

# Sorption of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) by Natural and Anthropogenic Carbonaceous Sorbents

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### Abstract

As a large number of perfluoroalkyl and polyfluoroalkyl substances (PFASs) has been extensively used in industrial and consumer products, many of these species are detected in the global environment and biota, including some carcinogenic ones. Perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) are examples of PFASs currently subject to strict regulatory and scientific scrutiny. There are many other analogous compounds, such as those used in aqueous film-forming foams (AFFFs), for which environmental fate and effect are little known. In addition, high chemical stability and hydrophilicity of PFASs pose challenges to effective treatment and mitigation of those present in groundwater and drinking water sources. The objective of this research was to elucidate interactions between PFASs and naturally occurring and engineered carbonaceous materials, the knowledge base needed for PFAS risk assessment and treatment.

The research first examined the interactions between commercial adsorbents with two most prominent PFAS species (PFOA and PFOS), to identify the ways in which water treatment efficiency for the PFASs can be improved. The study assessed the sorption of PFOS and PFOA onto as-received and surface-modified carbonaceous adsorbents using single-solute batch sorption experiments, and the main carbon characteristics controlling the uptake of PFASs were identified. Adsorbent surface chemistry played a more important role in controlling the extent of uptake than physical properties. High carbon surface basicity was closely linked to high PFOS and PFOA affinity. Prior to any modification of the carbon materials, synthetic polymer-based Ambersorb and activated carbon fibers were the most effective adsorbents due to their basic character. Surface modification, more so with ammonia gas treatment than with high-temperature thermal treatment, greatly improved sorption of PFOS and PFOA by wood-based carbons and activated carbon fibers.

The research then focused on the role that soil organic matter (SOM) and pyrogenic carbonaceous materials (PCMs) played in determining the transport potential of a range of perfluoroalkyl acids (PFAAs) and their chemical precursors (PrePFAAs). A novel dynamic HPLC-based column method was developed to determine distribution coefficients ( $K_{oc}$ ) between SOM and water at various conditions. PrePFAAs with betaine, sulfonamide betaine, and quaternary amine functional groups exhibited higher  $K_{oc}$  values than the PFAAs with the same perfluoroalkyl chain length.

Calcium ion had a positive impact on the sorption of anionic PFAAs to SOM while showing a negative impact on the PrePFAAs. Moreover, an increase in pH reduced sorption of all the PFASs to SOM.

In comparison, sorption of PFASs to PCMs (charcoal and soot) was stronger and less linear than SOM, indicating that PCMs could be a more significant sink to PFASs in the firefighting training sites where regular releases of AFFFs resulted in PFAS pollution of soil and groundwater. The role of PCMs was more pronounced than SOM at lower aqueous concentrations without an attenuation effect. Additionally, apparent sorption-desorption hysteresis exhibited by PCMs was sorbate-specific, and the soot had the highest hysteresis among all the sorbents.

These findings illustrate the importance of considering the surface chemistry of adsorbents, along with solution chemistry when investigating PFAS uptake by carbonaceous materials of different origins. Furthermore, the results obtained emphasize the need to evaluate the interactions between PrePFAAs and PCMs, in the efforts to delineate the behaviours of PFASs in soil and groundwater impacted by AFFFs, as well as to decide remediation strategies.

### Résumé

Un grand nombre de substances perfluoroalkyles et polyfluoroalkyles (PFASs) sont employées dans des produits industriels et de consommation. Beaucoup de ces espèces, dont certaines qui sont carcinogènes, sont détectées dans l'environnement et le biome global. Les acides perfluoroctane sulfoniques (PFOS) et carboxyliques (PFOA) sont des exemples de PFASs actuellement sujets à une surveillance scientifique et règlementaire stricte. Il y a aussi un nombre de composés analogues comme ceux fessant partis des mousses filmogènes aqueuses (AFFF) dont le sort et les effets environnementaux sont peu élucidés. De plus, la stabilité chimique élevée ainsi que l'hydrophilie des PFASs posent obstacle au traitement et atténuation efficace des substances présentes dans les eaux souterraines et les sources d'eau potable. L'objectif de la présente recherche est d'éclaircir les interactions entre les PFASs et les matières carbonées conçusses ou de provenance naturelle pour créer une base de savoir nécessaire à procéder à l'évaluation des risques ainsi qu'aux traitements possibles.

La présente recherche examine en premier les interactions entre adsorbants commerciaux et deux espèces de PFAS proéminentes (PFOA et PFOS) pour identifier les façons par lesquelles l'efficacité des méthodes de traitement d'eau peut être améliorée. L'étude évalue la sorption des PFOS et PFOA sur les adsorbants reçus comme tels et modifiés chimiquement de surface avec des essais de sorption en lots. Les caractéristiques primaires contrôlant l'étendue de l'adsorption des PFASs sont identifiées. La chimie de surface des adsorbant a un plus grand impact que les propriétés physiques. Une grande basicité de surface des matières carbonées est liée étroitement à une grande affinité pour PFOS et PFOA. Précédant toute modification des matières carbonées, les fibres de charbon actif et Ambersorb, adsorbant synthétique de base de polymères, sont les plus performants grâce à leur caractère basique. La modification de surface avec traitement par gaz d'azote plus que par traitement thermique de haute température améliore la sorption des PFOS et PFOA sur les charbons actifs et charbons à base de bois.

