly, the effect of 1–20 mgC/L SRFA on the adsorption of PFOS and PFOA was also investigated. All organic compounds described above were added to the reaction solution from their respective aqueous stock solutions, except for DGBE, which was added from the pure (> 99 %) DGBE stock.

To investigate the effect of ionic strength and Ca^{2+} on the adsorption of PFOS and PFOA, 1–100 mM NaCl and 0.1–2 mM CaCl_2 were added to the solution. Because varying the amount of CaCl_2 added to the solution also changed the ionic strength, the effect of Ca^{2+} could be confounded by the effect of ionic strength if the latter is not controlled. As such, in the experiments investigating the effect of Ca^{2+} , between 0 and 5.7 mM of NaCl was added so that the ionic strength was 7 mM in all experiments.

Adsorption of PFAS was initiated by adding different volumes of CAC slurry into the test tubes to obtain a CAC concentration ranging from 0.11 to 0.7 g/L. Subsequently, the test tubes were placed on an orbital shaker. After 72 hours, an aliquot was withdrawn from each test tube, transferred into an ultracentrifuge tube, and centrifuged at $230,000\times g$ for 105 min to separate CAC from the solution. To minimize the loss of PFAS to the ultracentrifuge tube wall, the tubes were first rinsed with two aliquots of the test solution to saturate the tube wall with PFAS before the final aliquot was transferred into the tube and centrifuged. Following CAC separation, 250 μL of the supernatant was taken out and subjected to PFAS analysis.

A separate set of experiments was conducted to investigate the kinetics of PFAS adsorption on CAC. In this set of experiments, test tubes were taken off of the orbital shaker at $t = 6\text{ h}$, 24 h , 48 h , 72 h , 120 h , and 168 h , and the reaction solutions were subjected to centrifugation to separate CAC. To investigate the affinity of PFAS to PP and glass test tubes, some reaction solutions did not contain CAC (i.e., control experiments).

All experiments were conducted in duplicate at $22\text{ }^\circ\text{C}$, and the average PFAS concentrations along with their range are presented.

Analysis. Benzene, DGBE, and TCE were analyzed by gas chromatography coupled with either flame ionization detection (benzene, DGBE) or electron capture detection (TCE). For the analysis

of PFAS, samples were diluted with methanol and isotopically labeled PFAS stock to obtain a final sample composition of 50/50 v/v water/methanol. Samples were analyzed on a Shimadzu 8030 LC/MS/MS, and the concentrations of PFAS were calculated using the isotopic dilution method. See Table 3-1 for the details on the instrument conditions and other information related to PFAS analysis.

Table 3-1. The quantitative method for PFAS analysis.

Instrument	Shimadzu LCMS-8030 Triple Quadrupole Mass Spectrometer				
Ionization	Negative electrospray				
Precolumn	Guard Column Thermo Scientific™ Acclaim 120 Å C18, 4.6 x 10 mm, 5 µm				
Column	Agilent Infinity Lab Poroshell 120 Å EC-C18, 3.0 x 50 mm, 2.7 µm				
Column oven temperature	30°C				
Injection volume	30 µL				
Mobile phases	A: 5 mM ammonium acetate in LCMS grade water B: LCMS grade Methanol				
Flow rate	0.5 mL/min				
Gradient profile	Time (min)	Eluent A Conc. (%)		Eluent B Conc. (%)	
	0	60		40	
	0.5	60		40	
	4.5	20		80	
	10	20		80	
	10.5	60		40	
	13.5	Stop			
Monitored ion transitions	Analytes	Ion transitions	Internal standards	Ion transitions	Calibration range (µg/L)
	PFBA	213 > 169	[¹³ C ₄]MPFBA	217 > 172	0.25–20
	PFPeA	263 > 219	[¹³ C ₅] MPFPeA	268 > 223	1–20
	PFOA	413 > 369	[¹³ C ₈] MPFOA	421 > 376	0.05–20
	PFBS	299 > 80	[¹³ C ₃] MPFBS	302 > 99	0.05–20
	PFHxS	399 > 80	[¹³ C ₃] MPHxS	402 > 99	0.05–20
	PFOS	499 > 80	[¹³ C ₈] MPFOS	507 > 99	0.05–20
	6:2 FTS	427 > 407	[¹³ C ₂]M6:2 FTS	429 > 81	0.05–20

PFAS isotherm modeling. Adsorption isotherm results were fitted using either the linear isotherm model $C_s = K_d C_w$ or the Freundlich isotherm model: $C_s = K_f C_w^n$. In these equations, K_d is the linear partition coefficient, K_f is the Freundlich constant $((\text{mg/g})(\text{mg/L})^{-n})$ and a measure of the adsorption capacity when $C_w = 1 \text{ mg/L}$, n is the exponential term indicative of the surface heterogeneity (when $n = 1$, the Freundlich model becomes the linear model), and C_s (mg/g) and C_w (mg/L) are the equilibrium concentrations of the contaminant in the solid and aqueous phases, respectively. C_w values were obtained from LC/MS/MS analysis, while C_s values were calculated based on PFAS mass balance: $C_s = \frac{C_0 - C_w}{C_{CAC}}$, with C_0 (mg/L) being the initial PFAS concentration, and C_{CAC} being the CAC concentration (g/L). It is noted that the Langmuir isotherm model was not considered, since under the experimental conditions employed in this study the resulting isotherms did not consist of a flat region (i.e., the region where C_s remains constant as C_w increases) required for proper fitting to the Langmuir model.

3.3. Results and Discussion

3.3.1 Adsorption kinetics

Less than 10 % of the initial PFAS was lost from the solution in the absence of the polymer-free CAC or the polymer-containing CAC after 168 hours (data not shown). The results of these control experiments suggest that the loss of PFAS in the presence of CAC (Fig. 3-1) was primarily due to adsorption to CAC. For the shorter-chain compounds PFBS and PFBA, the adsorption equilibrium was established after approximately 24 hours. For the longer-chain compounds PFOS and PFOA, their concentration in the solution quickly decreased during the first 24 hours and then gradually decreased further over the subsequent 144 hours. Considering that over 99 % of the initial mass of PFAS was adsorbed during the first 48 hours, the adsorption of each PFAS in the subsequent experiments was evaluated based on a contact time of $t = 72$ hours between the reaction solution and CAC.

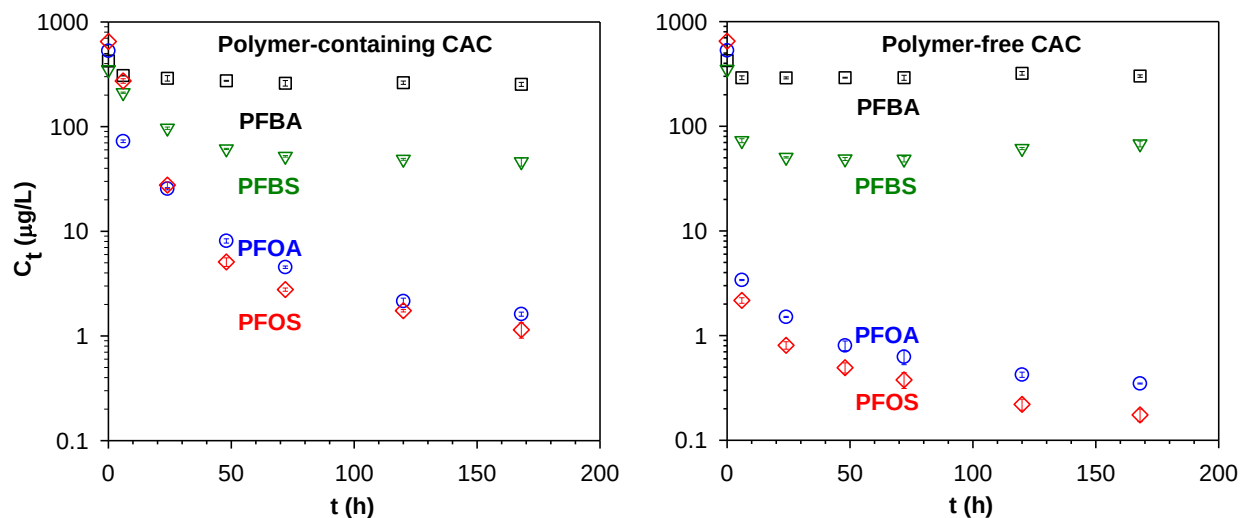


Figure 3-1. Adsorption kinetics of PFAS on the polymer-containing CAC and the polymer-free CAC. Reaction solutions contained 0.2 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), and one of the following PFAS: $[\text{PFBA}]_0 = 424 \mu\text{g/L}$, $[\text{PFOA}]_0 = 530 \mu\text{g/L}$, $[\text{PFBS}]_0 = 350 \mu\text{g/L}$, $[\text{PFOS}]_0 = 650 \mu\text{g/L}$.

3.3.2 Adsorption trend

There is a consensus that PFAS adsorption on AC is mainly driven by electrostatic and hydrophobic interactions (Du et al., 2014). The pH_{pzc} of both the polymer-containing and polymer-free CAC was determined to be 11.8, suggesting that the CAC surface would have been positively charged under the pH condition (i.e., 7.5–8.5) employed in the adsorption experiments conducted in this study. Thus, the adsorption of PFAS on CAC must have been partially driven by the electrostatic attraction between the positively charged CAC surface and the negatively charged sulfonate and carboxylate functional groups of PFAS. However, it is argued that this electrostatic attraction was not the dominant mechanism in our system, as otherwise shorter-chain PFAS would have been adsorbed to a greater extent than longer-chain PFAS (Parker et al., 2022). Instead, the affinity of PFAS to the polymer-containing CAC was in the following order: PFOS > 6:2 FTS > PFHxS > PFOA > PFBS > PFPeA > PFBA (Fig. 3-2). This trend suggests that hydrophobic interaction was generally the predominant adsorption mechanism. The two longest chain-length compounds PFOS and 6:2 FTS, which consist of 8 carbons, are the most hydrophobic among the 7 studied PFAS and, therefore, were adsorbed by the polymer-containing CAC to the greatest extent. Between PFOS and 6:2 FTS, the former compound exhibited a higher adsorption affinity, which could be attributable to the two fully fluorinated carbons (i.e., $-\text{CF}_2-\text{CF}_2-$) being more hydrophobic than the hydrogenated counterparts (i.e. $-\text{CH}_2-\text{CH}_2-$) (Krafft and Riess, 2015). Similarly, PFPeA, having one $-\text{CF}_2-$ longer than PFBA, was adsorbed by the polymer-containing CAC to a greater extent, whereas PFBS was adsorbed more than PFPeA because the $-\text{SO}_3^-$ headgroup is more hydrophobic than the $-\text{COO}^-$ headgroup (Parker et al., 2022).

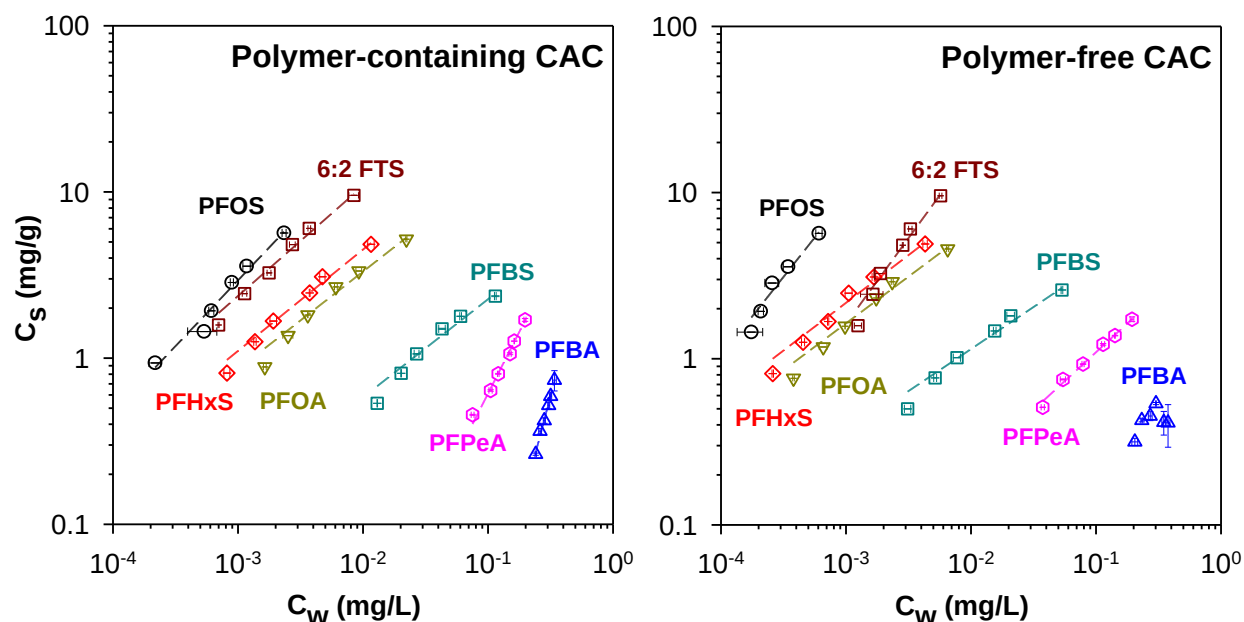


Figure 3-2. Isotherms for the adsorption of PFAS on the polymer-containing CAC and the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), and one of the following PFAS: $[\text{PFBA}]_0 = 424 \mu\text{g/L}$, $[\text{PFPeA}]_0 = 392 \mu\text{g/L}$, $[\text{PFOA}]_0 = 530 \mu\text{g/L}$, $[\text{6:2 FTS}]_0 = 1,100 \mu\text{g/L}$, $[\text{PFBS}]_0 = 350 \mu\text{g/L}$, $[\text{PFHxS}]_0 = 560 \mu\text{g/L}$, $[\text{PFOS}]_0 = 650 \mu\text{g/L}$. The dashed lines represent the fitting of the experimental data to the Freundlich model. The fitting parameters are presented in Table 3-2. With the two lowest polymer-free CAC dosages, only less than 5 % PFBA was removed from the reaction solution. Thus, the PFBA/Polymer-free CAC result (in the panel on the right) was not fitted.

For PFHxS and PFOA, their $\log K_{ow}$ values, which is an indicator of hydrophobicity, vary widely in the literature ($\log K_{ow} = 4.30\text{--}5.30$ for PFOA (Park et al., 2020; Arp et al., 2006; Wang et al., 2011; Jing et al., 2009), and $3.16\text{--}5.17$ for PFHxS (Jing et al., 2009; Gagliano et al., 2020)). Based on their relative retention times (4.9 min for PFHxS and 5.4 min for PFOA) on the C_{18} column in the LC/MS/MS analysis, PFOA might be more hydrophobic than PFHxS. However, CAC adsorbed more PFHxS than PFOA (Fig. 3-2), a trend that contradicts the hydrophobicity of these compounds. Parker et al. demonstrated that the electrostatic attraction to aminopropyl beads was stronger for PFOA than for PFHxS (Parker et al., 2022). Thus, the fact that more PFHxS was adsorbed by CAC than PFOA cannot be explained by electrostatic attraction either. While the

mechanisms of PFHxS and PFOA adsorption on CAC are not entirely clear at this point, our results are similar to that of Xiao et al., who reported that when the adsorbent was GAC Calgon Filtersorb300, the 30-day log K_d (L/kg) value of PFHxS (5.09 ± 0.01) was greater than that of PFOA (4.97 ± 0.04) (Xiao et al., 2017).

The trend of PFAS adsorption on the polymer-free CAC was generally similar to that on the polymer-containing CAC, except for 6:2 FTS (Fig. 3-2). This compound exhibited a greater adsorption affinity than PFHxS at C_w values greater than 3×10^{-3} mg/L, but its adsorption affinity was lower when $C_w < 3 \times 10^{-3}$ mg/L. In Fig. 3-2 (right panel), the adsorption isotherm of 6:2 FTS crosses that of PFHxS at around $C_w = 3 \times 10^{-3}$ mg/L.

When the isotherms describing the adsorption of each compound on the polymer-containing CAC and the polymer-free CAC were compared (Fig. 3-3), it was revealed that PFBA and 6:2 FTS exhibited a similar adsorption affinity to these two adsorbents under the studied C_w range. In contrast, PFBS, PFHxS, PFOS, PFPeA, and PFOA exhibited a greater adsorption affinity to the polymer-free CAC. It is speculated that the diminished adsorption in the presence of the polymers might be due to competitive sorption. This hypothesis is similar to that of Georgi et al., who attributed the diminished adsorption of monochlorobenzene (MCB) on AC colloids stabilized with dodecylbenzene sulfonate (SDBS) to the competition between MCB and SDBS (Georgi et al., 2015). Georgi et al. also speculated that the stabilizer would desorb from the AC surface once the CAC suspension was diluted by the groundwater (Georgi et al., 2015). The desorption and/or degradation of the stabilizing polymers following CAC barrier installation would free up adsorptive sites on CAC, thereby increasing the adsorption of PFAS. Additional research is needed to assess the desorption/degradation rate of the polymers used in the polymer-containing CAC.

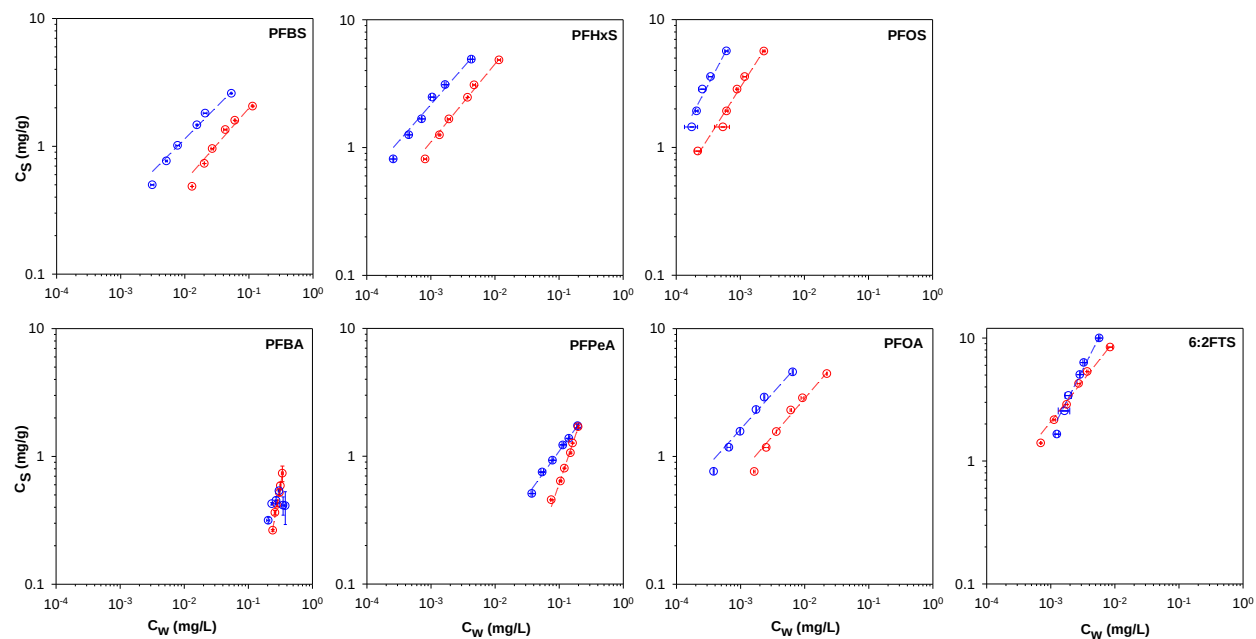


Figure 3-3. Isotherms for the adsorption of PFAS on the polymer-containing CAC (red circles) and the polymer-free CAC (blue circles). Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 ($\text{pH} = 7.5\text{--}8.5$), and one of the following PFAS: $[\text{PFBA}]_0 = 424 \mu\text{g/L}$, $[\text{PFPeA}]_0 = 392 \mu\text{g/L}$, $[\text{PFOA}]_0 = 530 \mu\text{g/L}$, $[\text{6:2 FTS}]_0 = 1,100 \mu\text{g/L}$, $[\text{PFBS}]_0 = 350 \mu\text{g/L}$, $[\text{PFHxS}]_0 = 560 \mu\text{g/L}$, $[\text{PFOS}]_0 = 650 \mu\text{g/L}$. The dashed lines represent the fitting of the experimental data to the Freundlich model. With the two lowest polymer-free CAC dosages, only less than 5 % PFBA was removed from the reaction solution. Thus, the PFBA/polymer-free CAC result was not fitted.

Table 3-2. The linear and Freundlich isotherm parameters for the adsorption of PFAS on PlumeStop® and polymer-free CAC (Fig. 3-2). The +/- values represent the 95 % confidence interval for each isotherm parameter.

PlumeStop®						Polymer-free CAC				
	Linear		Freundlich			Linear		Freundlich		
	K _d (L/g)	R ²	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²	K _d (L/g)	R ²	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²
PFBA	1.7 ± 0.26	0.77	1.7 ± 2.9	1 ± 0.26	0.77	Less than 5 % of PFBA was removed. Thus, no model can be fitted to the data.				
PFBS	22 ± 4	0.91	7.4 ± 1.8	0.57 ± 0.08	0.97	59 ± 14	0.91	12 ± 2.5	0.50 ± 0.06	0.98
PFHxS	482 ± 84	0.95	73.4 ± 21	0.61 ± 0.05	0.99	1,330 ± 269	0.93	113 ± 41	0.57 ± 0.06	0.98
PFOS	2,653 ± 264	0.98	531 ± 225	0.75 ± 0.07	0.97	9,579 ± 829	0.94	5,348 ± 8,468	0.92 ± 0.2	0.94
PFPeA	7.5 ± 0.6	0.97	7.5 ± 4.8	1 ± 0.34	0.97	9.9 ± 0.9	0.97	5.3 ± 0.8	0.69 ± 0.07	0.98
PFOA	233 ± 44	0.94	42 ± 11	0.58 ± 0.06	0.99	824 ± 172	0.93	79 ± 24	0.56 ± 0.05	0.99
6:2 FTS	1,133 ± 173	0.95	193 ± 71	0.65 ± 0.07	0.98	1,764 ± 99	0.97	1,764 ± 1,310	1 ± 0.13	0.97

The isotherms of PFBS, PFHxS, and PFOA seem to be better fitted by the Freundlich model ($R^2 = 0.97\text{--}0.99$) than by the linear model ($R^2 = 0.91\text{--}0.95$), whereas the isotherms of PFPeA could be described by either model ($R^2 = 0.97$ or 0.98) (Table 3-2). For PFOS and 6:2 FTS, while the R^2 values of the Freundlich fittings are similar or slightly greater than those of the linear fittings, there is high uncertainty associated with the K_f values. As such, it appeared that the PFOS and 6:2 FTS isotherms could be better described by the linear model. Note that a major assumption of the Freundlich model is that there is a distribution of surface sites with different adsorption affinity and that adsorbates will first occupy high-affinity sites (i.e., the “strong” sites), followed by adsorption on low-affinity sites. Since the C_s values in this study spanned over less than one order of magnitude (Fig. 3-2), PFAS may have been adsorbed to only the strong sites on the CAC surface. As such, whether the adsorption of PFAS on CAC obeys the linear or the Freundlich model may not be entirely discerned based on the experimental data, especially if experimental errors are factored in. It is also noted that the isotherm model used to describe PFAS adsorption could have implications for the prediction of barrier longevity. Specifically, a parameter that is often employed to describe the transport of contaminants in the subsurface is the retardation coefficient (R), which can be calculated by the following equations:

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad (1)$$

$$R = 1 + \frac{\rho_b}{\theta} K_f n C_w^{n-1} \quad (2)$$

with ρ_b being the soil dry bulk density (g/cm^3), θ the effective porosity (cm^3/cm^3), K_d being the linear partition coefficient, and K_f and n being the Freundlich isotherm parameters. Equation (1) is applicable to contaminants whose adsorption can be described by the linear isotherm model, whereas equation (2) is used when the adsorption obeys the Freundlich isotherm model. Assuming

a ρ_b value of 1.65 g/cm³, a θ value of 0.35 cm³/cm³, and a C_w value of 0.01 mg/L, the retardation values would be $R = 1.25 \times 10^7$ (based on equation 1) and $R = 5.94 \times 10^6$ (based on equation 2) when using the K_d , K_f , and n parameters for PFOS on the polymer-containing CAC (Table 3-2). While the two R values differ by less than an order of magnitude, it should be noted that R is independent of C_w in equation (1). Also, R is linearly proportional to K_d and K_f but is exponentially dependent on n . As a result, R is more sensitive to changes to n (i.e., changes in surface heterogeneity) than to K_d or K_f .

3.3.3 The effect of organics

Ethanol and 1,4-dioxane. The adsorption isotherms of PFOS and PFOA in the presence of varying concentrations of ethanol and 1,4-dioxane are presented in Fig. 3-4, and the associated isotherm parameters are presented in Table 3-3. As described above, the adsorption of PFOS on the polymer-free CAC could be better described by the linear model ($K_d = 9,579 \pm 829$ L/g). In the presence of either ethanol or 1,4-dioxane, the PFOS isotherms also seem to be better fitted to the linear model, because of the high uncertainty associated with the K_f values (Table 3-3). The K_d value increased from $7,545 \pm 921$ L/g and $7,698 \pm 505$ L/g (in the presence of $61.6 \mu\text{M}$ of ethanol and 1,4-dioxane, respectively) to $11,179 \pm 835$ L/g and $10,207 \pm 1,427$ L/g (in the presence of $616 \mu\text{M}$ ethanol and 1,4-dioxane, respectively). However, considering the uncertainty associated with these K_d values, as well as a lack of a clear trend between these values and the concentration of the co-contaminants, it could be concluded that 1,4-dioxane and ethanol did not have an appreciable effect on PFOS adsorption under the experimental conditions employed in this study. Similarly, there appeared to be no appreciable effect of these two co-contaminants on the adsorption of PFOA, except for when the concentration of 1,4-dioxane was $308 \mu\text{M}$, under which condition the K_f and n values were slightly higher (Table 3-3). Siriwardena et al. also observed that 1 mg/L ethanol (i.e., $22 \mu\text{M}$) did not appreciably affect the adsorption of PFOS on a bituminous coal-based (Filtrisorb F400, Calgon) and a coconut-based (CBC-OLC, Calgon) GAC (Siriwardena et al., 2019). On the contrary, they reported that the presence of ethanol enhanced the adsorption of PFOA on both adsorbents. However, this conclusion was based on a single-point isotherm experiment. Whether a similar effect of ethanol would be observed at a range of C_w and C_s is unclear. It should be noted that the effect of 1,4-dioxane and ethanol on the adsorption of PFOS and PFOA in our study could have been masked by the effect of methanol, whose concentration in the reaction solution

(0.1 v/v %, or 17.2 mM) was 28–280 times greater than those of 1,4-dioxane and ethanol. The concentration of methanol in our reaction solution was in the range similar to that in the PFAS adsorption studies by Guelfo and Higgins, 2013 (0.04 v/v %) and Higgins and Luthy, 2006 (0.2 v/v %). In PFAS adsorption experiments (in this study and in other studies), the presence of methanol in the reaction solution is not avoidable because PFAS stocks are made by dissolving PFAS in methanol.

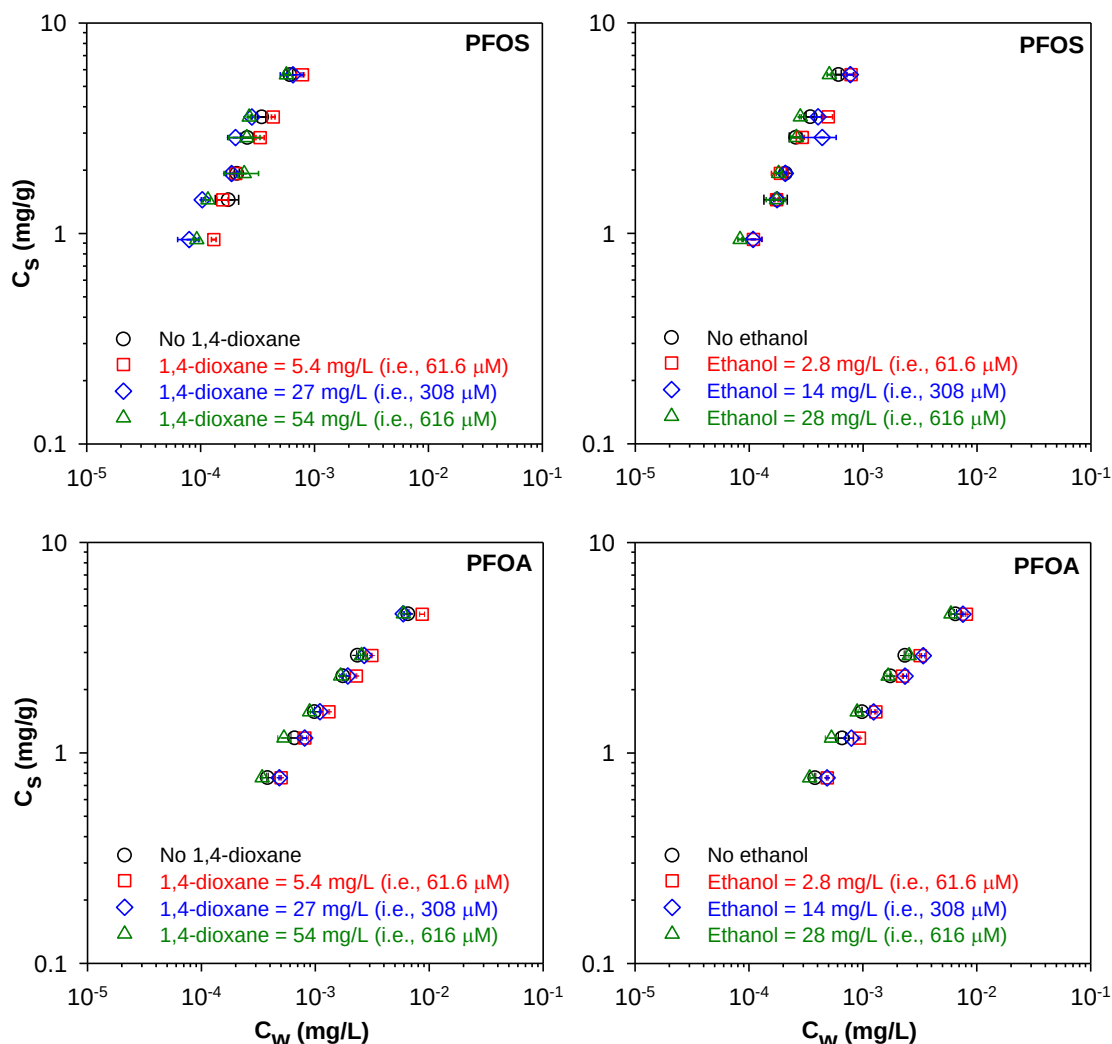


Figure 3-4. The effect of 1,4-dioxane (left panels) and ethanol (right panels) on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), either $[\text{PFOS}]_0 = 650 \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \mu\text{g/L}$, and either 1,4-dioxane or ethanol. The isotherm fitting parameters can be found in Table 3-3. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig S1 in the Appendix.

Table 3-3. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of 1,4-dioxane, ethanol, and DGBE (Figures 3-4 and 3-5). The +/- values represent the 95 % confidence interval for each isotherm parameter.

	Co-contaminant concentration (μM)	PFOS					PFOA				
		Linear		Freundlich			Linear		Freundlich		
		K_d (L/g)	R^2	K_f (mg/g)(mg/L) ⁻ⁿ	n	R^2	K_d (L/g)	R^2	K_f (mg/g)(mg/L) ⁻ⁿ	n	R^2
	0	9,579 $\pm$ 829	0.94	5,348 $\pm$ 8,468	0.92 $\pm$ 0.20	0.94	824 $\pm$ 172	0.93	79 $\pm$ 24	0.56 $\pm$ 0.05	0.99
1,4-dioxane	61.6	7,698 $\pm$ 505	0.98	2,842 $\pm$ 1,564	0.85 $\pm$ 0.08	0.99	616 $\pm$ 132	0.93	65 $\pm$ 19	0.55 $\pm$ 0.05	0.99
	308	9,523 $\pm$ 1,748	0.85	797 $\pm$ 1,068	0.68 $\pm$ 0.17	0.90	882 $\pm$ 129	0.96	131 $\pm$ 36	0.65 $\pm$ 0.05	0.99
	616	10,207 $\pm$ 1,427	0.85	2,997 $\pm$ 6,574	0.84 $\pm$ 0.28	0.85	892 $\pm$ 168	0.96	86 $\pm$ 15	0.57 $\pm$ 0.03	1.00
Ethanol	61.6	7,545 $\pm$ 729	0.95	1,694 $\pm$ 1,713	0.80 $\pm$ 0.13	0.96	656 $\pm$ 126	0.94	77 $\pm$ 21	0.58 $\pm$ 0.05	0.99
	308	7,389 $\pm$ 921	0.89	1,786 $\pm$ 3,029	0.81 $\pm$ 0.22	0.90	692 $\pm$ 116	0.97	87 $\pm$ 13	0.60 $\pm$ 0.03	1.00
	616	11,179 $\pm$ 835	0.95	11,181 $\pm$ 16,349	1.00 $\pm$ 0.18	0.95	980 $\pm$ 186	0.94	99 $\pm$ 35	0.59 $\pm$ 0.06	0.98
DGBE	61.6	2,603 $\pm$ 654	0.86	76 $\pm$ 39	0.45 $\pm$ 0.08	0.95	57 $\pm$ 27	0.76	8 $\pm$ 1.3	0.27 $\pm$ 0.04	0.97
	308	431 $\pm$ 111	0.94	34 $\pm$ 6	0.44 $\pm$ 0.03	0.99	6.8 $\pm$ 2.1	0.74	2.3 $\pm$ 0.4	0.23 $\pm$ 0.08	0.84
	616	245 $\pm$ 56	0.95	31 $\pm$ 4	0.47 $\pm$ 0.03	0.99	4.5 $\pm$ 0.7	0.93	2.01 $\pm$ 0.35	0.38 $\pm$ 0.11	0.88

DGBE. Contrary to 1,4-dioxane and ethanol, 61.6–616 μM DGBE significantly suppressed the adsorption of PFOS and PFOA (Fig. 3-5). For PFOA, the exponent term (n) in the Freundlich equation decreased from 0.56 ± 0.05 (in the absence of DGBE) to as low as 0.23 ± 0.05 (in the presence of 308 μM DGBE) (Table 3-3). For PFOS, its adsorption in the presence of DGBE could be better described by the Freundlich model rather than by the linear model, with the exponent term (n) varying between 0.45 ± 0.08 and 0.47 ± 0.03 . When the initial concentration of DGBE was 616 μM , 47 % and 92 % of DGBE were removed from the solution at the lowest (0.11 g/L) and highest (0.7 g/L) CAC concentrations, respectively (Fig. 3-6). Collectively, these results suggest that DGBE competed with PFOS and PFOA for high-affinity sites, resulting in the adsorption of PFOS and PFOA to sites with a wider adsorption energy range.

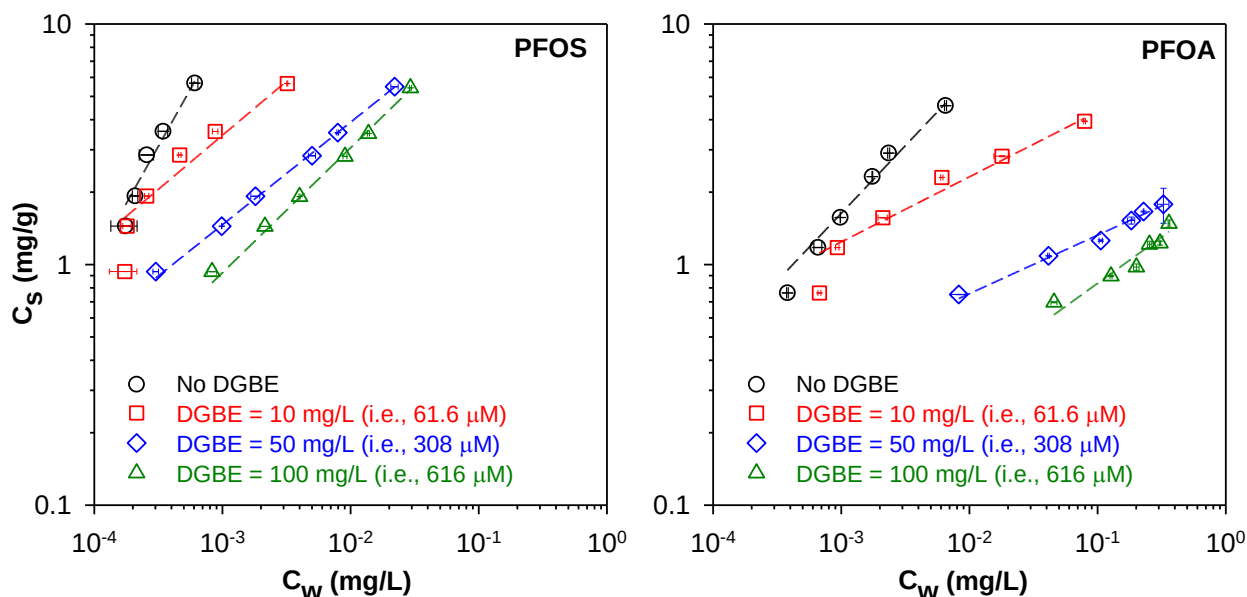


Figure 3-5. The effect of DGBE on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 ($\text{pH} = 7.5\text{--}8.5$), DGBE, and either $[\text{PFOS}]_0 = 650 \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \mu\text{g/L}$. The dashed lines represent the fitting of the experimental data to the Freundlich model. The fitting parameters are presented in Table 3-3.

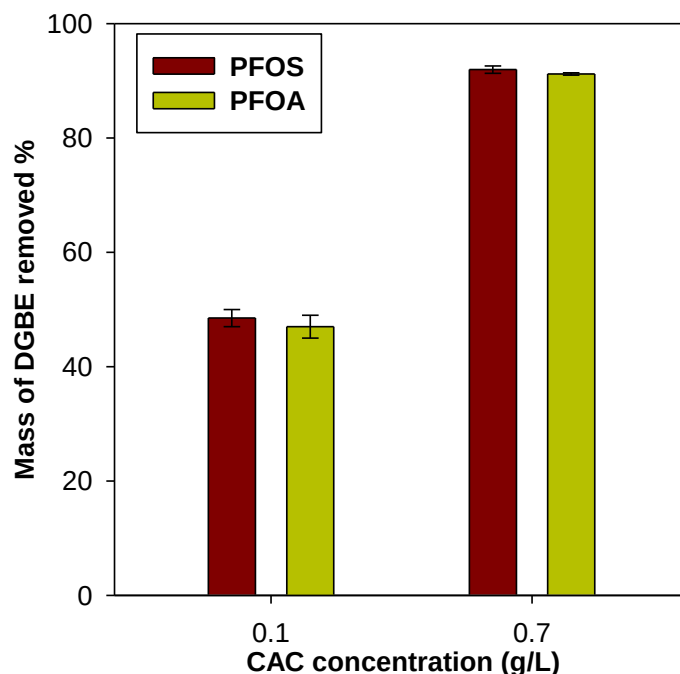


Figure 3-6. Mass of diethylene glycol butyl ether (DGBE) removed. Reaction solutions contained either 0.1 or 0.7 g/L CAC, 1 mM NaHCO₃ (pH = 7.5 - 8.5), [DGBE]₀ = 100 mg/L, and either [PFOS]₀ = 650 µg/L or [PFOA]₀ = 530 µg/L.

According to Harding-Marjanovic et al., some AFFF formulations contain at least 8 % (w/w) DGBE (Harding-Marjanovic et al., 2016). More recently, Titaley et al. reported that the concentration of DGBE in 37 AFFF formulations ranged from 26 to 420 g/L (Titaley et al., 2022). At contaminated sites, DGBE is expected to be more mobile than PFAS since it is relatively hydrophilic ($\log K_{ow} = 0.56$) (Hansch et al., 1995). DGBE also could be biodegraded under both aerobic and anaerobic conditions (Harding-Marjanovic et al., 2016; Yi et al., 2018). It could also volatilize (Titaley et al., 2022). As a result, after the release of DBGE-containing AFFFs, it is expected that the concentration of DGBE in groundwater would decrease due to volatilization, biodegradation, and dilution by groundwater. While little is known about how much DGBE could be present in plumes of PFAS, it was observed in this study that a DGBE concentration as low as 61.6 µM (i.e., 0.01 g/L) diminished the adsorption of PFOS and PFOA on CAC. The significant

adsorption (47–92 %, as mentioned above) of DBGE on CAC is somewhat unexpected. One possible explanation could be that the adsorption of DGBE on CAC was not driven by hydrophobic interactions. Although the mechanism of DGBE adsorption is not understood at this point, the results of this study suggest that the research on the fate and transport of PFAS in the subsurface should consider the effect of DGBE as well as other glycols (e.g., ethylene glycol, hexylene glycol, propylene glycol) that may be present in AFFFs.

Suwanee River Fulvic Acid. The adsorption of PFOS and PFOA decreased as the initial concentration of SRFA increased from 1 to 20 mgC/L (Fig. 3-7 and Table 3-4). The K_d values of PFOS adsorption when $[SRFA]_0 = 5$ mgC/L and 20 mgC/L were $6,856 \pm 854$ L/g and $2,461 \pm 527$ L/g, respectively. These values represent a decrease of 30 % and 75 %, compared with the K_d value ($9,579 \pm 829$ L/g) measured in the system where SRFA was absent. The K_d values for PFOA were 664 ± 139 L/g and 225 ± 64 L/g when $[SRFA]_0 = 5$ mgC/L and 20 mgC/L, respectively (versus $K_d = 824 \pm 172$ L/g when SRFA was absent). (While some isotherms could be better fitted to the Freundlich model, the isotherm parameters K_f and n varied simultaneously as the chemistry of the reaction solution changed. Hence, the linear partition coefficient K_d values were compared). The inhibitory effect of DOM on the adsorption of PFAS has been attributable to the blocking of pores, particularly macropores, resulting in the preclusion of PFAS from entering into mesopores and micropores. However, it is speculated that pore blocking by SRFA was unlikely appreciable because SRFA is not significantly larger than PFOS (MW = 500 Da.) and PFOA (MW = 414 Da.). The average MW of SRFA ranges between 800 and 1,500 Da. (Thurman et al., 1982; Beckett et al., 1987; Aiken and Malcolm, 1987; Chin et al., 1994; Reid et al., 1990), although one study suggested that 36 % (based on the mass of dissolved carbon) of SRFA has an MW smaller than 500 Dalton (Remucal et al., 2012). Another explanation for the inhibitory effect of SRFA could be

the competition between SRFA and PFOS/PFOA for the same adsorptive sites on CAC. This hypothesis is similar to that of Yu et al., who reported that the effluent organic matter fraction of $< 1,000$ Da. significantly inhibited the adsorption of PFOS and PFOA on powdered activated carbon (Yu et al., 2012).

Compared to the effect that DGBE had on the adsorption of PFOS/PFOA, the effect of SRFA appeared to be less significant. For PFOS, the K_d value measured in the presence of 5 mgC/L of SRFA ($6,856 \pm 854$ L/g) was over 2.5 times greater than the K_d value ($2,603 \pm 654$ L/g) measured in the system with an initial DGBE concentration of 61.6 μ M, which is equivalent to 5.9 mg C/L of DOC. The effect of 5.9 mg C/L of DGBE on PFOS adsorption was similar to the effect caused by 20 mgC/L SRFA ($K_d = 2,461 \pm 654$ L/g). In the case of PFOA, 5.9 mgC/L DGBE had a greater inhibitory effect ($K_d = 57 \pm 27$ L/g) even compared to when as much as 20 mg C/L SRFA was present ($K_d = 225 \pm 64$ L/g). This greater effect of DGBE on PFOS and PFOA adsorption corroborates the hypothesis mentioned earlier, that the adsorption of DGBE might be driven by a mechanism other than hydrophobic interaction.

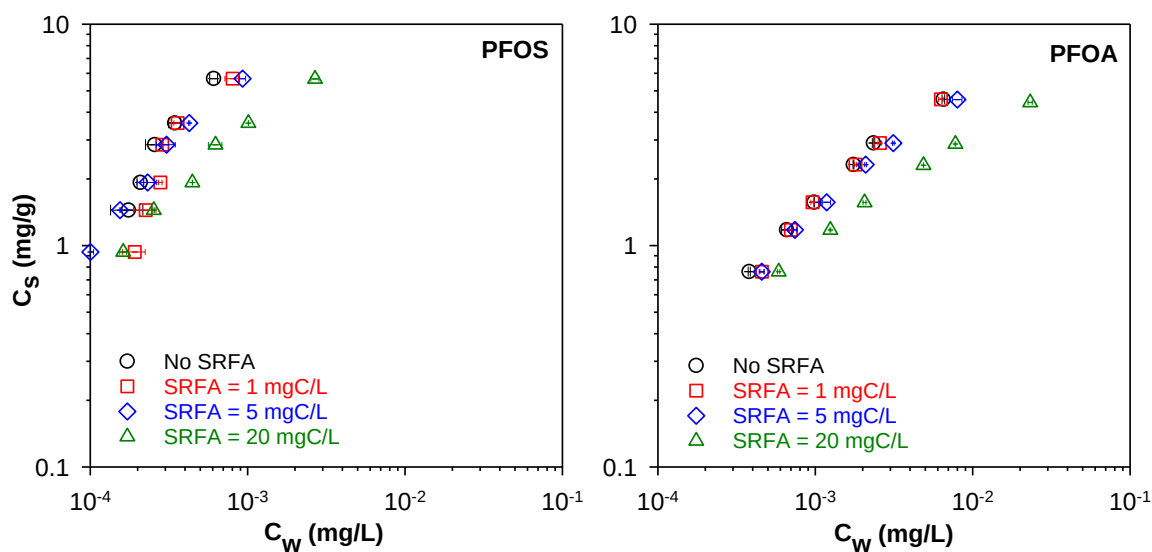


Figure 3-7. The effect of Suwannee River Fulvic Acid on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 ($\text{pH} = 7.5\text{--}8.5$), SRFA, and either $[\text{PFOS}]_0 = 650 \text{ } \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \text{ } \mu\text{g/L}$. The isotherm fitting parameters can be found in Table 3-4. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig. S2 in the Appendix.

Table 3-4. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of SRFA (Figure 3-7). The +/- values represent the 95 % confidence interval for each isotherm parameter.

PFOS						PFOA				
	Linear		Freundlich			Linear		Freundlich		
SRFA (mgC/L)	K _d (L/g)	R ²	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²	K _d (L/g)	R ²	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²
0	9,579 ± 829	0.94	5,348 ± 8,468	0.92 ± 0.2	0.94	824 ± 172	0.93	79 ± 24	0.56 ± 0.05	0.99
1	7,466 ± 993	0.86	3,089 ± 5,782	0.88 ± 0.25	0.86	845 ± 156	0.95	95 ± 27	0.59 ± 0.05	0.99
5	6,856 ± 854	0.95	881 ± 623	0.72 ± 0.09	0.97	664 ± 139	0.93	68 ± 18	0.56 ± 0.05	0.99
20	2,461 ± 527	0.92	159 ± 68	0.56 ± 0.06	0.98	225 ± 64	0.91	23.6 ± 3	0.44 ± 0.02	1.00

Benzene and TCE. The isotherms of PFOS and PFOA in the presence of benzene and TCE are presented in Fig. 3-8, and the corresponding isotherm parameters are presented in Table 3-5. In all experiments, the concentrations of benzene and TCE were below the detection limits (5 µg/L for benzene, 0.5 µg/L for TCE), suggesting that essentially all benzene and TCE were adsorbed by CAC. Meanwhile, the adsorption of PFOS was diminished compared to when benzene and TCE were absent. As the initial concentration of TCE increased from 0 to 0.5 mg/L and 8 mg/L, the K_d for PFOS decreased from $K_d = 9,579 \pm 829$ L/g to $6,140 \pm 1,592$ L/g and 514 ± 20 L/g, respectively. Compared to TCE, benzene had less of an impact on PFOS adsorption: the K_d values in the presence of 0.5 and 4.8 mg/L were $6,932 \pm 982$ L/g and $6,634 \pm 1,963$ L/g, respectively. The diminished PFOS adsorption by benzene and particularly by 8 mg/L TCE could be attributable to the competition between PFOS and these co-contaminants for adsorptive sites. Somewhat surprisingly, the adsorption of PFOA was not affected or was even enhanced by TCE and benzene, with K_d values in the presence of TCE or benzene being up to 2.5 times higher (Fig. 3-8 and Table 3-5). Previous studies have suggested that TCE NAPL could absorb contaminants and thus enhance their removal from the aqueous phase (Guelfo and Higgins, 2013; Jonker et al., 2003; Jonker and Barendregt, 2006). Although the concentrations of benzene and TCE in our study were much lower than their aqueous solubility ($> 1,000$ mg/L), it might be possible that the adsorbed benzene and TCE formed a NAPL phase inside CAC pores, thereby enhancing PFOA adsorption. While it is not possible to prove this hypothesis at this point, our result is similar to that of Siriwardena et al., who also reported that the adsorption of PFOA on GAC was enhanced in the presence of 1 mg/L TCE (Siriwardena et al., 2019). These similar observations indicate that additional research is needed to investigate whether the influence of TCE and benzene (and other co-contaminants) is dependent upon each PFAS/class of PFAS.

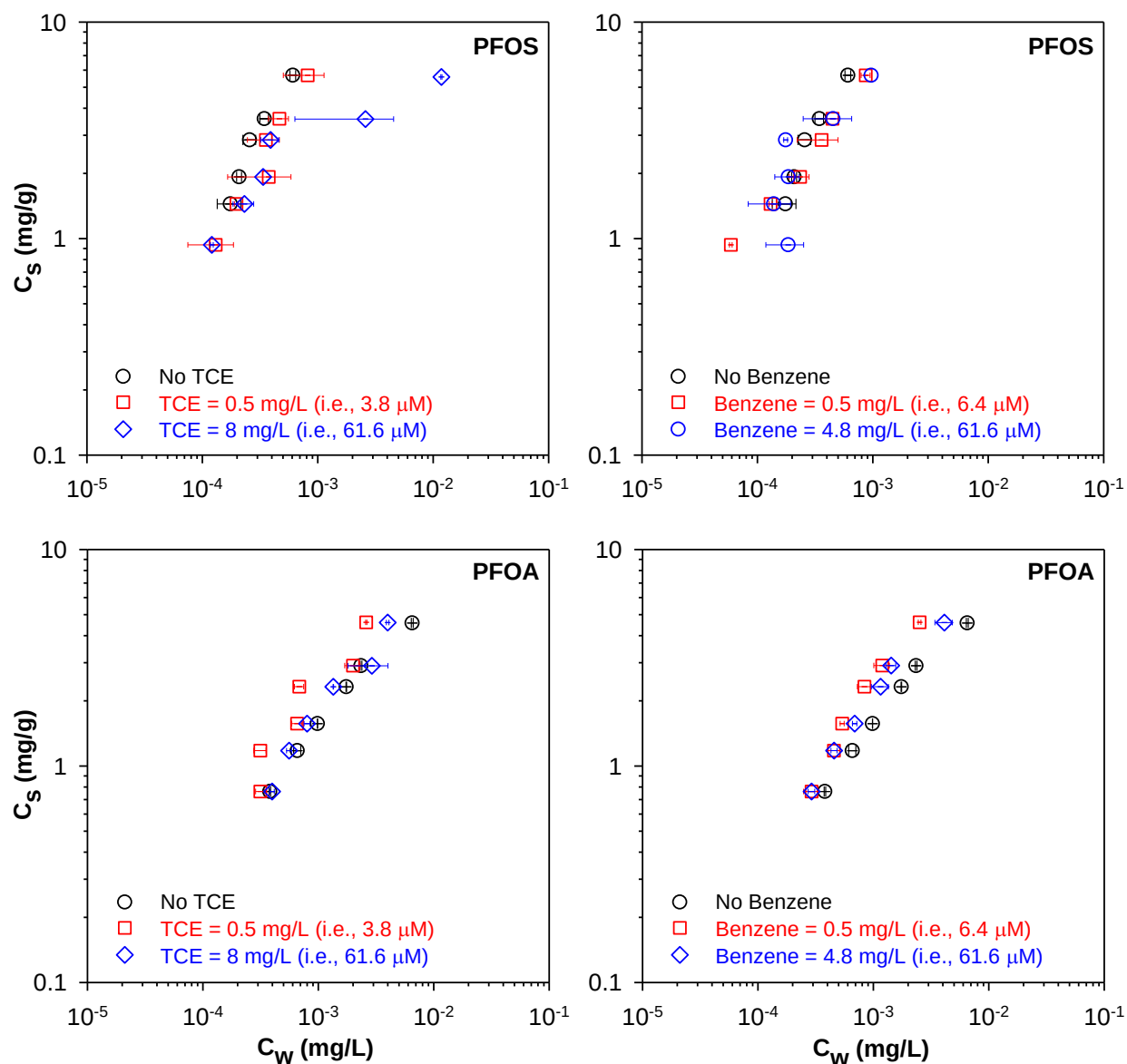


Figure 3-8. The effect of TCE and benzene on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), either TCE or benzene, and either $[\text{PFOS}]_0 = 650 \text{ } \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \text{ } \mu\text{g/L}$. The isotherm fitting parameters can be found in Table 3-5. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig. S3 in the Appendix.

Table 3-5. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of TCE and benzene (Fig. 3-8). The +/- values represent the 95 % confidence interval for each isotherm parameter.

	Co-contaminant concentration (μM)	PFOS					PFOA				
		Linear		Freundlich			Linear		Freundlich		
		K_D (L/g)	R^2	K_f (mg/g)(mg/L) ⁻ⁿ	n	R^2	K_D (L/g)	R^2	K_f (mg/g)(mg/L) ⁻ⁿ	n	R^2
	0	9,579 $\pm$ 829	0.94	5,348 $\pm$ 8,468	0.92 $\pm$ 0.20	0.94	824 $\pm$ 172	0.93	79 $\pm$ 24	0.56 $\pm$ 0.05	0.99
TCE	3.8	6,140 $\pm$ 1,592	0.61	0.61	423 $\pm$ 1,162	0.63	1,759 $\pm$ 307	0.88	186 $\pm$ 226	0.64 $\pm$ 0.19	0.88
	61.6	514 $\pm$ 240	0.78	19 $\pm$ 10	0.27 $\pm$ 0.09	0.86	1382 $\pm$ 274	0.84	140 $\pm$ 152	0.60 $\pm$ 0.18	0.88
Benzene	0.64	6,932 $\pm$ 982	0.93	692 $\pm$ 839	0.69 $\pm$ 0.16	0.93	2,048 $\pm$ 263	0.95	338 $\pm$ 229	0.72 $\pm$ 0.1	0.97
	61.6	6634 $\pm$ 1963	0.68	288 $\pm$ 636	0.57 $\pm$ 0.28	0.67	1274 $\pm$ 294	0.87	103 $\pm$ 65	0.57 $\pm$ 0.1	0.95

3.3.4 The effect of ionic strength and Ca^{2+}

Adsorption barriers have been proposed for the in-situ immobilization of PFAS at coastal sites (Bangert, 2023).¹²⁸ While the impact of ionic strength on the adsorption of PFAS by soils and inorganic minerals has been studied (Tang et al., 2010; Xiao et al., 2012; Wang et al., 2012; Wang et al., 2022), little is known about how ionic strength affects the adsorption of PFAS on AC. In this current study, it was observed that the affinity of PFOS to the polymer-free CAC was enhanced when the reaction solution contained 100 mM NaCl (Fig. 3-9). At this NaCl concentration, all C_w values for PFOS were less than 100 ng/L. Because the quantitation limit of PFOS in this study was 50 ng/L, there is a high uncertainty associated with the C_w values of this experiment. On the contrary, the adsorption of PFOS was not appreciably affected by the presence of either 1 mM or 10 mM NaCl. However, there were also high uncertainties associated with the C_w values of these experiments, which were all less than 500 ng/L. These high uncertainties might have masked any effect that NaCl had on the adsorption of PFOS. Alternatively, the minimal effect of NaCl in the 1–10 mM concentration range could have been due to PFOS molecules already having adequate access to high-affinity sites on CAC in the absence of NaCl. In all experiments, over 99.9 % of PFOS was removed even with the lowest CAC dosage (Fig. 3-9, the highest points in the PFOS isotherms). For PFOA, its adsorption on polymer-free CAC progressively increased as the concentration of NaCl increased (Fig. 3-9), with K_d in the presence of 100 mM NaCl ($6,010 \pm 716$ L/g) being over 7 times greater than the K_d in the absence of NaCl (824 ± 172 L/g) (Table 3-6). As discussed earlier, it is expected that electrostatic attractions exist between the positively charged CAC surface and the negatively charged PFOS and PFOA molecules. Because an increase in ionic strength would suppress electrostatic attraction (Saeidi et al., 2021), the enhanced PFOS and PFOA adsorption as the concentration of NaCl increased might be attributable

to the salting-out effect (Du et al., 2014). While Xiao et al. suggested that the salting-out effect was negligible for the adsorption of PFOS and PFOA on kaolinite in the presence of up to 1 mM NaCl (Xiao et al., 2011), the salting-out effect could be important at higher NaCl concentrations (e.g., 10–100 mM NaCl).

Similar to the effect of ionic strength, the effect of Ca^{2+} has been studied only for the adsorption of PFAS on sediments and soils but not on AC. In these previous studies with soils and sediments, the concentration of Ca^{2+} was varied by adding different amounts of Ca-containing salt (e.g., CaCl_2) to the solution. Because the addition of salt also impacts the ionic strength of the solution, the effect of Ca^{2+} could have been confounded by the effect of ionic strength. In the current study, the ionic strength of the solution was carefully controlled to 7 mM to separate these two effects. As can be seen from Fig. 3-9 and Table 3-6, the affinity of PFOS and PFOA to the polymer-free CAC progressively increased with increasing Ca^{2+} concentration. This enhanced adsorption could be attributable to Ca^{2+} ions serving as the bridge between the surface and the head group in PFAS, a hypothesis that was put forward previously (Wang et al., 2022). The positive effect of Ca^{2+} on the adsorption of PFAS indicates that the breakthrough of PFAS in CAC barriers will be retarded in groundwater containing high Ca^{2+} concentrations. In applications where CaCl_2 is injected into the subsurface to coagulate CAC particles and diminish their mobility (Niarchos et al., 2023a), the potential added benefit of CaCl_2 would be a greater PFAS immobilization immediately following CAC injection. However, this effect of CaCl_2 might dissipate over time as the concentration of Ca^{2+} decreases to the background level following dilution with groundwater.

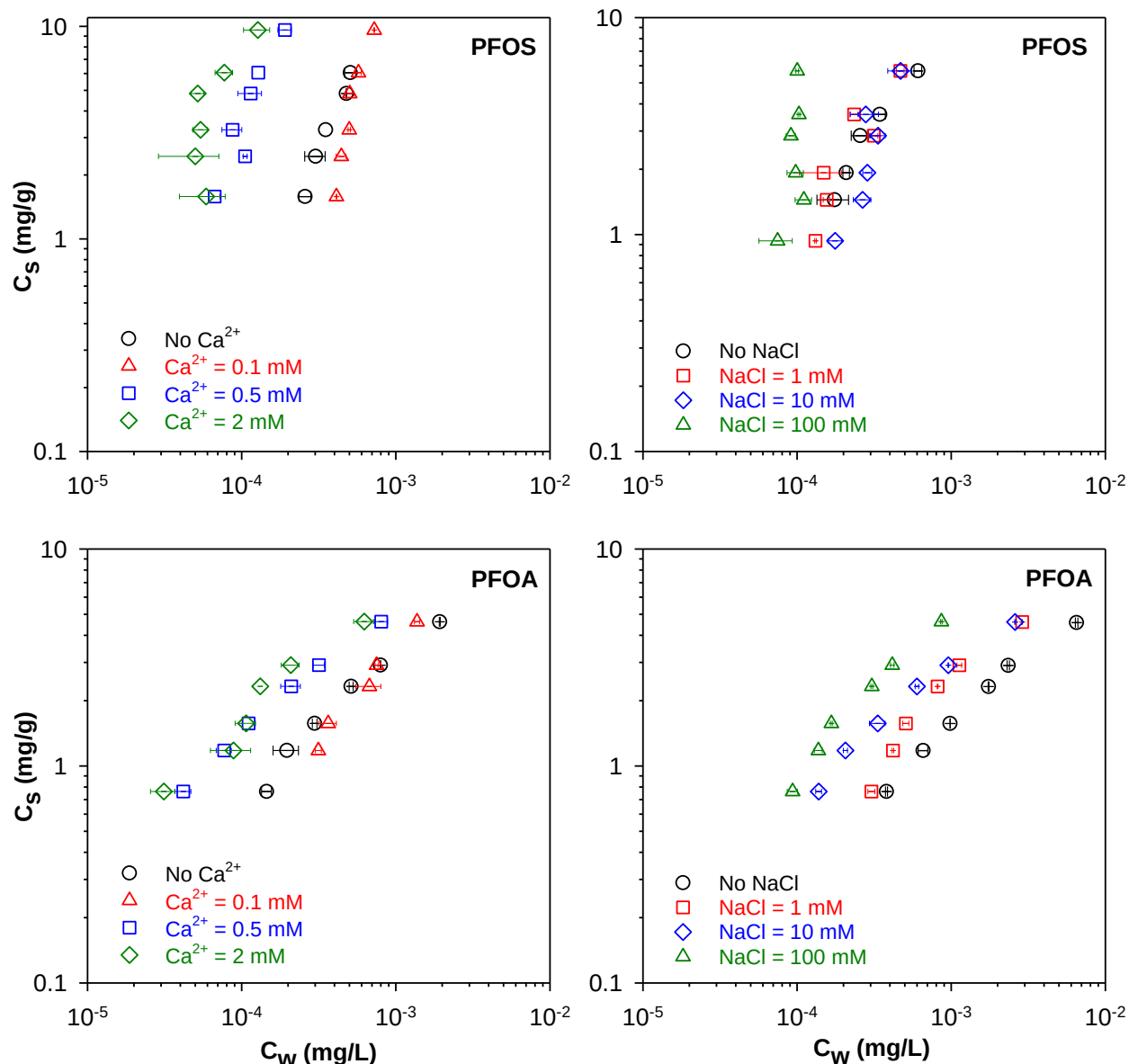


Figure 3-9. The effect of Ca^{2+} and ionic strength on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solution contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), and either $[\text{PFOS}]_0 = 1100 \text{ }\mu\text{g/L}$ (top left panel) or $[\text{PFOS}]_0 = 650 \text{ }\mu\text{g/L}$ (top right panel) or $[\text{PFOA}]_0 = 530 \text{ }\mu\text{g/L}$. To eliminate the effect of ionic strength in Ca^{2+} experiments, between 0 and 5.7 mM of NaCl was added so that the ionic strength was 7 mM in all Ca^{2+} experiments. The isotherm fitting parameters can be found in Table 3-6. For presentation clarity, the fitting lines were not included in this figure, but they can be found in Fig. S4 in the Appendix.

Table 3-6. The linear and Freundlich isotherm parameters for the adsorption of PFOS and PFOA on the polymer-free CAC in the presence of NaCl and Ca²⁺ (Fig. 3-9). The +/- values represent the 95 % confidence interval for each isotherm parameter.

		PFOS					PFOA				
		Linear		Freundlich			Linear		Freundlich		
Ca ²⁺ (mM)	NaCl (mM)	K _D (L/g)	R ²	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²	K _D (L/g)	R ²	K _f (mg/g)(mg/L) ⁻ⁿ	n	R ²
0	0	9,579 ± 829	0.94	5,348 ± 8,468	0.92 ± 0.20	0.94	824 ± 172	0.93	79 ± 24	0.56 ± 0.05	0.99
0	1	11,429 ± 1,547	0.84	11,433 ± 31,582	1.00 ± 0.34	0.84	1,853 ± 318	0.92	203 ± 118	0.64 ± 0.09	0.97
0	10	9,415 ± 2,085	0.65	9,417 ± 54,658	1.00 ± 0.73	0.64	2,078 ± 475	0.93	109 ± 34	0.53 ± 0.05	0.99
0	100	Due to high uncertainty, the experimental data was not fitted					6,010 ± 716	0.97	694 ± 296	0.71 ± 0.06	0.99
0	6	10,087 ± 944	0.94	10,087 ± 17,167	1.00 ± 0.23	0.94	2,774 ± 522	0.94	186 ± 71	0.59 ± 0.06	0.99
0.1	5.7	9,414 ± 2,192	0.93	9,415 ± 86,561	1.00 ± 1.2	0.93	3,564 ± 286	0.98	1,100 ± 791	0.83 ± 0.1	0.96
0.5	4.5	41,811 ± 7,808	0.84	41,811 ± 211,707	1.00 ± 0.55	0.84	6,570 ± 1,445	0.93	233 ± 120	0.55 ± 0.07	0.98
2	0	66,047 ± 14,715	0.6	64,920 ± 340,782	1.00 ± 0.57	0.59	8,457 ± 2,220	0.86	197 ± 158	0.51 ± 0.1	0.93

3.4. Conclusions

To date, PlumeStop CAC was applied to immobilize plumes of PFAS in situ at over a dozen sites around the world, including in the US, the UK, Canada, and Sweden (Carey et al., 2019; McGregor, 2020; McGregor, 2021; McGregor, 2022; Niarchos, 2023a). While the longevity of PlumeStop CAC barriers with respect to preventing PFAS breakthrough could be on the order of decades (Carey et al., 2019), the retention of PFAS by CAC barriers will be dependent upon site-specific factors such as the hydrogeology of the site, the mass of CAC injected and its distribution in the subsurface, the mass flux of PFAS entering the barrier, and the chemistry of the groundwater. This study investigated several solution parameters that may affect the adsorption of 7 PFAS on PlumeStop CAC. Key findings and their implications are summarized below:

- The adsorption of the seven studied PFAS on CAC was driven primarily by hydrophobic interactions, suggesting that hydrophilic compounds such as PFBA and PFPeA will be among the first compounds to break through CAC barriers. This is consistent with the observation made by Niarchos et. al., who reported that PFPeA was the first compound to break through a soil column loaded with CAC (Niarchos et al., 2022). Niarchos et al. also reported that due to competitive sorption, PFPeA was displaced by longer-chain compounds, resulting in PFPeA concentration overshooting (Niarchos et al., 2022). While shorter chain compounds are less bioaccumulative and therefore are less of a concern (e.g., the LHA for PFBS set by US EPA is 100,000 times greater than the LHA for PFOS), future regulatory limits for these compounds may become more stringent. As such, the retention and breakthrough of hydrophilic PFAS should be considered when designing and implementing in-situ CAC barriers.

- The adsorption of PFOS and PFOA by CAC was suppressed by SRFA and DGBE. Notably, DGBE, which is smaller and more hydrophilic than SRFA, had a greater inhibitory effect. While the mechanism through which DGBE inhibits the adsorption of PFOS and PFOA remains to be investigated, this result suggests that the effect of DGBE on the fate and transport of PFAS in the subsurface should be considered, as DGBE is an important component of many AFFF formulations.
- Benzene and TCE suppressed PFOS adsorption but had no effect or slightly enhanced PFOA adsorption, suggesting that the effect of benzene and TCE could be specific to each PFAS/class of PFAS. Because benzene, TCE, and other non-fluorinated contaminants could come along with PFAS in the groundwater at AFFF-impacted sites, additional research is needed to investigate their effect on the retention and breakthrough of PFAS in CAC barriers.
- By carefully controlling the ionic strength and the concentration of Ca^{2+} in the reaction solution, it was observed in this study that these two solution parameters enhanced the adsorption of PFOS and PFOA on CAC. As such, CAC barriers at coastal sites or at sites where the concentration of Ca^{2+} in groundwater is high may have greater longevity. Whether ionic strength and Ca^{2+} also have a positive effect on the adsorption of other PFAS by CAC remains to be investigated. The effect of other multivalent cations (e.g., Mg^{2+} , Al^{3+} , Fe^{3+}) on the adsorption of PFAS by CAC also should be studied.

It should be noted that the findings presented above concern the adsorption of PFAS on PlumeStop CAC. Whether these findings extend to other CAC materials remains to be explored.

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Chapter 4: An Investigation of the Effects of Aquifer Materials and Solution Chemistry on the Adsorption of PFAS by Colloidal Activated Carbon

by Seyfollah Gilak Hakimabadi, Hak-Hyeon Kim, and Anh Le-Tuan Pham. Manuscript prepared for journal submission.

4.1. Introduction

Colloidal activated carbon (CAC) barriers are becoming increasingly popular means of immobilizing per- and polyfluoroalkyl substances (PFAS) in situ, with several barriers deployed at PFAS-impacted sites around the world within the past five years (McGregor, 2018; Carey et al., 2019; McGregor, 2020a; McGregor and Benevenuto, 2021; McGregor and Zhao, 2021; Carey et al., 2022; Niarchos et al., 2023a). CAC barriers are created by injecting a suspension of CAC into the subsurface. These particles then deposit on aquifer materials, resulting in a stationary adsorption zone that retains PFAS and substantially reduces their mobility downgradient of the barrier. Compared to *ex-situ* adsorptive treatments, which involve extracting groundwater and treating it with adsorbents such as granular activated carbon (GAC) or ion exchange (IX) resins, immobilizing PFAS in situ has the potential to be more cost-effective because it could be less energy intensive and generates less remediation derived waste (Suthersan, 2005; Newell et al., 2022). However, PFAS breakthrough is expected to eventually occur once the adsorption sites in the barrier become saturated. To improve our understanding of the retention and breakthrough of PFAS in CAC barriers, research evaluating the adsorption of PFAS on CAC is crucial.

In the research reported in Chapter 3, the adsorption of several PFAS on two types of CAC was investigated. The research employed synthetic solutions consisting of one PFAS, 1 mM of NaHCO_3 , and inorganic and organic solutes (NaCl , Ca^{2+} , dissolved organic carbon (DOC), butyl carbitol, trichloroethylene, benzene, 1,4-dioxane, and ethanol). While the research provided important insights into the affinity of each PFAS to CAC, as well as the effects of inorganic and organic solutes, it did not consider the effect that aquifer materials may have on PFAS adsorption. Aquifer materials usually contain organic carbon, which adsorbs organic contaminants by hydrophobic effects (Higgins and Luthy, 2006; Li et al., 2018). Thus, the adsorption of PFAS on

aquifer materials could play an important role in reducing PFAS transport, especially the transport of hydrophobic PFAS such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS). On the contrary, the deposition of CAC to aquifer materials may reduce adsorptive sites available for PFAS sorption. If so, less mass of PFAS would be adsorbed to CAC when aquifer materials are present.

The research described in Chapter 3 also only compared the affinity of each PFAS to CAC using solutions containing one single PFAS. However, PFAS-contaminated groundwaters usually contain a mixture of PFAS that compete with each other for adsorptive sites. Previous studies have shown that the adsorption of shorter-chain, more hydrophilic compounds (e.g., perfluorobutane sulfonate (PFBS)) was substantially reduced in the presence of longer-chain, more hydrophobic compounds (e.g., PFOS) (Zhang et al., 2023; Singh et al., 2024). Therefore, there is a need for research that evaluates the adsorption of a mixture of PFAS on CAC. Additionally, the research described in Chapter 3 only investigated the effect of Ca^{2+} and DOC when only one of these solutes was present (i.e., the concentration of Ca^{2+} was 0.5 and 2 mM, while the concentration of DOC was 0 mM; the concentration of DOC was 1, 5, 20 mgC/L, while the concentration of Ca^{2+} was 0 mM). However, there could be a complex interplay between Ca^{2+} and DOC in the adsorption of PFAS. For example, functional groups such as carboxylate, hydroquinone, and amine in DOC could form complexes with Ca^{2+} (Adusei-Gyamfi et al., 2019), thereby reducing the Ca^{2+} available to form a bridge between PFAS and the CAC surface. In this case, the positive effect of Ca^{2+} on the adsorption of PFAS (Chapter 3) may be diminished in the presence of DOC. The adsorption of PFAS on CAC could also be affected by a complex interplay among other water chemistry parameters, such as the solution pH, ionic strength, and the concentration of Mg^{2+} (which is often a major cation present in groundwater).

The objective of this research was to investigate the effect of aquifer materials and typical groundwater constituents on the adsorption of several PFAS by CAC. To this end, a series of batch experiments were conducted to study the adsorption of PFOS, PFOA, and PFBS on CAC in the presence of six types of aquifer materials. Because the chemistry of the solution in these experiments was controlled by the aquifer material in contact with the solution, the results were also used to examine how solution chemistry influences PFAS adsorption. In particular, the solution chemistry at the end of the experiments was characterized, and the correlation among water chemistry parameters and the partition coefficient K_d for each PFAS was assessed using principal component analysis (PCA). In addition to the experiments with aquifer materials, six PFAS-impacted groundwater samples were fortified with a mixture of five PFAS (PFOS, PFOA, PFHxA (perfluorohexanoate), PFHxS (perfluorohexane sulfonate), and 6:2 FTS (6:2 fluorotelomer sulfonate), and CAC was added to the solution to evaluate the removal of these five PFAS. PCA was employed to assess the correlation among K_d and the chemistry parameters of the groundwater samples.

4.2. Materials and Method

4.2.1. Materials

Single PFAS were purchased from Sigma Aldrich (PFHxA, PFHxS, PFOA, and PFOS) and Toronto Research Chemicals (6:2 FTS). These PFAS were dissolved in methanol to generate single-compound stocks with concentrations ranging between 900 and 6,500 mg/L. A CAC stock, which consists of CAC (1–2 μm) suspended in water, was provided by Regenesis (San Clemente, California, USA). All other chemicals were purchased from either Sigma Aldrich or Fisher Scientific.

The aquifer materials used in this study were those employed by Xu and Thomson (Xu and Thomson, 2009). These materials were collected from various sites in Canada and the United States and were denoted as Borden, DNTS, LSU, USU, MAAP, and NFF. Xu and Thomson sieved these materials with a No. 10 mesh sieve (2 mm) and subsequently characterized the physico-chemical properties of the fractions passed through the sieve. Selected properties reported by Xu and Thomson are reproduced in Table 4-1. For this current study, each aquifer material sample was sieved with a No. 80 mesh sieve (i.e., 177 μm), and the fraction passed through the sieve was autoclaved and used.

A 1 mM sodium bicarbonate (NaHCO_3) buffer solution was prepared daily by adding NaHCO_3 to 18.2 $\text{M}\Omega\cdot\text{cm}$ Milli Q water (Millipore).

Table 4-1. Properties of aquifer materials (from Xu and Thomson, 2009)

ID	Description	Bulk mineralogy	Effective grain size (d10) (mm)	pH	Cation exchange capacity (CEC) (cmol +ve/Kg)	TOC (mg/g)
Borden	Fine/medium sand	Quartz, plagioclase, calcite, trace magnetite, and ilmenite	0.075	8.4	3.5	0.24
DNTS	Fine to medium silt sand	Quartz	0.003	6.1	2.6	0.28
LSU	Sand and silty sand	Quartz, calcite, aragonite, trace feldspars	0.065	8.6	12.8	1.84
USU	Sand and silty sand	Quartz, calcite, aragonite, trace feldspars	0.085	8.8	8.3	0.878
MAAP	Sand	Quartz	0.15	7.0	0.9	0.77
NFF	Loamy fine sand	Quartz	0.075	3.7	5.7	3.93

Six PFAS-impacted groundwater samples (GW 1–6) were obtained from industrial partners that supported this research. Upon arrival, groundwater samples were subjected to analyses for pH, cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}), anions (Cl^- , NO_3^- , phosphate, and SO_4^{2-}), DOC, and inorganic carbon (IC). The samples were stored at 4 °C until use.

4.2.2. Adsorption experiments

Adsorption experiments with aquifer materials. To evaluate the effect of aquifer materials on the adsorption of PFOS, PFOA, and PFBS by CAC, reaction suspensions containing 500 g/L of an aquifer material in water were constructed by adding 7.5 g of an autoclaved and sieved aquifer material and 15 mL of the buffer solution to a 50-mL polypropylene (PP) test tube. In total, there were 198 test tubes. The test tubes were placed on an orbital shaker for one week to allow species in the aquifer material to leach into the solution. Subsequently, the test tubes were divided into three sets. Set 1, consisting of 72 test tubes, was used to evaluate the adsorption of PFBS, PFOS, or PFOA onto aquifer materials. For Set 2 (54 test tubes), CAC was added to each test tube to obtain a CAC concentration of 0.33 g/L. Thus, the mass ratio of CAC to aquifer material in each tube was 0.066 %. For Set 3 (72 test tubes), the aquifer material in each tube was separated by centrifugation at 4,300×g for 20 min, and the supernatants (12 mL) collected from 18 test tubes were subjected to analysis for pH, DOC, IC, cations, and anions. The supernatants in the 54 remaining test tubes in Set 3 were transferred using a pipette to clean PP test tubes, which were then spiked with CAC (0.33 g/L).

To initiate adsorption, an aliquot (12–15 µL) of a methanolic stock of either PFOS, PFOA, or PFBS was added. The targeted initial concentration of each compound was: [PFBS]₀ = 900 µg/L (~ 3.0 µM), [PFOA]₀ = 1,200 µg/L (~ 2.9 µM), and [PFOS]₀ = 1,390 µg/L (~ 2.8 µM). Following the PFAS addition, test tubes were again placed on the orbital shaker for another week. Subsequently, Set 1 tubes were centrifuged at 4,300×g for 20 min, and the supernatant (~10 mL) of 18 tubes was subjected to analyses for pH, DOC, IC, cations, and anions. The supernatant of the 54 remaining test tubes was subjected to PFAS analysis. The suspensions in Set 2 and Set 3 tubes were filtered through a 0.02-µm aluminum oxide filter (Whatman Anotop). Results of a

preliminary experiment indicated that less than 1 % of PFBS, PFOS, or PFOA adsorbed to the filter. Less than 0.5 mL of the filtrate passed through the filter, the volume of which was only sufficient for PFAS analysis.

Another set of tubes, i.e., Set 4 (9 test tubes), was used to evaluate the adsorption of PFBS, PFOA, and PFOS on CAC in the buffer solution. To this end, CAC (0.33 g/L) and one of the studied PFAS (2.8–3.0 μM) were spiked into a PP tube containing 15 mL of the buffer solution, and the tube was placed on the orbital shaker. After one week, each solution was filtered through a 0.02- μm aluminum oxide filter, and the filtrate was subjected to analysis for PFAS. The experimental workflow described above is summarized in Fig. 4-1.

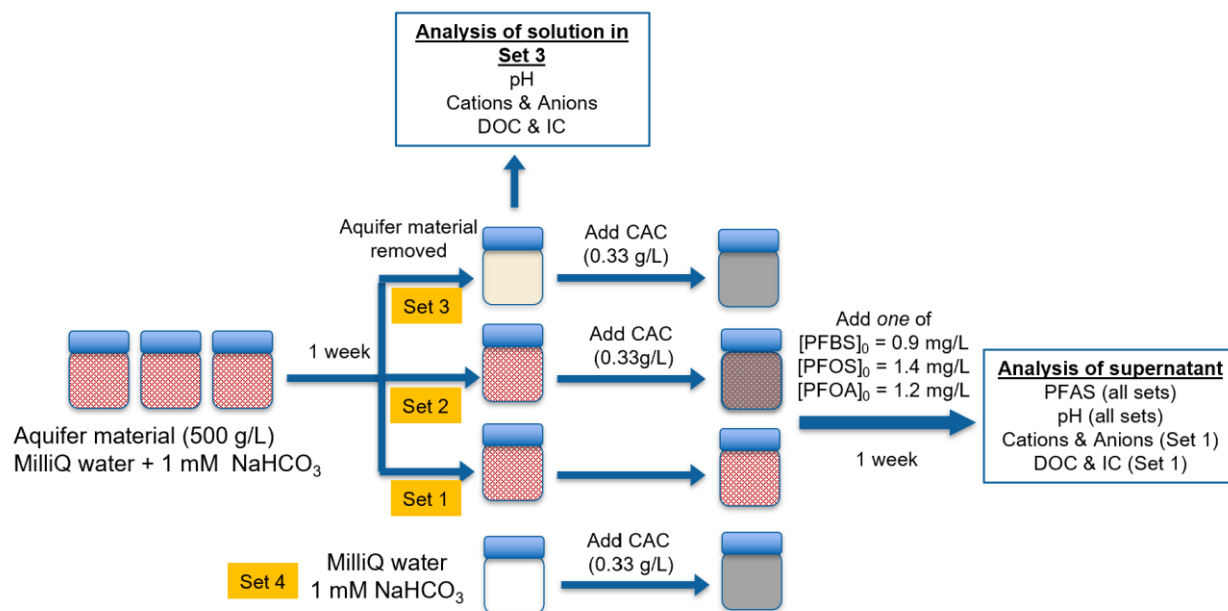


Figure 4-1. Schematic diagram illustrating the experimental approach employed to investigate the effect of aquifer materials on the adsorption of PFBS, PFOA, or PFOS. Each experimental set was conducted in triplicate.

In addition to the experimental test tube sets described above, a separate set of experiments (84 test tubes) was conducted to investigate the kinetics of PFBS, PFOS, or PFOA adsorption in the presence of CAC and selected aquifer materials. To this end, 7.5 g of either LSU or NFF and 15 mL of the buffer solution were added to 50 mL PP tubes, which were then shaken on the orbital shaker for one week. NFF (pH = 3.7) and LSU (pH = 8.6) were selected to represent acidic and slightly basic aquifer materials. Subsequently, aliquots of the CAC stock and the methanolic stock of PFBS, PFOS, or PFOA were added to obtain suspensions with initial concentrations similar to those described above. Test tubes were then shaken on the orbital shaker, and two test tubes were sacrificed at predetermined time intervals (i.e., $t = 6, 24, 48, 72, 120, 168,$ and 336 h). The suspension in each sacrificed tube was filtered through a $0.02\text{-}\mu\text{m}$ aluminum oxide filter, and the filtrate was subjected to analysis for PFAS.

Adsorption experiments with groundwater samples. Experiments were conducted to assess the adsorption of a mixture of 5 PFAS on CAC in 6 different groundwater samples. An aliquot of 750 mL of a groundwater sample was added to a high-density polyethylene (HDPE) bottle. To each bottle, methanolic stocks of PFHxA, PFOA, PFHxS, PFOS, and 6:2 FTS were added to obtain a solution of $1.3\text{ }\mu\text{M}$ of each PFAS (i.e., the total concentration of these 5 PFAS in the solution was $6.5\text{ }\mu\text{M}$; this total concentration included the initial mass of each of these PFAS that was present in the original water sample). Subsequently, aliquots of 50 mL of the PFAS-fortified water sample were transferred to PP tubes, and then different dosages of CAC were added to each test tube to obtain a CAC concentration of 0.05, 0.09, 0.18, 0.22, 0.34, 0.45, 0.69 g/L. The test tubes were shaken for one week on the orbital shaker, and CAC was separated by ultracentrifugation ($230,000\times g$ for 105 min) using the procedure reported in Chapter 3, and the supernatant was subjected to PFAS analysis.

To investigate the kinetics of PFAS adsorption, test tubes containing CAC (0.34 g/L) and either GW 1 or GW 6 that were fortified with PFAS were sacrificed at $t = 6, 24, 48, 72, 120, 168,$ and 336 h. The reaction solution collected from each test tube was centrifuged to separate CAC and the supernatant was subjected to PFAS analysis.

Chemical analysis. Solution pH was measured using an Oakton pH electrode. Cations and anions were measured on a Thermo Dionex Aquion Ion Chromatograph. DOC and IC were measured on a Shimadzu TOC-L Total Organic Carbon Analyzer. PFAS were measured on a Shimadzu 8030 Liquid Chromatograph Tandem Mass Spectrometer (LC/MS/MS) following the procedure described in our previous study (Hakimabadi et al., 2023). The list of analytes and their limit of detection (LOD) and quantitation (LOQ) are reported in Table S1 in the Appendix.

Data analysis. The concentration of PFAS adsorbed (C_s , mg/g) was calculated based on:

$C_s = \frac{C_0 - C_w}{C_{adsorbent}}$, where C_0 (mg/L) is the initial concentration of PFAS, C_w is the concentration of PFAS measured in the supernatant, and $C_{adsorbent}$ is the concentration of AC (g/L) or the concentration of aquifer material in the absence of AC (i.e., in experimental Set 1). The partition coefficient K_d (L/Kg) was calculated using the following equation: $K_d = \frac{C_s}{C_w}$.

Principal component analysis (PCA) was performed using Origin 2024 (OriginLab Corporation, 2024) to create PCA biplots that describe the correlation among K_d and five water chemistry parameters, including pH, ionic strength, and the concentrations of Mg^{2+} , Ca^{2+} , and DOC.

4.3. Results and Discussion

4.3.1. Adsorption in the presence of aquifer materials

Experimental Set 1 (i.e., the PFAS/aquifer material systems). Of the studied PFAS, PFBS adsorbed the least to the six aquifer materials (Fig. 4-2), which is consistent with the hydrophilic nature of this shorter-chain compound. The affinity of PFOA ($\log K_d$ (L/kg) = 3.0–3.8) to the aquifer materials was higher than that of PFOS ($\log K_d$ (L/kg) = 2.7–3.5). PFOS ($\log K_{ow}$ = 5.26–5.43) is more hydrophobic than PFOA ($\log K_{ow}$ = 4.3–5.3) because PFOS has one $-CF_2$ more and the $-SO_3^-$ functional group is more hydrophobic than the $-COO^-$ functional group (Parker et al., 2022). The reason why less PFOS was adsorbed on the studied aquifer materials is not clear, and this warrants further investigation.

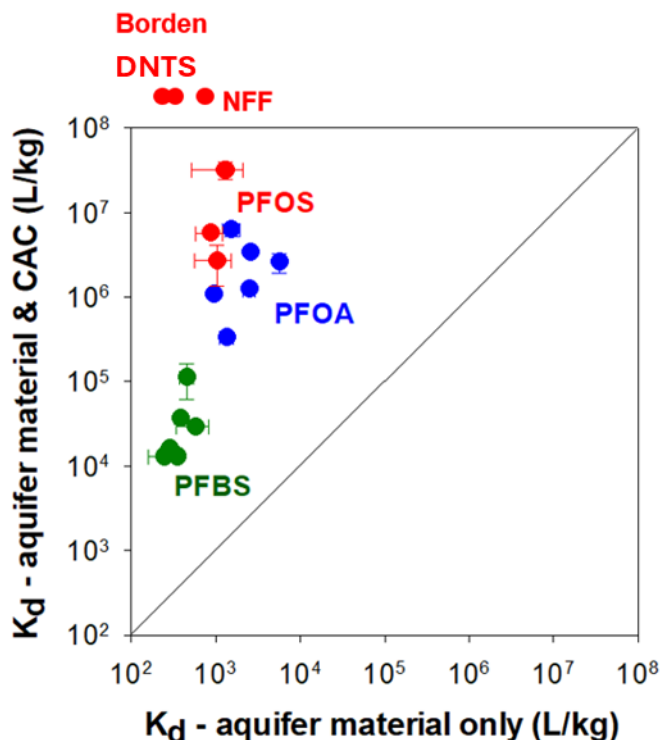


Figure 4-2. Comparison of K_d values for the adsorption of PFBS, PFOA, and PFOS in Experimental Set 1 (i.e., suspensions containing only aquifer materials) and Experimental Set 2 (i.e., suspensions containing aquifer materials and CAC). Suspension composition: 1 mM NaHCO_3 , 500 g/L of aquifer material, 0.33 g/L CAC (in Experimental Set 2), and either $[\text{PFBS}]_0 = 900 \mu\text{g/L}$ ($\sim 3.0 \mu\text{M}$), $[\text{PFOA}]_0 = 1,200 \mu\text{g/L}$ ($\sim 2.9 \mu\text{M}$), or $[\text{PFOS}]_0 = 1,390 \mu\text{g/L}$ ($\sim 2.8 \mu\text{M}$). In the CAC/Borden, CAC/DNTS, and CAC/NFF systems, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for these systems. In the plot, the red circles representing these systems are positioned using the K_d value obtained from Experimental Set 3 for the x-axis and a K_d of $> 10^8$ for the y-axis. Experiments were conducted in triplicate, and average values along with one standard deviation (i.e., error bar) are presented.

At the end of the adsorption experiment, the chemistry of the solution in each test tube was characterized (Table 4-3). The solution was in contact with an aquifer material for two weeks (i.e., one week of initial contact, and another week of contact following PFAS addition). Overall, the chemistry of the solution reflects the properties of the aquifer material. The solution that was in contact with NFF, which is an acidic aquifer material ($\text{pH} = 3.7$; see Table 4-1), had a pH of 3.4. The pH of the solutions in contact with Borden, LSU, MAAP, and USU ($\text{pH} = 7.0\text{--}8.8$) ranged

between 7.4 and 8.1, while the pH of the solution in the test tube containing DNTS (pH = 6.1) was 6.6.

The concentration of DOC ranged between 5.5 mg/L and 30.3 mg/L, with the highest DOC concentration observed in the solutions that were in contact with NFF and USU. These two aquifer materials contain the highest concentration of organic carbon (NFF: 3.93 mg/g TOC; USU: 1.84 mg/g TOC). While Borden contains the lowest concentration of TOC (0.24 mg/g), the solution in contact with Borden contained the third-highest DOC concentration (12.9 mg/L). This result suggests that the organic matter of Borden was more susceptible to leaching than the organic matter of DNTS, LSU, and MAAP.

The concentrations of Ca^{2+} in the solutions in contact with DNTS (0.03 mM) and MAAP (0.03 mM) were the lowest, consistent with their mineralogy (i.e., quartz). The concentration of Ca^{2+} in the solution in contact with NFF, also a quartz material, was 0.13 mM. In contrast, Borden, LSU, and USU contain either calcite and/or aragonite, and the concentration of Ca^{2+} in the solutions in contact with these aquifer materials was substantially higher, ranging between 0.58 mM and 1.85 mM. Lastly, the ionic strength of the solution in contact with the aquifer materials ranged between 0.8 mM and 23.7 mM. The ionic strength was the highest in the LSU (17.5 mM) and NFF (23.7 mM) test tubes, suggesting that the inorganic species in these aquifer materials are more susceptible to leaching.

Table 4-2. Chemistry of the solution that was in contact with aquifer material after 1 week (Experimental Set 3) and 2 weeks (Experimental Set 1)

Soil ID	pH		Ca ²⁺ (mM)		Mg ²⁺ (mM)		Ionic Strength ^a (mM)		DOC (mg/L)	
	After the 1 st week	After the 2 nd week	After the 1 st week	After the 2 nd week	After the 1 st week	After the 2 nd week	After the 1 st week	After the 2 nd week	After the 1 st week	After the 2 nd week
Borden	7.7	7.6	0.42	0.58	0.004	0.01	1.6	2.01	8.8	12.9
DNTS	6.8	6.6	0.02	0.03	0.01	0.02	1.3	1.4	5.1	5.5
LSU	7.4	7.4	1.34	1.85	0.47	0.64	14.2	17.5	17.7	19.9
MAAP	8	7.8	0.02	0.03	0.005	0.004	0.7	0.8	1.2	5.6
NFF	3.2	3.4	0.20	0.13	0.25	0.23	20.8	23.7	26.1	30.3
USU	8	8.1	0.55	0.73	0.08	0.11	4.0	4.8	6.6	11.5

^a Ionic strength was calculated based on the concentrations of cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and anions (Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻)

Experimental Set 2 (i.e., the PFAS/aquifer material/CAC systems). As reported in Chapter 3, over 99% of the initial mass of PFBS, PFOS, and PFOA was adsorbed by CAC during the first 24 hours. In the presence of either LSU or NFF, more than 80 % of the mass of these PFAS removed from the solution during the first 6 hours (Fig. 4-3). The adsorption of PFBS reached equilibrium after 2 days, whereas the adsorption of PFOA and PFOS reached equilibrium after 7 days. While the rate of PFAS adsorption on CAC in the presence of the other four aquifer materials was not investigated, it was deemed that a contact period of 168 hrs would also result in adsorption equilibrium in these systems.

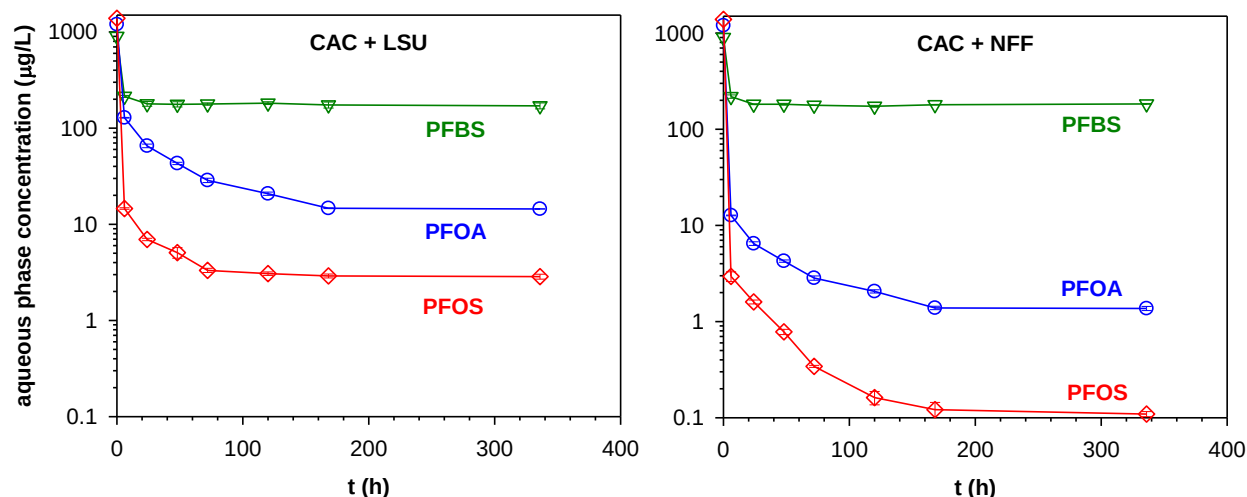


Figure 4-3. Aqueous phase concentration profiles of PFBS, PFOA, and PFOS. Reaction solutions contained 0.33 g/L CAC, 1 mM NaHCO_3 , 500 g/L of either LSU or NFF, and one of the following PFAS: $[\text{PFBS}]_0 = 900 \text{ } \mu\text{g/L}$, $[\text{PFOA}]_0 = 1,200 \text{ } \mu\text{g/L}$, or $[\text{PFOS}]_0 = 1,390 \text{ } \mu\text{g/L}$. The solution pH was 7.4 (in the system containing LSU) and 3.4 (in the system containing NFF). Experiments were conducted in duplicate and average values are presented. The error bars represent the min/max range of aqueous concentrations.

The K_d values calculated in Experimental Set 2 were a few orders of magnitude greater than those of Experimental Set 1, with $\log K_d$ (L/kg) ranging from 4.1–5.1 for PFBS, and 5.5–6.8 for PFOA (Fig. 4-2). For PFOS, the $\log K_d$ values were 6.4, 6.7, and 7.5 in the CAC/LSU, CAC/USU, and CAC/MAAP systems, respectively. In the CAC/Borden, CAC/DNTS, and CAC/NFF systems, all PFOS mass was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for these systems. As seen in Fig. 4-2, all data points are significantly above the 1:1 line, indicating that PFBS, PFOA, and PFOS predominantly (> 99 %) adsorbed to CAC over the aquifer materials.

Experimental Set 3 (i.e., aquifer materials removed prior to PFAS and CAC addition) and Experimental Set 4 (1 mM NaHCO₃). Between the solutions that were in contact with aquifer materials for two weeks (i.e., the solutions in Experimental Set 1) and the solutions in Experimental Set 3, which were in contact with aquifer materials for one week, the solution pH differed by ≤ 0.2 pH unit, while the solution ionic strength differed by less than 25 % (Table 4-3). These results suggest that the leaching of inorganic species from these aquifer materials occurred mostly during the first week of contact. On the contrary, there was a substantial increase in the DOC concentration between one and two weeks when the solution was in contact with Borden (an increase of 47 %), MAAP (an increase of 367 %), and USU (an increase of 76 %).

The log K_d for the adsorption of the studied PFAS on CAC in the buffer solution (i.e., 1 mM NaHCO₃) were 4.56 ± 0.05 (PFBS), 6.4 ± 0.05 (PFOA), and 7.04 ± 0.02 (PFOS). The adsorption affinity trend of PFBS < PFOA < PFOS is consistent with the trend reported in Chapter 3. In Experimental Set 3, the log K_d values were 4.2–5.4 (PFBS), 6.0–7.5 (PFOA), and 6.6–7.6 (PFOS) (Fig. 4-4). The lowest adsorption of all three PFAS was observed in the solutions previously in contact with LSU. This could be attributable to the DOC (19.9 mg/L) present in these solutions competing with PFAS for adsorptive sites on CAC. In the research reported in Chapter 3, it was observed that the adsorption of PFOS and PFOA on CAC decreased by 75 % when the concentration of Suwanee River Fulvic Acid increased from 0 to 20 mgC/L. However, all three PFAS were adsorbed to the highest extent in the solutions in contact with NFF, even though the DOC concentration in this solution (30.3 mg/L) was 50 % greater than that in the solutions in contact with LSU. A possible explanation for this result could be that the pH of the solution (3.4) previously in contact with NFF was substantially lower than the pH of the solutions in contact with the other aquifer materials (6.8–8.0). Studies have shown that as pH decreases, the adsorption of

anionic PFAS increases, owing to the increasing electrostatic attraction between the surface and the negatively charged functional groups in the PFAS molecules (Du et al., 2014). In the solutions in contact with NFF, the suppression of PFAS adsorption by the high DOC concentration may have been outweighed by the enhancement of adsorption due to the solution's acidic pH.

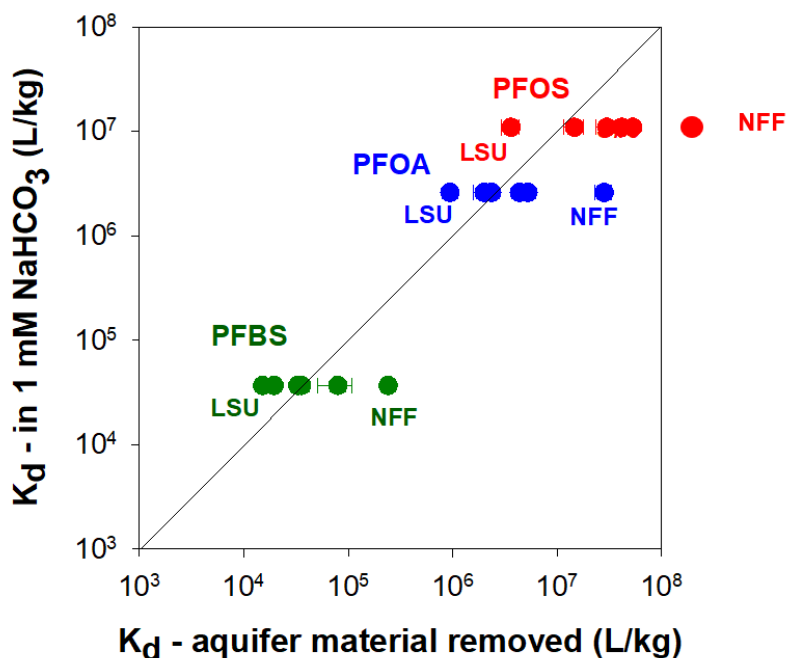


Figure 4-4. Comparison of K_d values for the adsorption of PFBS, PFOA, and PFOS on CAC in Experimental Set 3 (i.e., suspensions containing solutions that were previously in contact with aquifer materials, but the materials were removed prior to CAC addition) and in the buffer solution (i.e., solutions containing 1 mM NaHCO₃ and CAC). Suspension composition: 0.3 g/L CAC (in Experimental Set 2), and either [PFBS]₀ = 900 µg/L (~ 3.0 µM), [PFOA]₀ = 1,200 µg/L (~ 2.9 µM), or [PFOS]₀ = 1,390 µg/L (~ 2.8 µM). In the system that was in contact with NFF, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for this system. In the plot, the red circle representing this system is positioned using the K_d value obtained from the experiment with the buffer solution for the x-axis and a K_d of $> 10^8$ for the y-axis. Experiments were conducted in triplicate, and average values are presented along with one standard deviation (i.e., error bar).

It should be noted that the adsorption of PFAS on CAC is dependent not only on the solution pH and DOC but also on other factors, including the solution ionic strength and the concentration

of Ca^{2+} . Therefore, PCA biplots were assessed to further investigate the effect of solution chemistry on the adsorption of PFBS, PFOA, and PFOS to CAC (Fig. 4-5).

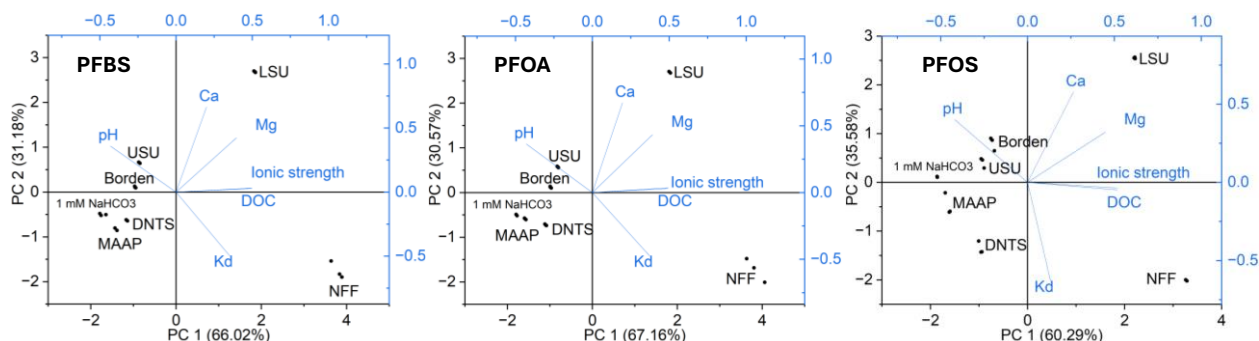


Figure 4-5. The correlation between K_d values of PFAS adsorption on CAC and five solution chemistry parameters. The angles between the vectors represent the correlation between the parameters. In the system that was incubated with NFF, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated for this system. Therefore, in the PFOS plot, the dots representing the NFF system are positioned by using the highest K_d value among the K_d values of all systems. The location of each observation point on the plot relative to each parameter vector represents the magnitude of the parameter for the observation point. For example, the pH of the solution increases in the direction pointed by the pH arrow, and the NFF point is located in the opposite direction because the solution incubated with NFF has the lowest pH. On the contrary, the NFF point is located in the direction pointed by the K_d arrow, as K_d is the highest in the solution incubated with NFF.

The PCA biplots suggest that the adsorption of all three PFAS decreases as pH increases, which is consistent with what is known about the effect of pH on the adsorption of anionic PFAS (Du et al., 2014). The biplots also show that an increase in the concentration of DOC or ionic strength results in an increase in the adsorption of PFBS and PFOA but does not affect PFOS adsorption. For PFBS and PFOA, there is a weak correlation between K_d and the concentration of Ca^{2+} or Mg^{2+} , while for PFOS, the correlation is negative.

In the research reported in Chapter 3, the effects of Ca^{2+} , ionic strength, and organic carbon on the adsorption of PFOS and PFOA by CAC were investigated separately. It was observed that the

adsorption of these two compounds increased as the solution ionic strength or the concentration of Ca^{2+} increased. In contrast, an increase in the concentration of DOC resulted in decreased adsorption. Therefore, the results herein are not consistent with the results reported in Chapter 3, suggesting that there could be a complex interplay of various water chemistry parameters, which may confound the effect of each parameter. It is speculated that the effect of DOC on K_d could be confounded by the effect of Ca^{2+} when both species were present simultaneously. Specifically, the complexation between DOC and Ca^{2+} (Adusei-Gyamfi et al., 2019) could diminish the enhanced adsorption of the studied PFAS by Ca^{2+} (which may serve as a bridge between the surface and PFAS molecules, as discussed in Chapter 3). On the other hand, the DOC - Ca^{2+} complexation could neutralize the functional groups on DOC that carry a negative charge, thereby suppressing the repulsion between the DOC sorbed on CAC and the negatively charged PFAS molecules. Recently, Molé et al. reported that there was no significant difference in the adsorption of PFBA, PFHxA, and PFOA on Intraplex[®] CAC between the solution containing 10 mg/L of Suwanee River Natural Organic Matter (SRNOM) and that containing 10 mg/L SRNOM as well as 1 mM CaCl_2 (Molé et al., 2024). Although the properties (e.g., pH_{pzc} , porosity) of Intraplex[®] CAC are significantly different from the CAC used in this study, and SRNOM is more hydrophobic than SRFA, the results of Molé et al. as well as the results reported herein indicate that the interplay among water chemistry parameters on the adsorption of different PFAS on CAC requires additional research. It should also be noted that the effect of DOC on K_d was assessed solely based on the concentration of DOC in the solution. However, DOC varies widely in terms of its elemental composition, functional group, and molecular size, which could affect how it competes with PFAS for adsorptive sites and the extent of complexation formation with Ca^{2+} . For example, large dissolved organic matter molecules could inhibit PFAS adsorption to a greater extent than smaller

dissolved organic matter molecules due to the pore-blocking effect (Yu et al., 2012). Thus, additional research is needed to characterize DOC properties (e.g., molecular weight and functional group) and investigate the effect of DOC properties on the adsorption of PFAS on CAC.

Effect of aquifer material on the adsorption of PFBS, PFOS, and PFOA on CAC. The K_d values obtained from Experimental Sets 2 and 3 were presented on the same plot to examine the effect of aquifer materials on the adsorption of the three studied PFAS on CAC (Fig. 4-6).

In the systems where the solution was in contact with NFF, all mass of PFOS was removed from the solution by CAC, regardless of whether NFF was present (Set 2) or was removed prior to CAC addition (Set 3). Thus, the effect of the presence/absence of NFF on the adsorption of PFOS on CAC could not be assessed. For the 17 pairs of K_{d-S2} and K_{d-S3} , there were 11 pairs whose values differed by $\leq 50\%$, suggesting that the presence of aquifer materials in these systems did not appreciably affect the adsorption of the studied PFAS on CAC (Fig. 4-6). Of the remaining six pairs that were outside the $\pm 50\%$ area in the plot, K_{d-S2} of PFBS and PFOA was 19 and 11 times smaller than the respective K_{d-S3} for the NFF pair; K_{d-S2} of PFOS was 7 times smaller than the respective K_{d-S3} for the USU pair; and K_{d-S2} of PFOA was approximately three times smaller than the respective K_{d-S3} for the USU pair. A possible explanation for the diminished adsorption observed in the presence of NFF, USU, and LSU could be due to the hetero-aggregation of CAC and these aquifer materials, thereby diminishing the number of CAC adsorptive sites accessible to PFAS molecules. However, the hetero-aggregation should have affected the adsorption of all three PFAS. Another possible explanation could be that, as mentioned previously, the USU system in Set 2 contained 76 % more DOC than that in the system wherein USU was removed prior to CAC addition (i.e., Set 1). This additional mass of DOC in the solution may have competed with PFOS for sorptive sites on CAC, thereby diminishing PFOS adsorption. However, the adsorption of

PFOA and PFBS also should have been diminished, which was not the case. Thus, these incidents of diminished adsorption in the presence of aquifer materials appeared to be random.

There were two incidents of enhanced PFOS adsorption when Borden and DNTS were present, although the extent of enhancement could not be determined because all mass of PFOS was removed from the solution (and, therefore, K_{d-S2} could not be calculated). The enhanced adsorption of PFOS in the presence of Borden and DNTS also could not be explained.

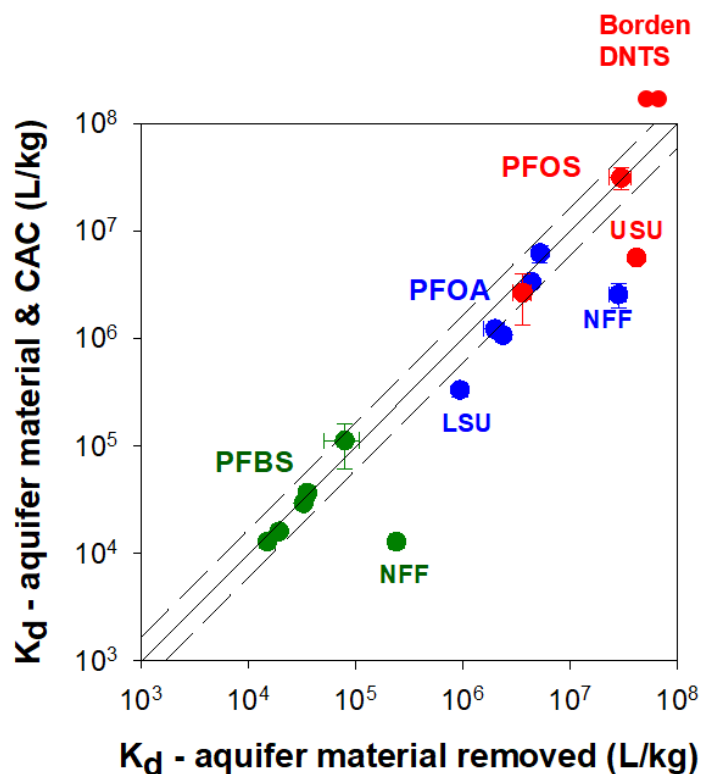


Figure 4-6. Comparison of K_d values for the adsorption of PFBS, PFOA, and PFOS on CAC in Experimental Set 3 (K_{d-S3}) and Experimental Set 2 (K_{d-S2}). In the system that was in contact with NFF, all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$) in both experimental sets, and K_d could not be calculated. Thus, there is no data point on the plot for K_d representing the NFF systems. In the systems wherein the solution was incubated with either Borden or DNTS for 2 weeks (i.e., Experimental Set 2), all mass of PFOS was removed from the solution (i.e., $C_w < \text{LOD}$), and thus K_d could not be calculated. In the plot, the red circles representing these systems are positioned using the K_{d-S3} value obtained from the experiment wherein Borden and DNTS were removed after 1 week (i.e., Experimental Set 3) and a K_d of $> 10^8$ for the y-axis. The region within the two dashed lines is where K_{d-S3} and K_{d-S2} are different by less than 50 %. Experiments were conducted in triplicate, and average values are presented along with one standard deviation (i.e., error bar).

4.3.2. Adsorption of a mixture of 5 PFAS in groundwater samples

Groundwater chemistry and the concentration of native PFAS. The measured water chemistry parameters of the groundwater samples are presented in Table 4-4. The concentration of DOC and ionic strength of GW 6 are significantly higher than those of the other groundwater samples. GW 6 was collected near a source zone of a contaminated site. No additional information about the origin of this sample was available.

The concentrations of the PFAS in each sample are presented in Table 4-5. Of the 24 PFAS measured, seven compounds were non-detect in all samples. The compounds that were most frequently detected and/or presented at a high concentration ($> 10 \mu\text{g/L}$ in at least one sample) include PFOS, PFOA, PFHxA, PFHxS, 6:2 FTS, and 8:2 FTS.

Table 4-3. Water chemistry parameters of groundwater samples.

ID	pH	Ca ²⁺ (mM)	Mg ²⁺ (mM)	Ionic strength (mM) ^a	DOC (mg/L)
GW 1	7.6	< LOQ ^b	0.14	1.9	0.5
GW 2	7	1.01	0.24	5.9	12.4
GW 3	7	1.28	0.33	3.7	8.5
GW 4	7	< LOQ ^b	0.05	1.7	4.7
GW 5	7.9	< LOQ ^b	< LOQ ^b	0.04	10.8
GW 6	5.5	< LOQ ^b	0.56	57.9	290.2

^a Ionic strength was calculated based on the concentrations of cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and anions (Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, CO₃²⁻)

^b LOQ of Ca²⁺ = 0.03 mM; LOQ of Mg²⁺ = 0.04 mM

Table 4-4. PFAS originally presented in the groundwater samples (unit: µg/L).

ID	GW 1	GW 2	GW 3	GW 4	GW 5	GW 6
PFBA	0.1	4.4	1.6	0.1	2.1	0.8
PFPeA	0.1	2.5	8.5	0.1	0.7	0.5
PFHxA	0.6	21.9	16.6	0.3	11.1	1.9
PFHpA	0.2	3.2	3	0.1	1.8	0.2
PFOA	0.6	1.9	15.7	0.1	3.6	1.2
PFNA	< LOQ	0.1	< LOQ	< LOQ	< LOQ	< LOQ
PFDA	< LOQ	0.1	< LOQ	< LOQ	< LOQ	< LOQ
PFBS	0.7	2.1	2.5	0.1	7.3	0.4
PFPeS	0.7	1.6	< LOQ	0.1	5.3	< LOQ
PFHxS	4.2	6.2	48.1	1.7	29.8	< LOQ
PFHpS	0.2	0.3	< LOQ	< LOQ	1.4	< LOQ
PFOS	2.3	10.4	162.6	3.5	64.2	32.4
PFNS	< LOQ	< LOQ	< LOQ	< LOQ	0.1	< LOQ
4:2FTS	< LOQ	0.1	< LOQ	< LOQ	< LOQ	< LOQ
6:2FTS	0.3	135.8	49.3	< LOQ	< LOQ	9.1
8:2FTS	< LOQ	1.6	23.9	< LOQ	< LOQ	29.8
FOSA	< LOQ	< LOQ	0.8	< LOQ	< LOQ	< LOQ

Adsorption kinetics. The result of the kinetic experiments with GW 6 reveals that the adsorption of all 5 PFAS on CAC (0.34 g/L) reached equilibrium after 120 or 168 hrs (Fig. 4-7). In the experiment with GW 1, the concentration of PFOS in the solution dropped below LOQ after 5 days, and thus, it was not possible to determine the time required for the adsorption of PFOS to reach equilibrium. For the other 4 PFAS, their aqueous phase concentrations measured at 168 hrs and 336 hrs differ by less than 5 %, which is within the uncertainty of PFAS analysis (± 10 %). This result suggests that the adsorption of these compounds reached equilibrium after 168 hrs.

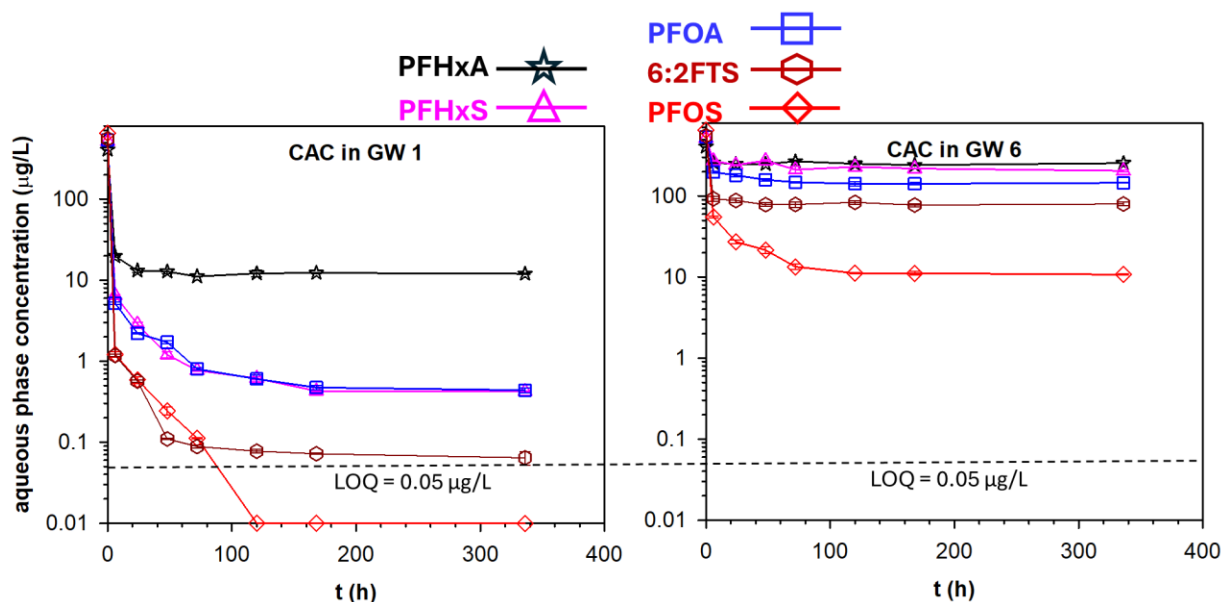


Figure 4-7. Aqueous phase concentration profiles of the studied PFAS in GW 1 and GW 6 PFBS, PFOA, and PFOS. Reaction solutions contained: 0.34 g/L CAC, and a mixture of the following PFAS: $[\text{PFHxA}]_0 = 407 \mu\text{g/L}$, $[\text{PFHxS}]_0 = 519 \mu\text{g/L}$, $[\text{PFOA}]_0 = 537 \mu\text{g/L}$, $[\text{PFOS}]_0 = 649 \mu\text{g/L}$, $[\text{6:2 FTS}]_0 = 555 \mu\text{g/L}$, and several other PFAS at concentrations $< 10 \mu\text{g/L}$ (see Table 4-5 for the list of the other PFAS and their concentrations). The solution pH in the experiments with GW 1 varied between 7.1 and 7.6, while the pH in the experiments with GW 6 varied between 5.3 and 5.5. Experiments were conducted in duplicate and average values along with a range (i.e., error bar) are presented.

Adsorption of 5 PFAS at various CAC dosages. While the rate of PFAS adsorption at other CAC concentrations and in the presence of the other four GWs was not investigated, given the equilibrium time of 120 or 168 hrs observed for PFAS adsorption in GW 1 and GW 6, it was deemed that a contact period of 168 hrs would also result in adsorption equilibrium.

The affinity of the studied PFAS to CAC was in the following order: PFOS > 6:2 FTS > PFOA ~ PFHxS > PFHxA, with two exceptions: 1) the adsorption of 6:2 FTS in GW 4 decreased at CAC concentrations of 0.05 g/L and 0.09 g/L and 2) in GW 5, 6:2 FTS was the compound adsorbed to the greatest extent. The adsorption affinity trend among the studied PFAS is consistent with the adsorption being driven by the hydrophobic effect. PFHxA, the most hydrophilic compound of the 5 studied PFAS, was adsorbed to the lowest extent (Fig. 4-8).

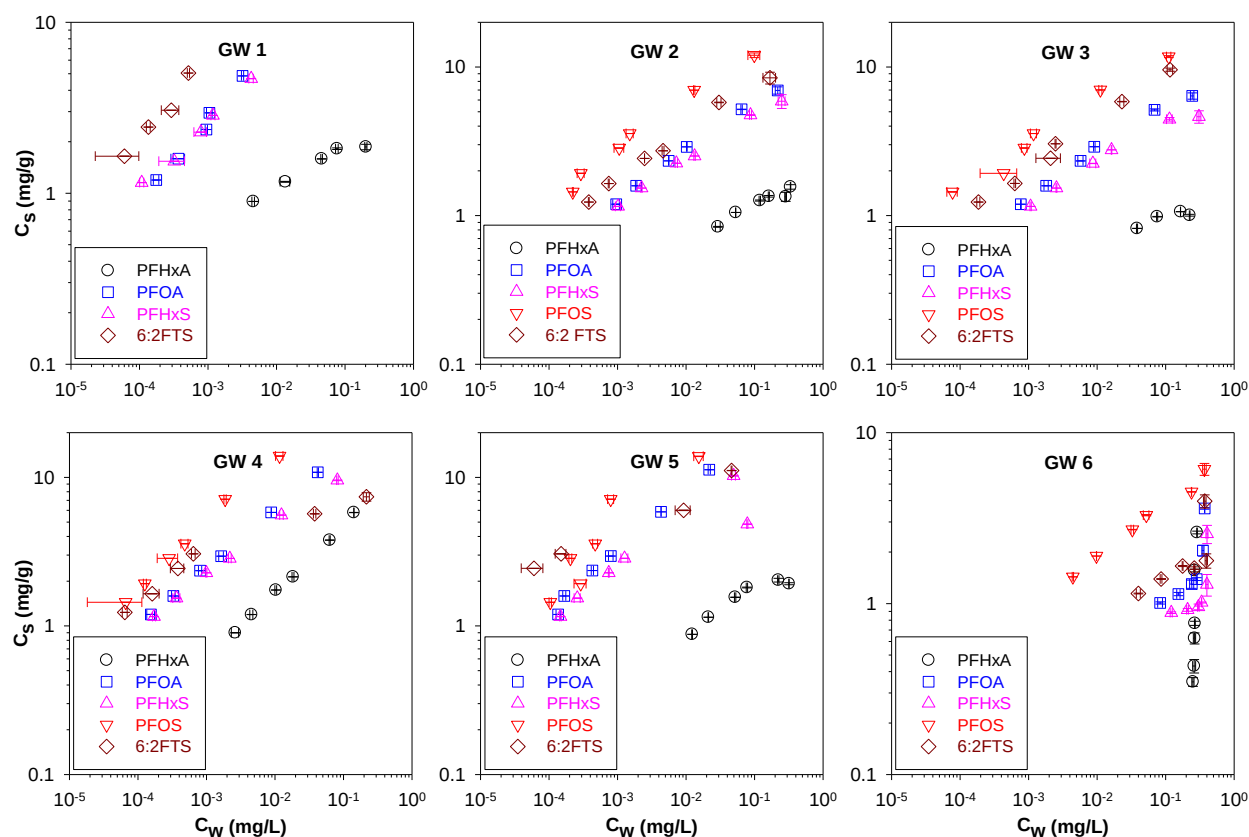


Figure 4-8. Adsorption of PFHxA, PFOA, PFHxS, 6:2 FTS, and PFOS on CAC in 6 groundwater types. For GW 1 experiment, reaction solutions contained 0.09, 0.18, 0.22, 0.34, 0.45 g/L, and 0.69 g/L CAC. Since all PFOS and 6:2 FTS mass was removed at CAC = 0.45 g/L and 0.69 g/L, in the GW 2–6 experiments, the reaction solution contained 0.05, 0.09, 0.18, 0.22, 0.34, and 0.45 g/L CAC. All groundwaters also contained a mixture of the following PFAS: $[PFHxA]_0 = 407 \mu\text{g/L}$, $[PFHxS]_0 = 519 \mu\text{g/L}$, $[PFOA]_0 = 537 \mu\text{g/L}$, $[PFOS]_0 = 649 \mu\text{g/L}$, $[6:2 \text{ FTS}]_0 = 555 \mu\text{g/L}$, and several other PFAS at $< 10 \mu\text{g/L}$ (see Table 4-5 for the list of the other PFAS and their concentrations). Experiments were conducted in duplicate and average values along with a range (i.e., error bar) are presented.

The studied PFAS was adsorbed to the lowest extent in GW 6. While this result might be attributable to the presence of a high concentration of DOC in this water sample (which could compete with PFAS for adsorptive sites on CAC), there could be confounding effects among water chemistry parameters on the adsorption of PFAS, as discussed earlier. To further investigate the effect of solution chemistry on the adsorption of the studied PFAS on CAC, PCA biplots were created. K_d values were calculated using the data points of the systems containing 0.22 g/L CAC.

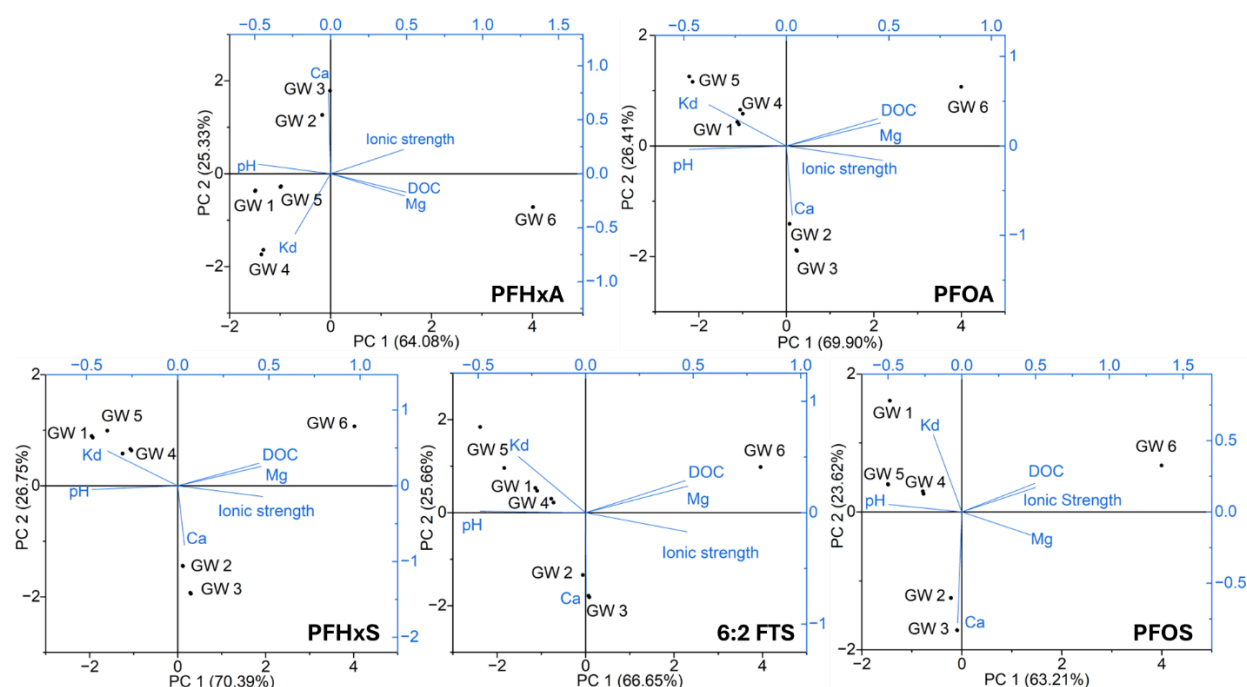


Figure 4-9. The correlations between K_d of PFAS adsorption on CAC and five solution chemistry parameters in groundwater samples. K_d values were calculated using the data points which represented systems containing 0.22 g/L CAC in the isotherms shown in Fig. 4-8.

The PCA biplots (Fig. 4-9) suggest that the K_d describing the adsorption of PFHxA, PFOA, PFHxS and 6:2 FTS decreases as DOC increases, which is consistent with the competitive effect of DOC on PFAS adsorption observed in Chapter 3 but inconsistent with the effect of DOC on PFBS and PFOA adsorption observed in solutions in contact with aquifer materials (Fig. 4-5). Moreover, there is no correlation between K_d of PFOS and DOC. Surprisingly, for all 5 PFAS, there is a positive correlation between K_d and pH, which contradicts the consensus that the adsorption of anionic PFAS is enhanced as the solution pH decreases (Du et al., 2014). It is also surprising that K_d and the solution ionic strength are inversely correlated for 4 compounds (PFHxA, PFOA, PFHxS, and 6:2 FTS), while no correlation between these two parameters is observed for PFOS. Additionally, there is an inverse correlation between K_d and the concentration of Ca^{2+} and Mg^{2+} , suggesting that these cations suppressed the adsorption of PFAS. This effect of

Ca^{2+} is the opposite of that reported in Chapter 3, once again suggesting that there could be a complex interplay among various water chemistry parameters on K_d , which may confound the effect of each parameter. It should also be noted that the groundwater samples used in these studies may contain solutes beyond those measured in this study. For example, since these groundwater samples were collected from AFFF-impacted sites, they likely contain PFAS precursors that were not measured by the analytical method employed. Depending on the nature and the concentration of these precursors, they could affect the adsorption of the studied PFAS differently in each groundwater sample. Thus, it is recommended that laboratory experiments designed to evaluate the retention of PFAS in a CAC barrier should employ site-specific groundwater and aquifer materials.

4.4. Conclusion

Over the past few years, there has been an increasing interest in implementing CAC barriers to immobilize plumes of PFAS in situ. To improve our understanding of the retention and breakthrough of PFAS in CAC barriers, the research reported here investigated the adsorption of several PFAS on CAC, employing solutions containing aquifer materials as well as actual groundwater samples. The key findings are:

- The mass of PFBS, PFOA, and PFOS removed from the solution in the presence of CAC and aquifer materials was a few orders of magnitude greater than the mass removed when only aquifer materials were present. This result suggests that in a CAC barrier, PFAS would be predominantly adsorbed to CAC than to aquifer materials.
- Under the experimental conditions employed in this study, the presence of aquifer materials did not appreciably affect the adsorption of PFBS, PFOA, and PFOS on CAC. There were a few incidents of less mass of the studied PFAS removed from the solution and one incident of more mass of the studied PFAS removed when aquifer materials were present. However, these incidents appeared to be random.
- In six actual groundwater samples that were fortified with a mixture of PFOS, 6:2 FTS, PFOA, PFHxS and PFHxA, the affinity of these PFAS to CAC was in the following order: PFOS > 6:2 FTS > PFOA ~ PFHxS > PFHxA, with two exceptions: 1) the adsorption of 6:2 FTS in GW 4 decreased at CAC concentrations of 0.05 g/L and 0.09 g/L, and 2) in GW 5, 6:2 FTS was the compound adsorbed to the greatest extent. The adsorption affinity trend among the studied PFAS is consistent with the adsorption being driven by the hydrophobic effect.

- PCA analyses of the results obtained from the experiments with aquifer materials and groundwater samples demonstrated that there was a weak/no correlation between the partition coefficient K_d for each PFAS and the major water chemistry parameters, including the solution pH, ionic strength, and the concentrations of Ca^{2+} , Mg^{2+} , and DOC. Given that there could be a complex interplay between the factors affecting the adsorption of PFAS on CAC, laboratory experiments designed to evaluate the retention of PFAS in a CAC barrier should employ site-specific groundwater and aquifer materials.

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Chapter 5: The Effect of Particle Size on the Adsorption of PFOS, PFOA, and PFBS by Granular, Powdered, and Colloidal Activated Carbons

by Seyfollah Gilak Hakimabadi, Najmeh Jaber, Abdelrahman Awad, Charles-François de Lannoy, Peter Brodersen, Neil R. Thomson, and Anh Le-Tuan Pham. Manuscript prepared for journal submission.

5.1. Introduction

Activated carbon (AC) is the most popular type of adsorbent for the removal of aqueous contaminants from drinking water, municipal and industrial wastewater, and groundwater (Bans and Goyal, 2005). AC can be produced from a variety of source materials (e.g., lignite or bituminous coal, coconut shells, and wood) (Pollard et al., 1992) and pulverized to fine granules or powders. Typically, granular AC (GAC) has an average diameter of $> 177 \mu\text{m}$ (ASTM Standard D2862-10, 2014), while powdered AC (PAC) has a diameter between 10 to $177 \mu\text{m}$ (ASTM Standard D5158-98, 2019), and the diameter of colloidal AC (CAC) ranges from 0.1 to $3 \mu\text{m}$ (Georgi et al., 2015). GAC and PAC have been widely used in drinking water, wastewater, and ex-situ groundwater treatment systems, while PAC and CAC have become popular for in-situ groundwater treatment applications (Kopinke, 2008; Patmont et al., 2015; Fan et al., 2017). The proven utility of ACs has attracted additional interest in recent years owing to their ability to adsorb per- and polyfluoroalkyl substances (PFAS) (Murray et al., 2019; Liu et al., 2020; Niarchos et al., 2023a), which are highly resistant to biological and chemical degradation.

The adsorption of contaminants on AC can generally be described by an intraparticle diffusion model where diffusion from the external surface into meso- and micro-pores is considered the rate-limiting step (Matsui et al., 2009). Consistent with this conceptual model, it has been demonstrated that the rate of adsorption is inversely proportional to the AC size (i.e., the adsorption rate follows $\text{CAC} > \text{PAC} > \text{GAC}$) (Yu et al., 2009; Matsui et al., 2009; Hansen et al., 2010; Bonvin et al., 2016). Nevertheless, there appears to be no consensus on how reducing AC particle size affects adsorption affinity, particularly the adsorption affinity to PAC versus CAC. Pan et al. reported that decreasing AC particle size from $30 \mu\text{m}$ to less than a few μm resulted in a decrease in the adsorption affinity for lower molecular weight adsorbates (e.g., phenol, geosmin, salicylic acid, 2-

methylisoborneol) but increased the adsorption affinity for higher molecular weight adsorbates (e.g., Suwannee River natural organic matter) (Pan et al., 2017). In another study, Bakkaloglu et al. demonstrated that pulverizing a bituminous coal PAC ($\sim 21 \mu\text{m}$) resulted in a CAC ($\sim 0.42 \mu\text{m}$) with a lower adsorption capacity for carbamazepine, and attributed this behavior to a smaller surface area and micropore volume compared to the parent PAC (Bakkaloglu et al. 2021). In the same study, the authors compared PAC versus CAC by synthesizing data from their study and 11 studies by others and concluded that CACs have a similar or greater adsorption affinity for hydrophobic compounds ($\log K_{ow} > 3$) compared to PACs, but lower adsorption affinity for hydrophilic compounds ($\log K_{ow} < 3$) (see Fig. 5 in Bakkaloglu et al., 2021).

Only a few studies have directly compared the adsorption rate and affinity of GAC versus PAC for PFAS, and there is no published study that directly compares the affinity of PAC and CAC for PFAS. Yu et al. reported that the adsorption of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) on a coal-based GAC (900–1,000 μm) and PAC ($< 100 \mu\text{m}$, created by grinding GAC) reached equilibrium within 168 h and 4 h, respectively, and that the affinity of these PFAS to PAC was greater than to GAC (Yu et al., 2009). Hansen et al. investigated the adsorption of a mixture of PFAS on a coal-based GAC (180–400 μm) and PAC (80 % $< 45 \mu\text{m}$) and observed that the affinity to PAC was greater (Hansen et al., 2010). In addition to these two studies, there have been a myriad of other studies that investigated the adsorption of PFAS on GAC, PAC, or CAC (e.g., Hansen et al., 2010; Zhi and Liu, 2015; Senevirathna et al., 2010; Ochoa-Herrera and Sierra-Alvarez, 2008; Siriwardena et al., 2019; Inyang and Dickenson, 2017; Zhang et al., 2016; Yu et al., 2012; Qu et al., 2009; Yu and Hu, 2011; Chularueangaksorn et al., 2014; Liang et al., 2011; Rattanaoudom et al., 2012; Yao et al., 2014; Qian et al., 2017; Söregård et al., 2020; Deng et al., 2015; Du et al., 2015; Murray et al., 2019; Park et al., 2020; Qu et al.,

2009; Umeh et al., 2023). Unfortunately, the findings of these studies cannot be readily compared because the experimental conditions employed varied widely (e.g., solution chemistry, type of PFAS and initial concentrations, and type and dosage of AC).

To address this knowledge gap mentioned above, four commercial ACs (three granular and one powdered) were pulverized by grinding and micromilling to create PACs and CACs, and the adsorption of perfluorobutane sulfonic acid (PFBS), PFOA, and PFOS by these adsorbents (11 in total) was investigated. A detailed characterization of the properties of the adsorbents was also performed.

5.2. Materials and Methods

Adsorbent preparation and characterization. Three commercial GACs, obtained from Calgon Carbon Corporation, were Filtrasorb 400 (F400, made from bituminous coal), OLC 12×40 (OLC, made from coconut shells), and Acticarbone BGX (ArtiC, made from wood). These materials were used either as received or as the source material for the preparation of PAC and CAC. To produce a PAC, the parent GAC was manually ground in a ceramic mortar and pestle, and the resulting powder was sieved through a No. 100 mesh (i.e., 150 μm). A CAC was created by wet milling a slurry consisting of 100 mg PAC and 5 mL Milli-Q water for 30 minutes. Milling was performed using a bench-top micronizing mill (McCrone) consisting of a polypropylene container and agate (i.e., SiO_2) beads. The milled slurry was collected in a beaker, dried at 104 °C, and then transferred to a screw-top glass vial. In addition, a commercial PAC (WPC PAC, made from coconut shells) was obtained from Calgon Carbon Corporation and used as received or wet milled to create CAC. All AC materials were stored in a desiccator until used.

The particle size of the GACs was obtained from the factsheets available from Calgon Carbon Corporation. The particle size distribution (PSD) of the PACs and CACs was analyzed on a Horiba LA-960 laser scattering analyzer. The surface area and pore volume distribution of all adsorbents were determined using an N₂ gas sorption analyzer (Anton-Paar Autosorb iQ and ASiQwin C-MP). The surface elemental composition of the adsorbents was determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha). For XPS analysis, AC powders were smeared on a 10 mm × 10 mm double-sided tape, which was then placed in the instrument. One analysis was performed for each sample, using a spot size of 400 μm × 200 μm. The method described by Saeidi et al. was used to measure pH_{PZC}. (Saeidi et al., 2020).

PFAS adsorption. Adsorption experiments were conducted in high-density polyethylene (HDPE) bottles that contained 250 mL reaction solution prepared from Milli-Q water (Millipore). All reaction solutions consisted of 1 mM NaHCO₃ and one of the following PFAS: [PFBS]₀ = 900 μg/L (~ 3 μM), [PFOA]₀ = 1,200 μg/L (~ 2.9 μM), or [PFOS]₀ = 1,390 μg/L (~ 2.8 μM). These three PFAS were used because of their differences in functional group and hydrophobicity. PFOS (log *K_{ow}* = 5.26–5.43) and PFOA (log *K_{ow}* = 4.30–5.30) are relatively hydrophobic, while PFBS (log *K_{ow}* = 1.98–2.82) is relatively hydrophilic (Arp et al., 2006; Park et al., 2020; Gagliano et al., 2020). These three compounds are also among the six PFAS that have a maximum contaminant level (MCL) proposed by the US Environmental Protection Agency (EPA) (US EPA, 2024). Preliminary experiments showed that the adsorption of these PFAS to the HDPE bottle walls was insignificant (i.e., < 10 %). To initiate adsorption, a known mass of an AC, determined using an analytical balance (precision: 0.001 g), was added to the reaction solution. Prior to weighing, the selected AC was dried at 104 °C for 2 hours to minimize adsorbed moisture.

Two sets of experiments were conducted. The objective of the first set was to assess PFAS adsorption kinetics, while the objective of the second set was to evaluate the adsorption of PFAS at different adsorbent dosages. For the first set, 0.02 g AC was added to the 250 mL solution (concentration of 0.08 g/L) in the experiments with GACs, ActiC PAC, and ActiC CAC, or 0.01g (0.04 g/L) in all other PAC and CAC experiments. Following AC addition, the bottles were shaken on an orbital shaker for 6, 24, 48, 72, 120, and 168 hrs. At each time point, a bottle was sacrificed, and the AC in the reaction solution was separated by centrifugation. To minimize adsorption loss to the centrifuge tube walls, the tube was rinsed twice with the reaction solution to coat the tube walls with PFAS. Subsequently, 12 mL of the reaction solution was transferred into the tube and centrifuged at 230,000×g for 60 min. Following centrifugation, 10 to 250 µL of the supernatant was withdrawn from the tube and subjected to PFAS analysis. In the second experimental set, the AC concentrations were 0.02, 0.03, 0.04, 0.08, 0.15, and 0.2 g/L. All bottles were shaken for 72 hrs. Following shaking, the AC was separated by centrifugation, and an aliquot of supernatant was removed and analyzed for PFAS.

Information on PFAS analyses can be found in Hakimabadi et al. (2023). All experiments were performed in duplicate at room temperature ($21 \pm 1^\circ\text{C}$). The concentration of PFAS adsorbed (C_s , mg/g) was estimated based on $C_s = (C_0 - C_w)/C_{AC}$ where C_0 (mg/L) is the initial concentration of PFAS, C_w is the concentration of PFAS in the aqueous phase and C_{AC} is the concentration of AC (g/L).

5.3. Results and Discussion

5.3.1 Adsorbent properties

All N₂ sorption isotherms were Type IV (Fig. S5 in Appendix), Thus, the specific surface area (SSA) and micro- and mesopore volumes were calculated from the isotherm using the slit-pore density functional theory (DFT) model.

Of the four parent ACs used in this study (i.e., GACs and WPC PAC), ActiC GAC was substantially different from the other three materials. First, the SSA of ActiC GAC (1,230 m²/g) is 1.4 to 1.7 times greater than those of F400 GAC (698 m²/g), OLC GAC (790 m²/g), and WPC PAC (853 m²/g) (Table 5-1). Second, the pH_{pzc} of ActiC GAC (5.1) is in the acidic range, whereas the pH_{pzc} of the other parent AC materials (12–12.8) is in the basic range (Table 5-1). Additionally, ActiC GAC is the only material with a mesopore volume (0.894 mL/g) greater than the micropore volume (0.479 mL/g). In comparison, the mesopore volume of F400 GAC (0.13 mL/g) is 2.7 times less than the micropore volume (0.352 mL/g), while the mesopore volume of OLC GAC (0.012 mL/g) and WPC PAC (0.011 mL/g) are 30 and 33 times less than the micropore volumes, respectively (0.366 mL/g for OLC GAC and 0.373 mL/g for WPC PAC). The predominance of micropores in the OLC GAC and WPC PAC is reflective of coconut shell source material (Laine and Yunes, 1992; Daud and Ali, 2004).

Overall, the CACs used in this study are 10 to 50 times smaller than their PAC parents, which in turn are 4 to 100 times smaller than their GAC parents (see Table 5-1, and Figs. S6 and S7 in Appendix). The SSAs, micropore volumes, and mesopore volumes of ActiC ACs are within 15 % of each other. Similarly, the SSA and micropore volumes of the F400, OLC ACs differ by < 15 %. For WPC PAC and CAC, their SSAs differ by 23 %, while their micropore volumes differ by <

15 %. These results indicate that grinding and/or milling did not appreciably affect SSA and micropore volume. On the contrary, the mesopore volume of the F400, OLC, and WPC ACs generally increased (by as much as 8 times) as the particle size decreased. Previous studies attributed an increase in mesopore volume as particle size decreases to be the result of either the creation of new pores or the aggregation of small particles, which could form interparticle pores (Bakkaloglu et al., 2021).

Table 5-1. Physical and chemical characteristics of ACs: particle size, surface area, and pore volume.

	Particle size (μm)				Surface area (m2/g)	Pore volume (mL/g)		pH _{pzc}	Elemental composition			
						Slit-pore DFT						
	90 wt % (μm)	D10 (μm)	D50 (μm)	D90 (μm)	Slit-pore DFT	Micropore W < 2 nm	Mesopore 2 < W < 37 nm		C (%)	N (%)	O (%)	S (%)
F400 GAC	550–750				698	0.352	0.130	12.8	93.9	0.4	5.5	0.2
F400 PAC		11	65	171	765	0.390	0.124	12.8	92.3	0.5	7.0	0.2
F400 CAC		0.8	1.2	1.9	771	0.370	0.255	9.8	85.5	0.4	13.9	0.2
OLC GAC	425–1700				790	0.366	0.012	12.8	91.4	0.4	8.3	0.0
OLC PAC		5	17	38	769	0.376	0.018	12.6	92.8	0.4	6.8	0.0
OLC CAC		0.6	1.2	2.1	797	0.399	0.066	9.8	88.9	0.1	10.9	0.1
ActiC GAC	425–1700				1230	0.479	0.894	5.1	85.2	0.2	14.7	0.0
ActiC PAC		29	107	191	1373	0.536	1.020	5.1	92.5	0.3	7.3	0.0
ActiC CAC		1.2	2.5	4.5	1378	0.551	1.020	4.7	91.9	0.2	7.9	0.0
WPC PAC		4	12	24	853	0.373	0.011	12	88.8	0.3	10.8	0.0
WPC CAC		1	1.7	2.7	674	0.340	0.091	10.3	87.0	0.4	12.6	0.0

Grinding GAC parent materials to create PACs resulted in either a decrease (OLC and ActiC) or an increase (F400) in the surface oxygen concentration (Table 5-1). The decrease in surface oxygen concentration could be attributable to particle breakage, which created new surfaces that are less oxidized, whereas an increase in surface oxygen could be due to increased surface exposure to air, resulting in oxidation. The results indicate that F400 was more prone to oxidation than OLC and ActiC under the grinding conditions employed. Milling of PACs, which should be more mechanically aggressive than manual grinding, resulted in an increase in the surface oxygen concentration for all four materials. The greatest increase was observed for F400 (7.0 % O in PAC and 13.9 % O in CAC), which corroborates the hypothesis that this material is more susceptible to oxidation. Concurrent with an increase in the surface oxygen concentration, the pH_{pzc} of the CACs decreased (by as much as three units) compared to the pH_{pzc} of PACs. Several studies have also observed this inverse relationship between the oxygen concentration and pH_{pzc} among CAC and their PAC parents (Partlan et al., 2016; Amaral et al., 2016; Chen et al., 2018; Takaesu et al., 2019; Abulikemu et al., 2023).

5.3.2 Affinity of PFAS to wood-based, coconut shell-based, and coal-based ACs

GACs. Adsorption equilibrium of PFBS, PFOA, and PFOS on GACs was not visually observed by 168 hrs, except for the adsorption of PFBS on OLC GAC and ActiC GAC, which attained equilibrium by 48 hrs (Fig. 5-1, top row of panels). The observed slow adsorption rate of PFAS on GACs is consistent with the results reported by others (Yu et al., 2009; Xiao et al., 2017; Wu et al., 2020). In the study by Xiao et al., 2017, the equilibrium for the adsorption of a mixture of 11 PFAS on Filtrasorb 300 GAC (a coal-based GAC) was not reached by 30 days.

Of the three GACs, ActiC GAC adsorbed the least PFAS mass (< 50 % of the initial mass). ActiC GAC has a pH_{pzc} of 5.1 (Table 5-1), and under the experimental pH employed (i.e., 7.9–

8.5), the surface would be negatively charged. Thus, the repulsion between the surface and the negatively charged head group (-COO^- and SO_3^-) presumably hindered adsorption. In contrast, the surface of F400 GAC and OLC GAC (both adsorbents have a pH_{pzc} of 12.8) would be positively charged and, therefore, attract the negatively charged PFBS, PFOA, and PFOS molecules.

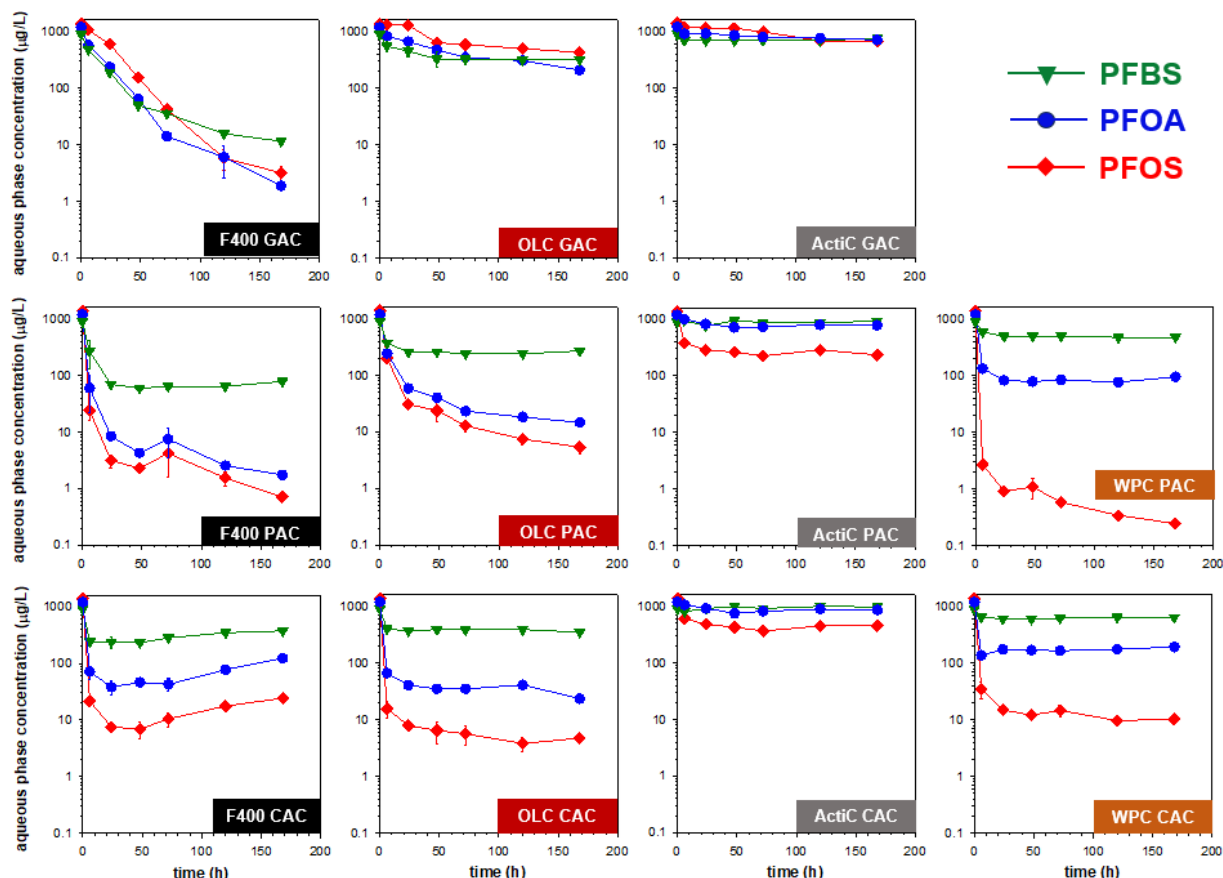


Figure 5-1. Aqueous phase concentrations of PFBS, PFOA, and PFOS as a function of time. Reaction solutions contained 1 mM NaHCO_3 ($\text{pH} = 7.9\text{--}8.5$) and one of the following PFAS: $[\text{PFBS}]_0 = 900 \mu\text{g/L}$, $[\text{PFOA}]_0 = 1,200 \mu\text{g/L}$, or $[\text{PFOS}]_0 = 1,390 \mu\text{g/L}$. The concentration of AC was either 0.08 g/L in the experiments with GACs, ActiC PAC, and ActiC CAC, or 0.04 g/L (in all other PAC and CAC experiments). The error bars represent the min/max of aqueous phase data from duplicate bottles.

Significantly more mass (30–100 times) of the PFAS was adsorbed on F400 GAC than on OLC GAC. There are two possible explanations for this difference. First, while F400 GAC and OLC

GAC possess similar SSA ($698 \text{ m}^2/\text{g}$ for F400 GAC; $790 \text{ m}^2/\text{g}$ for OLC GAC) and microporous volume (0.352 mL/g for F400 GAC; 0.366 mL/g for OLC GAC), the mesoporous volume of F400 GAC (0.13 mL/g) is over 10 times greater than that of OLC GAC (0.012 mL/g). As a result, there are likely more adsorptive sites in the mesopores of F400 GAC. Second, the surface of F400 GAC (which contains 5.5 % O) is more hydrophobic than the OLC GAC surface (8.3 % O) and, thus, would possess a higher affinity for PFAS adsorption.

PACs. Compared to the adsorption rates in the GAC systems, the adsorption rates in the PAC systems were faster, with equilibrium reached in less than 48 hrs for the adsorption of PFBS on all four PACs, PFOA on ActiC and WPC PACs, and PFOS on ActiC PAC (Fig. 5-1, middle row of panels). The faster adsorption rates of the studied PFAS on PACs are attributable to the smaller particle size of PACs ($d_{90} = 24\text{--}191 \text{ }\mu\text{m}$) compared to their parent GACs ($425\text{--}1700 \text{ }\mu\text{m}$), giving rise to shorter diffusion distances.

Similar to the GAC experiments, ActiC PAC ($\text{pH}_{\text{pzc}} = 5.1$) adsorbed the least mass of the studied PFAS ($< 85 \%$), even though (i) the concentration of ActiC PAC (0.08 g/L) was a factor of two higher than the adsorbent concentration in the experiments with the other PACs (0.04 g/L), and (ii) ActiC PAC possesses the greatest SSA ($1,373 \text{ m}^2/\text{g}$, versus $765\text{--}853 \text{ m}^2/\text{g}$ for the other PACs), micropore volume (0.546 mL/g , versus $0.373\text{--}0.390 \text{ mL/g}$), and mesopore volume (1.020 mL/g , versus $0.011\text{--}0.124 \text{ mL/g}$). This suggests that the repulsion between PFAS and the surface was the dominant factor that inhibited PFAS adsorption on ActiC PAC.

Although the SSA and micropore volume of WPC PAC ($853 \text{ m}^2/\text{g}$, 0.373 mL/g) are comparable to those of F400 PAC ($765 \text{ m}^2/\text{g}$, 0.390 mL/g) and OLC PAC ($769 \text{ m}^2/\text{g}$, 0.376 mL/g), less PFBS and PFOA mass was adsorbed on WPC PAC than on the other two adsorbents. (Since equilibrium had not been reached in any of the PFOS/PAC systems, the adsorption behavior of PFOS is not

discussed). At equilibrium, the aqueous phase concentration of PFBS was $473 \pm 19 \mu\text{g/L}$ in the WPC PAC system, $240 \pm 10 \mu\text{g/L}$ in the OLC PAC system, and $72 \pm 8 \mu\text{g/L}$ in the F400 PAC system. While the adsorption of PFOA on F400 and OLC PACs had not reached equilibrium by 168 hrs, the aqueous phase concentrations ($2\text{--}20 \mu\text{g/L}$) in these systems at 168 hrs were lower than the equilibrium concentration ($95 \pm 10 \mu\text{g/L}$) in the WPC PAC system. The lower adsorption affinity to WPC PAC could be attributable to its smaller mesopore volume (0.011 mL/g , versus 0.018 mL/g of F400 PAC and 0.13 mL/g of OLC PAC) and more hydrophilic surface ($10.8 \% \text{ O}$, versus $7.0 \% \text{ O}$ of F400 PAC and $6.8 \% \text{ O}$ of OLC PAC). The pH_{pzc} of WPC PAC (12.0) is also slightly lower than those of F400 PAC (12.8) and OLC PAC (12.5). Thus, the surface of WPC PAC, which was less positively charged, would exert a weaker attraction force on the studied PFAS molecules.

Between F400 PAC and OLC PAC, more mass of the PFAS was adsorbed on F400 PAC. This is attributable to the mesopore volume of F400 PAC (0.124 mL/g) being approximately 7 times larger than that of OLC PAC (0.018 mL/g), since the SSA, micropore volume, and surface oxygen content values for these two PACs differ by $< 5 \%$.

CACs. The rates of PFBS, PFOA, and PFOS adsorption in the CAC systems were faster than those in the GAC and PAC systems, with most ($> 90 \%$) of mass loss from the aqueous solution occurring during the first 6 hours (Fig. 5-1, bottom row of panels). This observation is consistent with the adsorption being controlled by intraparticle diffusion since CACs ($d_{50} = 1.2\text{--}2.5 \mu\text{m}$) are smaller than PACs by approximately 10–50 times. As in the ActiC GAC and PAC systems, the adsorption of PFAS in the ActiC CAC system was not appreciable ($< 70 \%$). This is again attributable to the repulsion between the -COO^- and -SO_3^- functional groups of the studied PFAS and the negatively charged surface of ActiC CAC, which has a pH_{pzc} of 4.7 . More PFAS mass was adsorbed on OLC

CAC than on WPC CAC, with an aqueous phase concentration at 168 hrs in the OLC CAC experiment of 351 ± 29 $\mu\text{g/L}$ (PFBS), 24 ± 2 $\mu\text{g/L}$ (PFOA), and 5 ± 1 $\mu\text{g/L}$ (PFOS), compared to the concentration in the WPC CAC experiment of 645 ± 23 $\mu\text{g/L}$ (PFBS), 194 ± 9 $\mu\text{g/L}$ (PFOA), and 10 ± 1 $\mu\text{g/L}$ (PFOS). The greater adsorption on OLC CAC is likely attributable to a larger SSA, micropore, and mesopore volumes, and a more hydrophobic surface (OLC CAC: $797 \text{ m}^2/\text{g}$, 0.465 mL/g , $10.9 \% \text{ O}$, versus WPC CAC: $674 \text{ m}^2/\text{g}$, 0.431 mL/g , $12.6 \% \text{ O}$).

A notable feature in the aqueous phase concentration profiles of the F400 CAC systems was that the concentrations decreased during the first 48 hrs and then gradually increased. For example, the PFOS aqueous concentration decreased from $1,390 \mu\text{g/L}$ to $7 \pm 2 \mu\text{g/L}$ and then increased to $24 \pm 2 \mu\text{g/L}$. A possible explanation might be that the surface of F400 CAC was gradually oxidized and became more hydrophilic throughout the experiment (i.e., “aged”), resulting in the release of the sorbed PFAS. However, this hypothesis warrants further investigation.

5.3.3 Effect of particle size reduction on PFAS adsorption

Less PFAS mass was adsorbed on CAC materials than on their parent PAC materials, resulting in higher aqueous phase concentrations in the CAC systems (Fig. 5-1). For example, the PFBS equilibrium concentration in the WPC CAC and WPC PAC systems was $645 \pm 23 \mu\text{g/L}$ and $473 \pm 19 \mu\text{g/L}$, respectively. The PFOS aqueous phase concentration (at equilibrium) in the WPC CAC system was $10 \pm 1 \mu\text{g/L}$, while the concentration in the WPC PAC system was $0.2 \pm 0.05 \mu\text{g/L}$ (and may have decreased further had the experiment continued). As another example, the lowest concentrations of PFOS and PFOA in the F400 CAC experiment were $7 \pm 2 \mu\text{g/L}$ and $43 \pm 11 \mu\text{g/L}$, respectively, while those in the F400 PAC experiment were $< 2 \mu\text{g/L}$ at the end of the experiment and still decreasing.

The adsorption of the studied PFAS on GACs, PACs, and CACs was further compared based on the experiments that employed reaction solutions consisting of a similar initial concentration of PFAS but varying AC concentrations. Fig. 5-2 presents the relationship between C_s and C_w in these experiments (referred to as the C_s – C_w profile from this point forward). Note that for the systems wherein adsorption equilibrium had not been established at the end of the experiment (12 out of 33 systems), the C_s – C_w profile does not represent an adsorption isotherm, and thus, C_s and C_w were not fitted to an isotherm model. Instead, a 72-h partition coefficient K_{d-72h} (L/g) = C_s/C_w was calculated for every experimental data, and the average value, $K_{d-72h-av}$, was calculated and reported (Table 5-2).

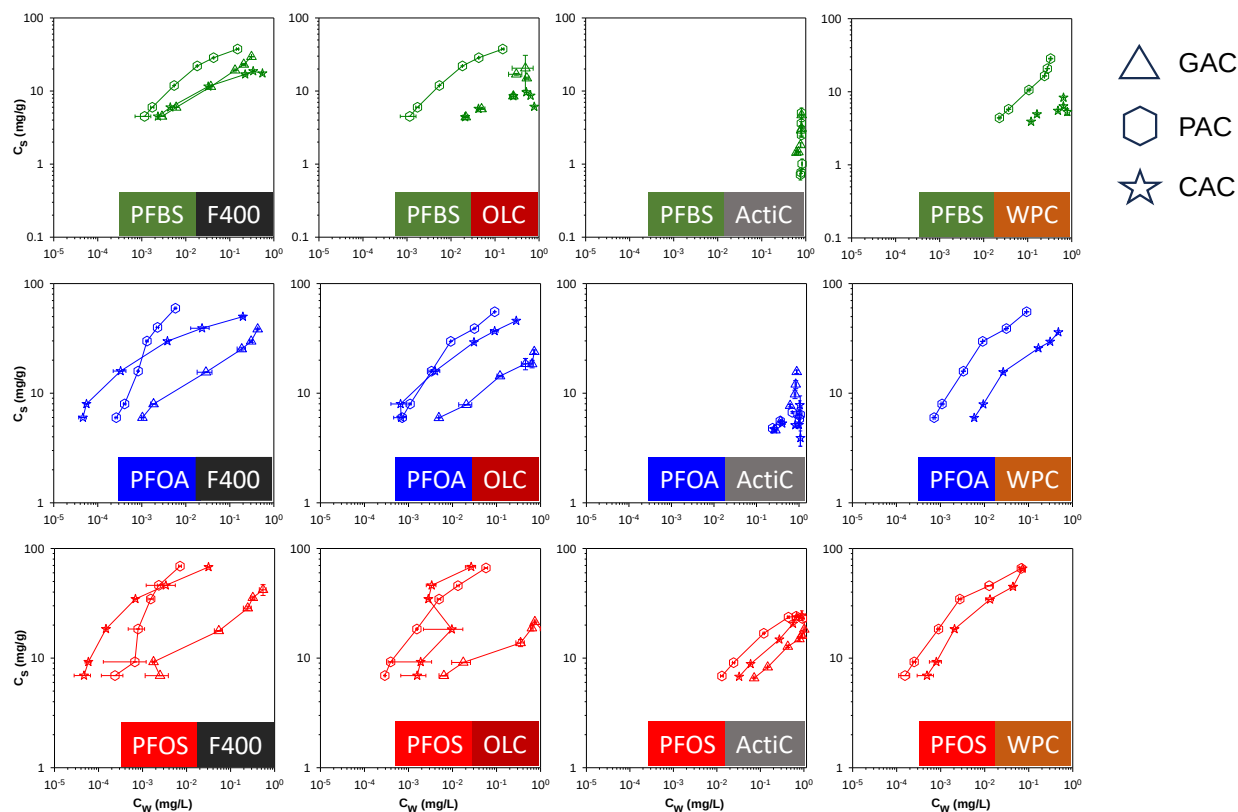


Figure 5-2. The relationship between adsorption density (C_s) and aqueous phase concentration (C_w). Note that for the systems wherein adsorption equilibrium had not been established at the end of the experiment (12 out of 33 systems), the C_s – C_w relationship does not represent an adsorption isotherm. The lines

connecting the data points are only meant to enhance the visual comparison of $C_s - C_w$ relationships. Reaction solutions contained 1 mM NaHCO₃ (pH = 7.9–8.5), 0.02, 0.03, 0.04, 0.08, 0.15, and 0.2 g/L AC, and one of the following PFAS: [PFBS]₀ = 900 µg/L, [PFOA]₀ = 1,200 µg/L, or [PFOS]₀ = 1,390 µg/L. The contact time between the solution and AC was 72 h. The error bars represent the min/max of aqueous phase data from duplicate bottles.

Table 5-2. 72-hour six-point average K_d values (L/Kg) for the adsorption of PFAS on ACs.

	$K_{d-72h-av} \times 10^{-3}$ (L/Kg)		
	PFBS	PFOS	PFOA
F400 GAC	545 ± 54	1,635 ± 412	1,864 ± 188
F400 PAC	2,065 ± 356	27,136 ± 10,955	18,890 ± 674
F400 CAC	635 ± 6	90,662 ± 18,614	57,489 ± 9,952
OLC GAC	86 ± 11	320 ± 96	314 ± 29
OLC PAC	130 ± 3	11,975 ± 741	4,257 ± 144
OLC CAC	70 ± 2	9,105 ± 3641	4,990 ± 1,689
ActiC GAC	3.5 ± 0.3	39 ± 2	15 ± 1
ActiC PAC	2.9 ± 0.4	194 ± 11	11 ± 1
ActiC CAC	No sorption	85 ± 1	11 ± 1
WPC PAC	113 ± 3	20,784 ± 2,983	3,202 ± 224
WPC CAC	17 ± 0	7,320 ± 1,959	464 ± 16

WPC PAC and WPC CAC. Previous studies reported that pulverizing PAC into CAC decreased SSA and micropore volume while increasing mesopore volume (Patlan et al., 2016; Chen et al.,

2018; Bakkaloglu et al., 2021). In the current study, the SSA and micropore volume of WPC CAC were less than those of WPC PAC by 21 % and 9 %, respectively, while the mesopore volume of WPC CAC was approximately 8 times greater than that of WPC PAC. Despite having less mesopore volume, WPC PAC adsorbed more mass of the studied PFAS, with $K_{d-72h-av}$ of WPC PAC being 2–40 times greater than $K_{d-72h-av}$ of WPC CAC (Table 5-2). The difference between WPC PAC and WPC CAC can be clearly seen in Fig. 5-2, which shows that the C_s-C_w profiles of the WPC PAC systems lie to the left of the profiles of the WPC CAC systems. Note that the PFOS/WPC PAC system had not reached equilibrium after 72 hrs (Fig. 5-1). Thus, once adsorption equilibrium is reached, the difference between the adsorptions of PFOS on WPC PAC and WPC CAC would be more pronounced. Possible explanations for the lower mass the studied PFAS adsorbed by WPC CAC include: (i) with a lower pH_{pzc} (10.3), the surface of WPC CAC would be less positively charged than the surface of WPC PAC ($pH_{pzc} = 12$) and, thus, would exert a weaker attraction force on the studied PFAS molecules; and (ii) the surface of WPC CAC (12.6 % O) is more hydrophilic than that of WPC PAC (10.8 % O).

ActiC ACs. The adsorption of PFBS and PFOA on ActiC was minimal and are not discussed. The extent of PFOS mass adsorbed was in the following order: ActiC GAC < ActiC CAC < ActiC PAC (Fig. 5-2). The lowest PFOS mass sorbed for the ActiC GAC system is partly due to the slow rate of adsorption, as equilibrium was not reached at $t = 72$ hrs (Fig. 5-1). (As mentioned earlier, PFOS adsorption on ActiC PAC and CAC reached equilibrium within 48 h). ActiC PAC adsorbed slightly more PFOS mass than ActiC CAC $K_{d-72h-av}$ (194 ± 11 L/g) vs $K_{d-72h-av}$ of ActiC CAC (85 ± 1 L/g). Milling ActiC PAC resulted in ActiC CAC that possesses similar pH_{pzc} , SSA, and micropore and mesopore volumes (Table 5-2). However, the surface of ActiC CAC contains slightly more O than

that of ActiC PAC (7.9 % O versus 7.3 % O). Thus, the less mass of PFOS sorbed to ActiC CAC compared to ActiC PAC is attributable to the more hydrophilic nature of the ActiC CAC surface.

F400 ACs. Less mass of the PFOS and PFOA was adsorbed on F400 GAC than on F400 PAC and F400 CAC (Fig. 5-2), which is attributable, in part, to the slow rate of adsorption on F400 GAC (Fig. 5-1). Interestingly, the mass of PFBS adsorbed on F400 GAC was less than the mass adsorbed on F400 PAC but was either equal or greater (at $C_w > 5 \times 10^{-4}$ mg/L) than the mass adsorbed on F400 CAC (Fig. 5-2). F400 CAC adsorbed the least PFBS mass among the three adsorbents. This could be attributable to the more hydrophilic surface (13.9 % O), which contains 2 and 2.5 times more O than the surface of F400 PAC (7.0 % O) and F400 GAC (5.5 % O).

Between F400 PAC and F400 CAC, the adsorption extent depended on the type of PFAS and the aqueous concentration. As mentioned, more mass of PFBS was adsorbed on F400 PAC than on F400 CAC, with the entire C_s – C_w profile for PFBS on F400 PAC positioned to the left of the profile of PFBS on F400 CAC. The $K_{d-72h-av}$ of the PAC system ($2,065 \pm 356$ L/g) was three times greater than that of the CAC system (635 ± 6 L/g) (and because PFBS adsorption in these systems reached equilibrium within 48 hours (Fig. 5-1), $K_{d-72h-av}$ is the partition equilibrium constant in this case). More mass of PFOA and PFOS was adsorbed on PAC at lower AC masses (i.e., at higher C_w values) compared to CAC, but less mass of these compounds was adsorbed when more AC mass was present. Note that unlike in the F400 CAC system, the adsorption of PFOA and PFOS in the F400 PAC system had not reached equilibrium after 72 h (Fig. 5-1). As the adsorption of PFOS and PFOA on F400 PAC progresses, the C_s – C_w profiles for these compounds would move further to the left. Thus, it can be expected that once adsorption equilibrium is reached, more PFOA and PFOS would be adsorbed on F400 PAC than on F400 CAC for the systems with more AC mass.

F400 PAC and F400 CAC have comparable surface areas ($1,037 \text{ m}^2/\text{g}$ and $1,020 \text{ m}^2/\text{g}$) and micropore volumes (0.390 mL/g and 0.370 mL/g). Although the mesopore volume of F400 CAC (0.255 mL/g) is two times greater than that of F400 PAC (0.124 mL/g), it adsorbed less PFBS at all C_w values and less PFOA and PFOS at higher C_w values, as mentioned above. This could be attributable to the more hydrophilic nature of the F400 CAC surface, which contains almost two times more O than the surface of F400 PAC (13.9 % versus 7.0 %). Also, the surface of F400 CAC ($\text{pH}_{\text{pzc}} = 9.8$) is less positively charged than the surface of F400 PAC ($\text{pH}_{\text{pzc}} = 12.8$) and, thus, would exert a weaker attraction force on the studied PFAS molecules.

OLC ACs. The PFAS adsorption trends among OLC GAC, PAC, and CAC are similar to those of F400 ACs. First, OLC GAC adsorbed all three PFAS the least. Second, more mass of PFBS was adsorbed on OLC PAC than on OLC CAC at all C_w values. Third, more mass of PFOA was adsorbed on OLC PAC at higher C_w (i.e., in the systems with lower adsorbent concentration). Finally, the masses of PFOS adsorbed on OLC PAC and OLC CAC were comparable when the adsorbent concentration was 0.04 g/L , but more mass of PFOS was adsorbed on OLC CAC at higher C_w (i.e., in the systems with lower adsorbent concentration). Note that, as in the F400 PAC systems, the adsorption of PFOS and PFOA on OLC PAC had not reached equilibrium.

The surface areas and microporous volumes of OLC PAC ($990 \text{ m}^2/\text{g}$, 0.376 mL/g) and OLC CAC ($1058 \text{ m}^2/\text{g}$, 0.399 mL/g) differ by $< 10 \%$, but the mesoporous volume of OLC CAC (0.066 mL/g) is 4 times greater than that of OLC PAC (0.018 mL/g). As with F400 CAC, the lower mass of PFAS adsorbed on OLC CAC is interpreted to be the result of its surface being more hydrophilic (10.9 % O, versus 6.8 % O of OLC PAC) and less positively charged ($\text{pH}_{\text{pzc}} = 9.8$, which is lower than the $\text{pH}_{\text{pzc}} = 12.6$ of OLC PAC).

Collectively, the results show that all four CACs adsorbed less PFBS, PFOA, and PFOS than their respective PAC parent. As mentioned earlier, the literature review performed by Bakkaloglu et al., indicated that compared to PACs, CACs have a similar or greater adsorption affinity for hydrophobic compounds ($\log K_{ow} > 3$), but lower adsorption affinity for more hydrophilic compounds ($\log K_{ow} < 3$) (Bakkaloglu et al., 2021). The three PFAS used in our study represent a hydrophilic (PFBS, $\log K_{ow} = 1.98\text{--}2.82$ (Park et al., 2020; Gagliano et al., 2020)) and more hydrophobic PFAS (PFOA, $\log K_{ow} = 4.30\text{--}5.30$ (Arp et al., 2006; Park et al., 2020; Gagliano et al., 2020); PFOS, $\log K_{ow} = 5.26\text{--}5.43$ (Arp et al., 2006; Park et al., 2020; Gagliano et al., 2020)). We note that our results neither corroborate nor disprove the trend observed by Bakkaloglu et al. since the $\log K_{ow}$ values of PFBS, PFOA, and PFOS mentioned above represent the values for the unionized form of these compounds and not the anionic form present under pH 7.9–8.5. Additional research comparing the adsorption of various types of PFAS (e.g., neutral, cationic, and zwitterionic compounds; compounds with different functional groups) on PACs and CACs under a wide range of solution chemistry conditions is warranted.

5.4. Conclusion

GACs, PACs, and CACs are being used or have been proposed for the removal of PFAS from drinking water, groundwater, and industrial wastewater streams. While there is a consensus that the rate of contaminant adsorption will increase with decreasing AC size, our study is the first that systematically assessed the effect of size reduction on PFAS adsorption affinity to AC. Specifically, we demonstrated that four types of CACs (two made from coconut shell, one made from bituminous coal, and one made from wood) adsorbed less PFBS, PFOA, and PFOS than their PAC precursors. This is attributable to the surface of CACs being more hydrophilic than that of PACs, which was the result of surface oxidation caused by milling. When selecting between PAC or CAC for in-situ adsorption barriers, two key factors need to be considered: 1) the adsorption performance of AC, and 2) the spatial distribution of AC mass in the subsurface. While the result of this research indicates the superior adsorption performance of PAC over CAC, additional data on the spatial distribution of PAC versus CAC in the PFAS-impacted site is needed to select the appropriate AC. We also demonstrated that ActiC ACs (which are made of wood) adsorbed PFBS, PFOA, and PFOS the least, despite having the highest surface area, micropore volume, and mesopore volume. The repulsion between the negatively charged surface of ActiC ACs ($\text{pH}_{\text{pzc}} = 5.1$) and the negatively charged head group of these PFAS molecules was identified to be the dominant factor that inhibited adsorption. While the adsorption of PFAS on ACs is primarily driven by hydrophobic interactions, the results of our study indicate that the role of electrostatic interaction should be considered when selecting AC type for PFAS treatment applications.

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Chapter 6: Implications and Recommendations

6.1 Implications

To the author's knowledge, the research described in this thesis is the first to investigate some of the major factors affecting the adsorption of PFAS on CAC. The research is also the first to systematically assess the effect of particle size reduction on the affinity of PFAS to AC. This chapter summarizes the key research findings and their implications, as well as suggests several areas for future research.

Firstly, it was concluded that the adsorption of PFOS, 6:2 FTS, PFHxS, PFOA, PFHxA, PFBS, PFPeA, and PFBA on CAC was driven primarily by hydrophobic interactions (Chapters 3 and 4). This result indicates that hydrophilic compounds such as PFBA and PFPeA will be among the first compounds to breakthrough in CAC barriers. While shorter-chain compounds are less bioaccumulative (Buck et al., 2011; Brendel et al., 2018), future regulatory limits for these compounds may become more stringent (Health Canada, 2023; US EPA, 2024). As such, the retention and breakthrough of hydrophilic PFAS should be considered when implementing in-situ CAC barriers.

Secondly, more mass of PFOS and PFOA was adsorbed to the polymer-free CAC than polymer-containing CAC. For in situ remediation, the polymer-containing CAC is commonly used to achieve a better distribution of CAC mass in the subsurface. Therefore, this result suggests that the performance of in-situ adsorption barriers may improve over time if the polymer is biodegraded or desorbed after CAC injection.

Thirdly, the effect of various organic co-contaminants on the adsorption of PFOS and PFOA was observed to be compound-specific (Chapter 3). Under the experimental conditions employed, the adsorption of PFOS and PFOA by CAC was suppressed by DGBE, which is an important component in some AFFF formulations (Harding-Marjanovic et al., 2016; Titaley et al., 2022). While benzene and TCE suppressed PFOS adsorption, these two co-contaminants had no effect or slightly enhanced PFOA adsorption. Because DGBE, benzene, TCE, and other non-fluorinated contaminants could come along with PFAS in the groundwater at AFFF-impacted sites, additional research is needed to investigate their effect on the retention and breakthrough of PFAS in CAC barriers.

Furthermore, in the experiments with synthetic solutions that were free of aquifer materials, an increase in either the solution ionic strength or the concentration of Ca^{2+} increased the adsorption of PFOS and PFOA on CAC, whereas an increase in the concentration of DOC diminished the adsorption of these two compounds (Chapter 3). However, in experiments with aquifer materials (Chapter 4), the effect of Ca^{2+} and DOC on the adsorption of PFOS and PFOA on CAC was the opposite. Moreover, in experiments with actual groundwater samples (Chapter 4), the effect of ionic strength and Ca^{2+} on the adsorption of PFOS and PFOA on CAC was also the opposite of the effect reported in Chapter 3. It is hypothesized that interplays among water chemistry parameters may confound the effect of each parameter. The results of this study indicate that site-specific groundwater and aquifer materials should be employed in laboratory experiments designed to evaluate the retention of PFAS in a CAC barrier.

Additionally, it was demonstrated that four types of CACs (two made from coconut shell, one made from bituminous coal, and one made from wood) adsorbed less PFBS, PFOA, and PFOS than their PAC precursors (Chapter 5). This was attributable to the surface of CACs being more

hydrophilic than that of PACs, which was the result of surface oxidation caused by milling. It was also observed that wood-based adsorbed PFBS, PFOA, and PFOS the least, despite having the highest surface area, micropore volume, and mesopore volume. The repulsion between the negatively charged surface of these ACs ($\text{pH}_{\text{pzc}} = 5.1$) and the negatively charged head group of these PFAS molecules was identified to be the dominant factor that inhibited adsorption. While the adsorption of PFAS on ACs is primarily driven by hydrophobic interactions, the results of our study indicate that the role of electrostatic interaction should be considered when selecting AC type for PFAS treatment applications.

6.2 Recommendations

The research presented in this thesis is not without limitations. Firstly, the research only focused on eight anionic PFAS. While the studied compounds are the ones that currently drive PFAS regulations and are pervasive at AFFF-impacted sites, it has been suggested that the number of PFAS that could be present at these sites could be in the range of several hundred to a few thousand compounds (Barzen-Hanson et al., 2017; Adamson et al., 2022). Some of these compounds are neutral (e.g., perfluorooctane sulfonamide (PFOSA)), cationic (e.g., fluorotelomer thiohydroxy ammonium (6:2 FtTHN⁺)), or zwitterionic (e.g., fluorotelomer sulfonamido betaines (FtB)) (Mejia-Avendaño et al., 2017; Nickerson et al., 2020). The mechanisms through which these compounds adsorb to surfaces could be different from those that control the adsorption of anionic PFAS. Also, some of these compounds could undergo biotransformation, generating perfluoro carboxylic acids and perfluoro sulfonic acids (Houtz et al., 2013; McGuire et al., 2014). The adsorption of these compounds and their biotransformation will likely affect the retention and breakthrough of PFAS in CAC barriers. Thus, additional research is needed to investigate the adsorption of these other compounds on CAC.

Additional information is also needed to investigate the occurrence of DGBE and other glycol ethers at AFFF-impacted sites. DGBE and other glycol ethers (e.g., dipropylene glycol monomethyl ether, tetraethylene glycol dimethyl ether) could be present in AFFF-impacted groundwater because these compounds are an important component in many AFFFs. Glycol ethers are added to AFFFs to help compatibilize various surfactants, prevent phase separation, lower the freezing point, and reduce the solution viscosity (Martin, 2012). According to Martin, the concentration of glycol ethers in AFFF concentrates could be as high as 40 wt. % (Martin, 2012). This is consistent with a recent finding that the concentration of DGBE in 37 AFFF formulations ranged from 26 to 420 g/L (Titaley et al., 2022). However, there is currently no data on the occurrence of DGBE and other glycol ethers at AFFF-impacted sites. Given that DGBE was observed to have a major influence on the adsorption of PFOS and PFOA on CAC, there is a need for research investigating the occurrence of glycol ethers at AFFF-impacted sites and the effect that these compounds may have on the fate and transport of PFAS.

In this research, benzene was chosen as a representative hydrocarbon that could be present in plumes of PFAS. However, the fuels used in firefight training activities were likely a mixture of hydrocarbons. Therefore, the effects of different types of hydrocarbons (e.g., diesel range organics (DRO)) (McGregor, 2023) and their concentration on the adsorption of PFAS by CAC warrant further investigation. Additionally, more experiments with actual groundwater samples collected from AFFF-impacted sites should be conducted to expand the database describing the adsorption of PFAS on CAC under different water chemistry conditions. It should be noted that most of the findings presented in this thesis, specifically Chapters 3 and 4, concern the adsorption of PFAS on PlumeStop CAC, a proprietary commercial product provided by Regenesis, (San Clemente, CA, US). Whether these findings extend to other CAC materials remains to be explored.

Finally, batch experiments were employed throughout this research. However, batch systems provide the most ideal conditions to maximize treatment due to high dosing, maximum contact, and long residence times. These conditions are not representative of in-situ conditions where there is less direct contact between CAC and the target compounds, and the residence time is controlled by the groundwater flow rate. Therefore, future research should investigate the adsorption of PFAS on CAC under conditions that are more representative of in-situ conditions (e.g., column and 2D box experiments).

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Appendix

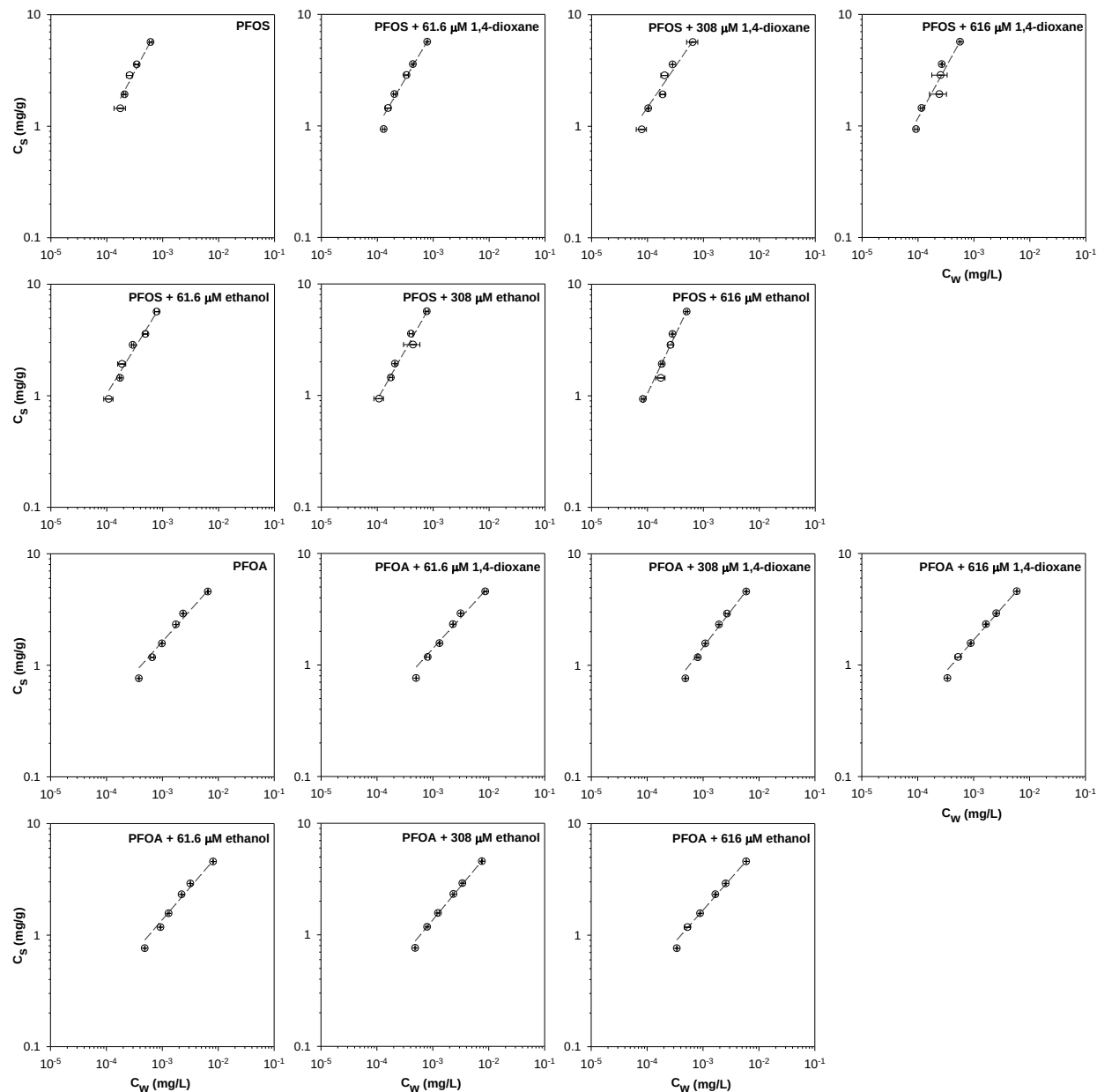


Figure S1. The effect of 1,4-dioxane and ethanol on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), either $[\text{PFOS}]_0 = 650 \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \mu\text{g/L}$, and either 1,4-dioxane or ethanol. The dashed lines represent the fitting of the experimental data to the Freundlich model.

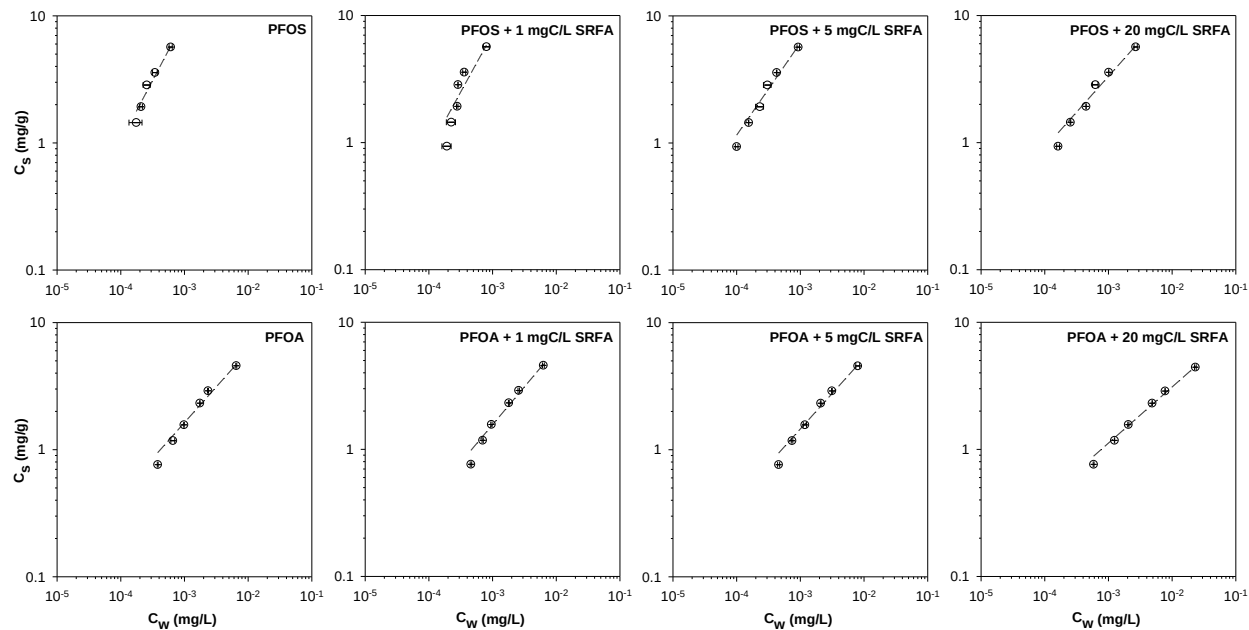


Figure S2. The effect of Suwannee River Fulvic Acid on the adsorption of PFOS and PFOA by the polymer-free CAC. Reaction solutions contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), SRFA, and either $[\text{PFOS}]_0 = 650 \text{ } \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \text{ } \mu\text{g/L}$. The dashed lines represent the fitting of the experimental data to the Freundlich model.

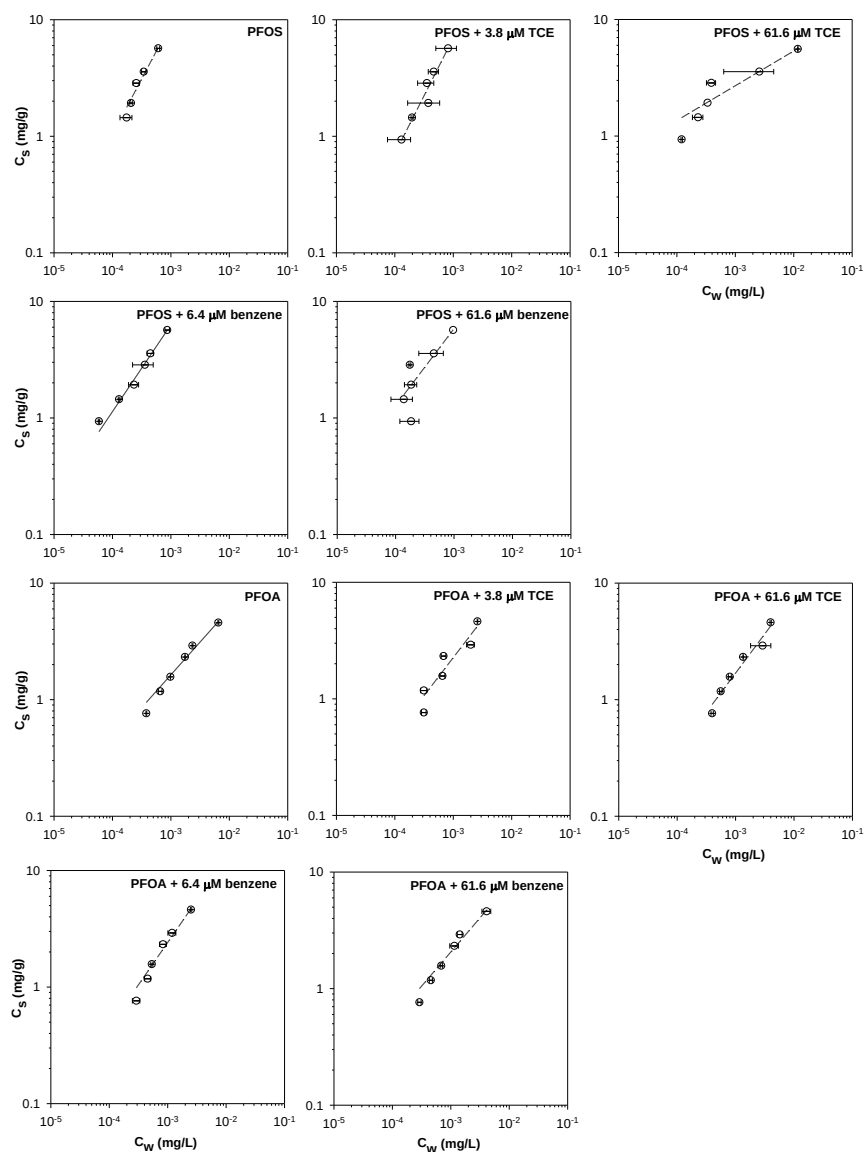


Figure S3. The effect of TCE and benzene on the adsorption of PFOS and PFOA by the polymer-free CAC. The reaction solution contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 ($\text{pH} = 7.5\text{--}8.5$), either TCE or benzene, and either $[\text{PFOS}]_0 = 650 \text{ } \mu\text{g/L}$ or $[\text{PFOA}]_0 = 530 \text{ } \mu\text{g/L}$. The dashed lines represent the fitting of the experimental data to the Freundlich model.

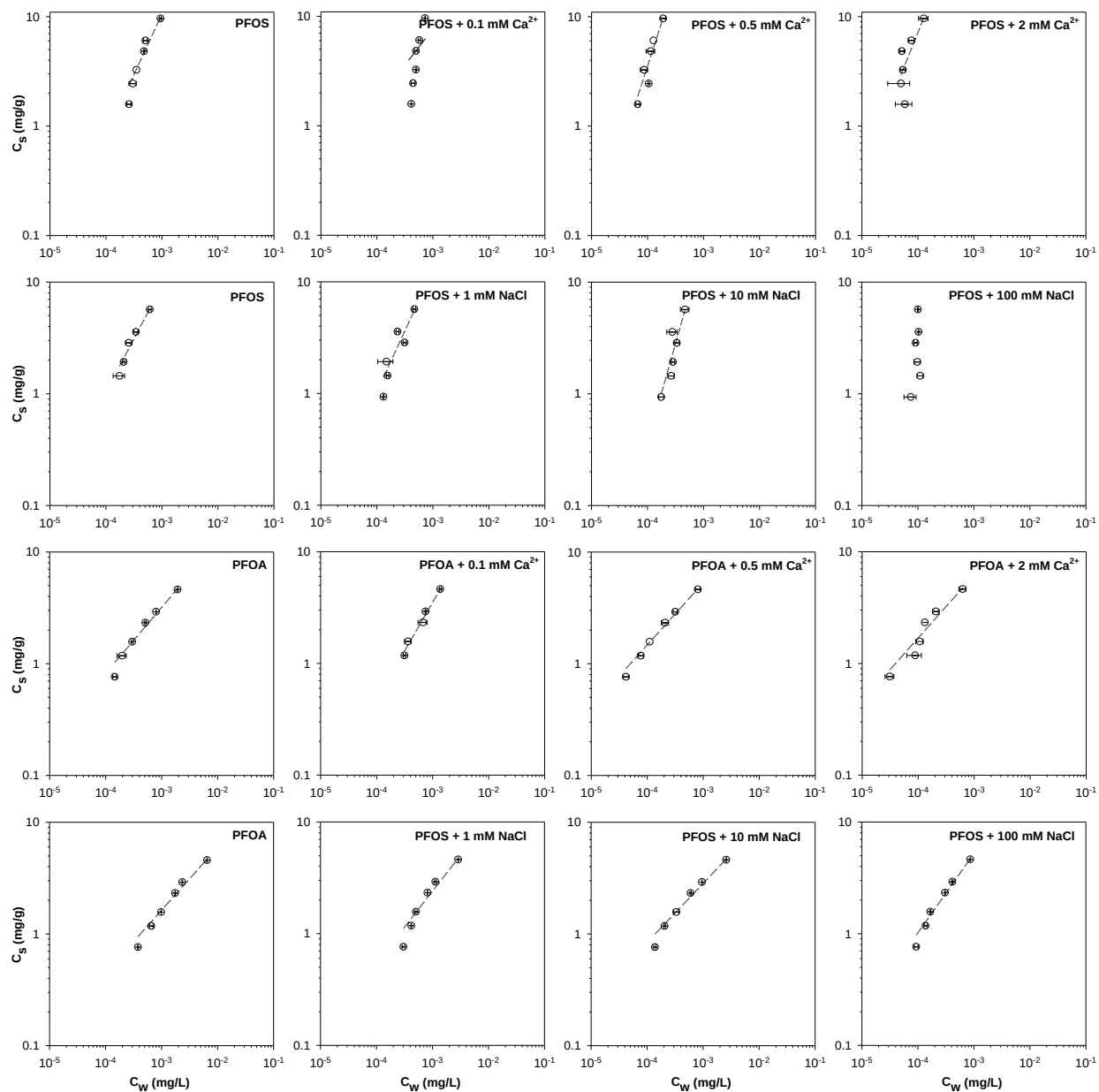


Figure S4. The effect of Ca^{2+} and ionic strength on the adsorption of PFOS and PFOA by the polymer-free CAC; Reaction solution contained 0.1–0.7 g/L CAC, 1 mM NaHCO_3 (pH = 7.5–8.5), and either $[\text{PFOS}]_0 = 1100 \mu\text{g/L}$ (first row panels) or $650 \mu\text{g/L}$ (second-row panels) or $[\text{PFOA}]_0 = 530 \mu\text{g/L}$. The dashed lines represent the fitting of the experimental data to the Freundlich model.

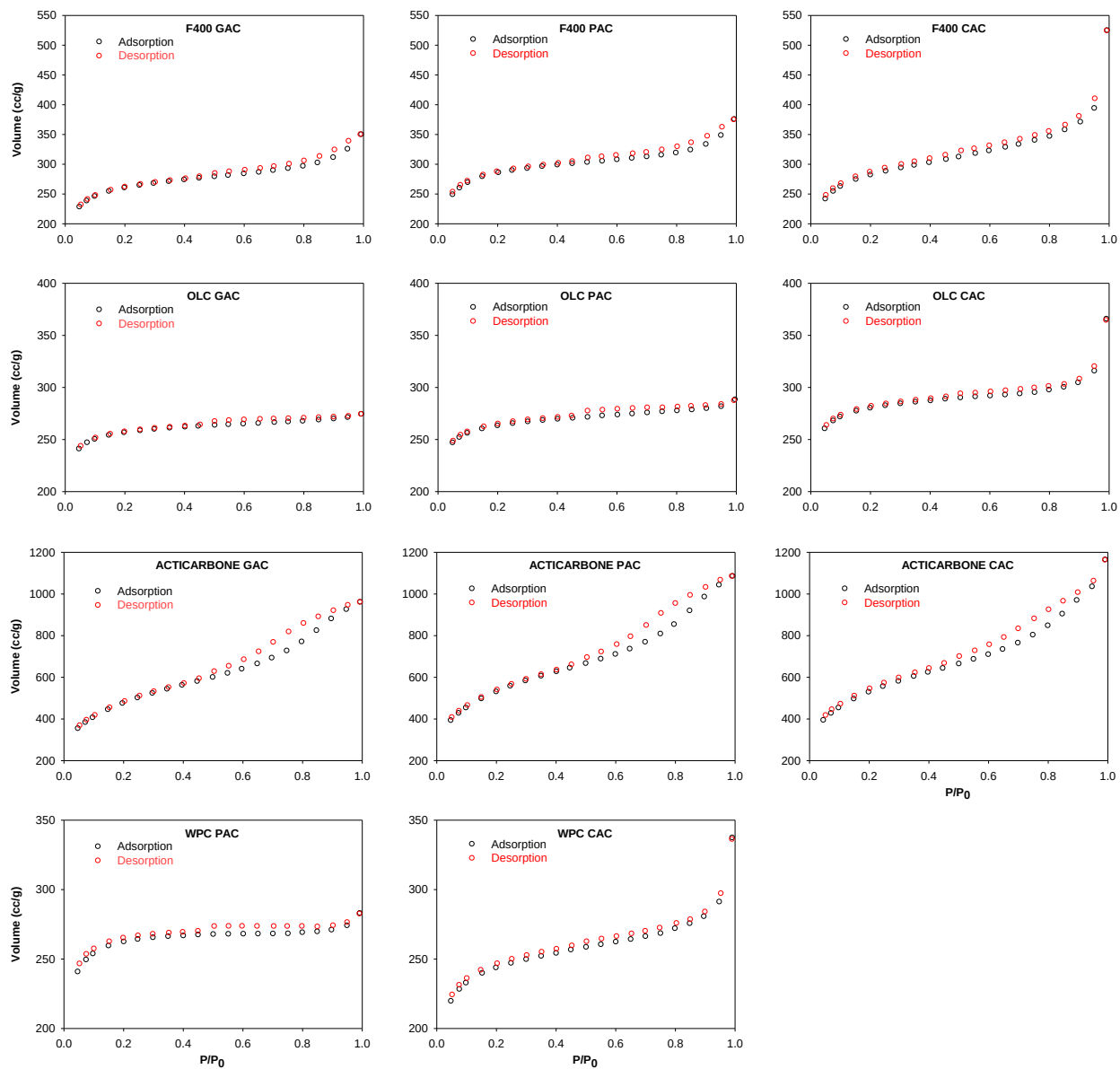
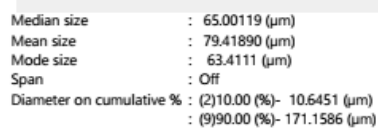


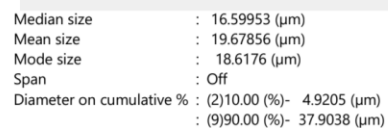
Figure S5. N_2 adsorption-desorption isotherms of GACs, PACs, and CACs.

F400 PAC



Cumulative % at diameter :

OLC PAC



Cumulative % at diameter :

148

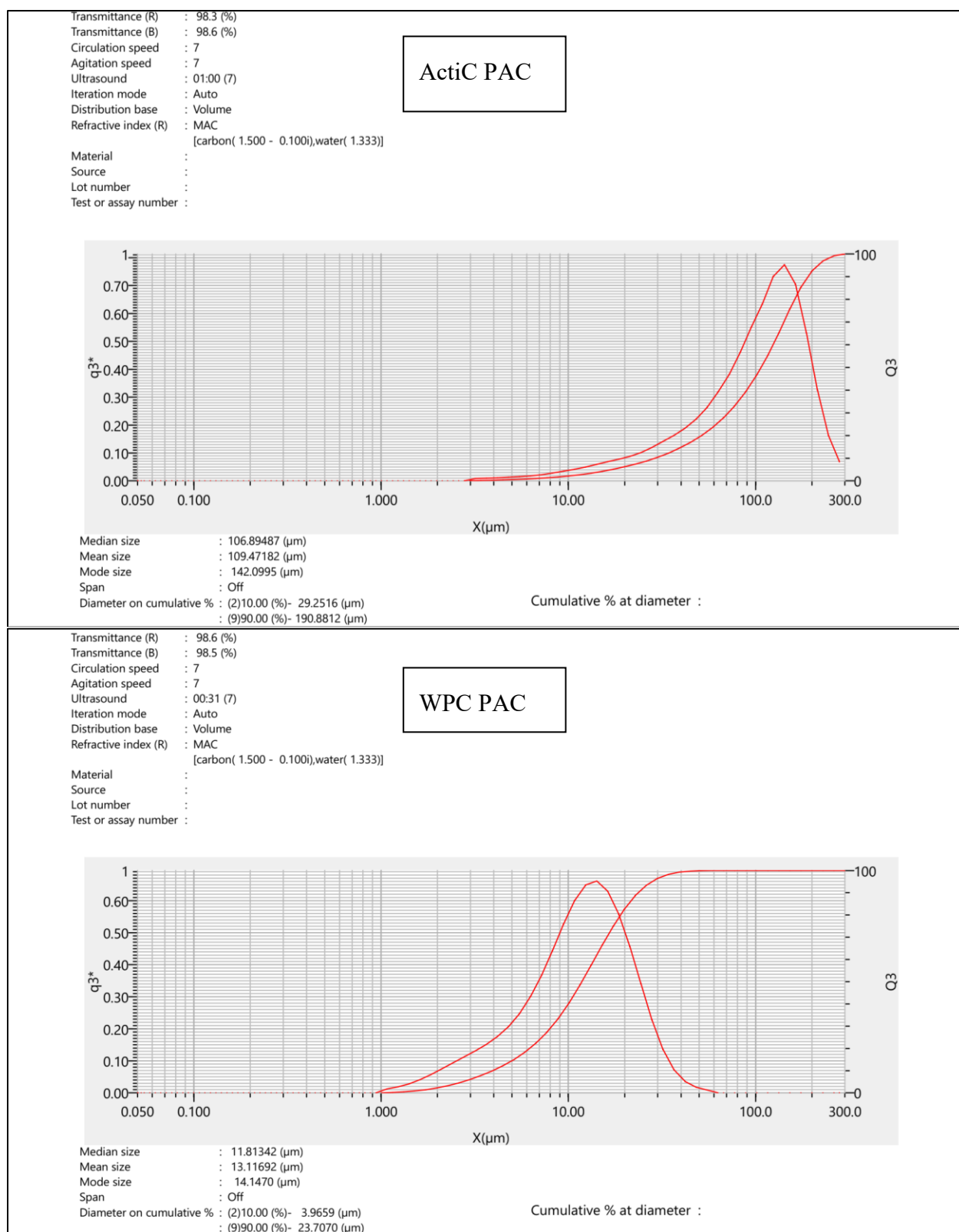


Figure S6. The particle size distribution of PACs (continued)

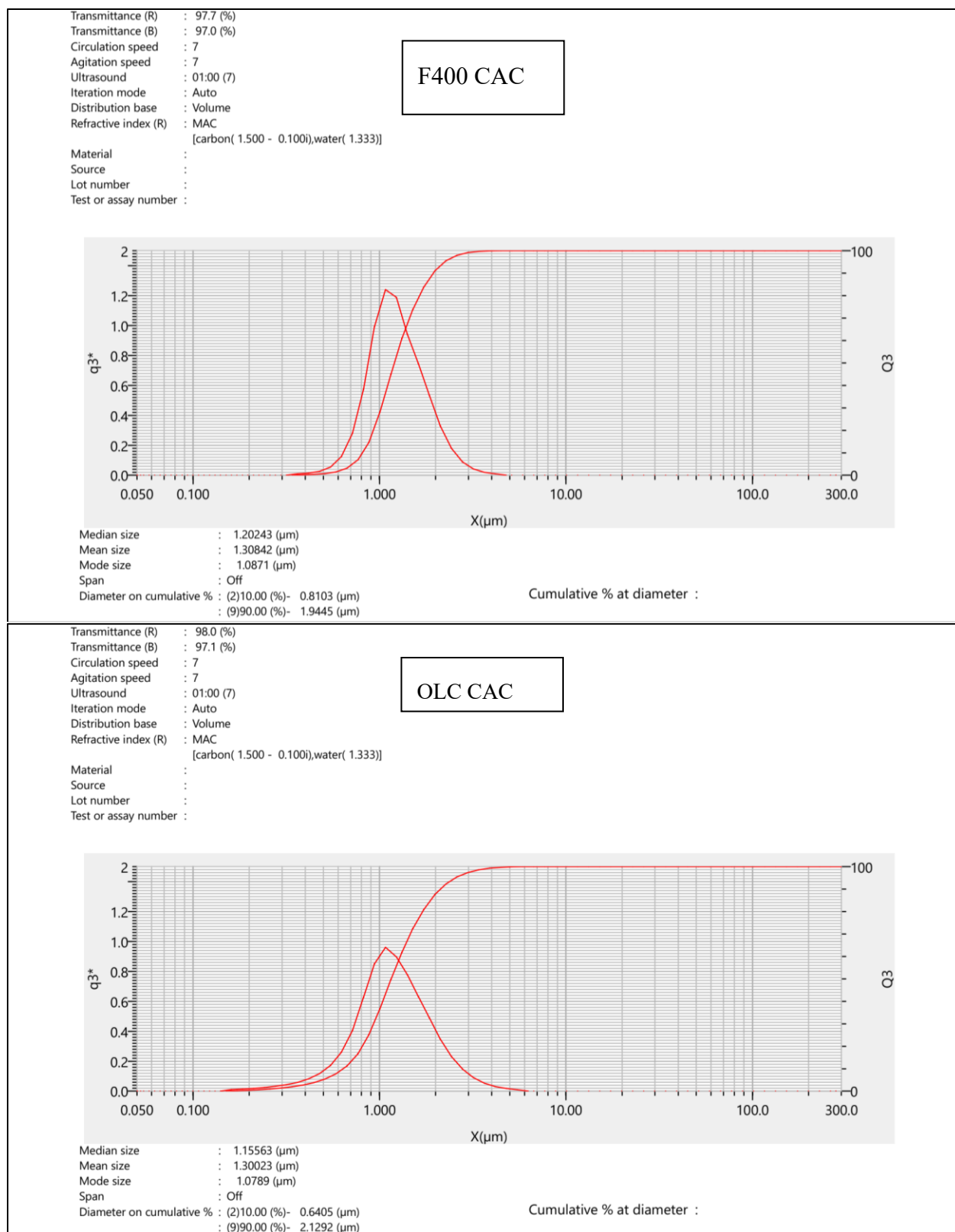
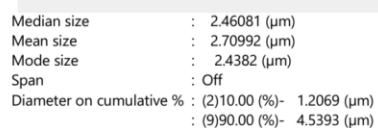


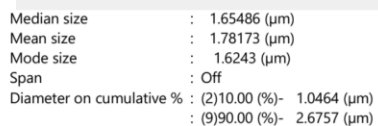
Figure S7. The particle size distribution of CACs

ActiC CAC



Cumulative % at diameter :

WPC CAC



Cumulative % at diameter :

Table S1. List of 24 PFAS and their limit of detection (LOD) and quantitation (LOQ).

Perfluorocarboxylic acids (PFCAs)				
	Analyte	Surrogate	LOD (µg/L)	LOQ (µg/L)
1	PFBA	[¹³ C ₄] MPFBA	0.1	0.5
2	PFPeA	[¹³ C ₅] MPFPeA	0.3	1
3	PFHxA	[¹³ C ₅] MPFHxA	0.01	0.05
4	PFHpA	[¹³ C ₄] MPFHpA	0.01	0.05
5	PFOA	[¹³ C ₈] MPFOA	0.01	0.05
6	PFNA	[¹³ C ₉] MPFNA	0.01	0.05
7	PFDA	[¹³ C ₆] MPFDA	0.01	0.05
8	PFUdA	[¹³ C ₇] MPFUdA	0.01	0.05
9	PFDoA	[¹³ C ₂] MPFDoA	0.01	0.05
10	PFTTrDA	[¹³ C ₂] MPFTTrDA	0.01	0.05
11	PFTeDA	[¹³ C ₂] MPFTeDA	0.01	0.05
Perfluorosulfonic acids (PFSAs)				
	Analyte	Surrogate	LOD (µg/L)	LOQ (µg/L)
12	PFBS	[¹³ C ₃] MPFBS	0.01	0.05
13	PFPeS	[¹³ C ₃] MPFBS	0.01	0.05
14	PFHxS	[¹³ C ₃] MPHxS	0.01	0.05
15	PFHpS	[¹³ C ₃] MPHxS	0.01	0.05
16	PFOS	[¹³ C ₈] MPFOS	0.01	0.05
17	PFNS	[¹³ C ₈] MPFOS	0.01	0.05
18	PFDS	[¹³ C ₈] MPFOS	0.01	0.05
Precursors				
	Analyte	Surrogate	LOD (µg/L)	LOQ (µg/L)
19	4:2FTS	[¹³ C ₂] M4:2FTS	0.01	0.05
20	6:2FTS	[¹³ C ₂] M6:2FTS	0.01	0.05
21	8:2FTS	[¹³ C ₂] M8:2FTS	0.01	0.05
22	FOSA	[¹³ C ₈] MFOSA	0.01	0.05
23	MeFOSAA	[² d ₂] MMeFOSAA	0.03	0.1
24	EtFOSAA	[² d ₂] MEtFOSAA	0.03	0.1