La recherche tourne ensuite sur le rôle que jouent des matières organiques du sol (SOM) et les matières carbonées pyrogènes (PCMs) sur le potentiel de propagation d'une gamme d'acides perfluoroalkyles (PFAAs) et leurs prédécesseurs chimiques (PrePFAAs). Une nouvelle méthode

dynamique sur colonne HPLC a été développée pour trouver les coefficients de distribution (K<sub>oc</sub>) entre SOM et l'eau dans des conditions variées. Les PrePFAAs avec des groupes fonctionnels de bétaine, bétaine sulfonamide et amine quaternaire démontrent des valeurs de K<sub>oc</sub> plus élevées que les PFAAs de même longueur de chaîne perfluoroalkyle. L'ion de calcium affecte positivement la sorption des PFAAs anioniques sur la SOM, mais affecte négativement celle des PrePFAAs. D'ailleurs, une croissance de pH réduit la sorption des tout PFAS au SOM.

Par comparaison, la sorption des PFASs aux PCMs (charbon et suie) est plus forte et moins linéaire que leur sorption sur SOM. Ceci peut indiquer que les PCMs peuvent être un puit de PFAS sur les sites d'entrainement de pompiers où une contamination de PFAS aux eaux et sols provient d'une application régulière de AFFF. Le rôle des PCMs est plus prononcé que celui de SOM à des bases concentrations aqueuses et sans atténuation. De plus. Une hystérèse sorption-désorption apparente démontrée par les PCMs est spécifique au sorbat. La suie a la plus haute hystérèse de tous les sorbants.

Ces constatations illustrent l'importance de considérer la chimie de surface des adsorbants en tandem avec la chimie des solutions lors de l'investigation de l'adhérence des PFASs sur des matières carbonées de différentes origines. En outre, les résultats obtenus renforcent le besoin d'étudier les interactions entre PrePFAAs et PCMs dans l'effort d'élucider le comportement des PFASs au sol et dans les eaux souterraines affectées par les AFFFS ainsi que pour formuler des stratégies de réhabilitation.

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# Nomenclature

Acronym	Name	Formula
PFAS	Perfluoroalkyl and polyfluoroalkyl substances	
PFAA	Perfluoroalkyl acid	F(CF <sub>2</sub> ) <sub>n</sub> COOH
		$F(CF_2)_nSO_3^-$
PrePFAA	Precursor to perfluoroalkyl acid	
PFCA	Perfluoroalkyl carboxylic acid	F(CF <sub>2</sub> ) <sub>n</sub> COOH
PFBA	Perfluorobutanoic acid	F(CF <sub>2</sub> ) <sub>3</sub> COOH
PFPeA	Perfluoropentanoic acid	F(CF <sub>2</sub> ) <sub>4</sub> COOH
PFHxA	Perfluorohexanoic acid	F(CF <sub>2</sub> ) <sub>5</sub> COOH
PFHpA	Perfluoroheptanoic acid	F(CF <sub>2</sub> ) <sub>6</sub> COOH
PFOA	Perfluorooctanoic acid	F(CF <sub>2</sub> ) <sub>7</sub> COOH
PFNA	Perfluorononanoic acid	F(CF <sub>2</sub> ) <sub>8</sub> COOH
PFDA	Perfluorodecanoic acid	F(CF <sub>2</sub> )9COOH
PFSA	Perfluoroalkyl sulfonic acid	$F(CF_2)_n SO_3^-$
PFBS	Perfluorobutane sulfonate	$F(CF_2)_4SO_3^-$
PFHxS	Perfluorohexane sulfonate	$F(CF_2)_6SO_3^-$
PFOS	Perfluorooctane sulfonate	$F(CF_2)_8SO_3^-$
n:2 FTSA	n:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>n</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
4:2 FTSA	4:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
6:2 FTSA	6:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
8:2 FTSA	8:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
PFOSB	Perfluoroctanesulfonamide betaine	$\begin{array}{l} F(CF_2)_8SO_2NH(CH_2)_3N^+(CH_3)_2CH_2COO\\ H\end{array}$
PFOAB	Perfluorooctaneamide betaine	F(CF <sub>2</sub> ) <sub>7</sub> CONH(CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> COOH
6:2FTAB	6:2 Fluorotelomer sulfonamide betaine	$F(CF_2)_6CH_2CH_2SO_2NH(CH_2)_3N^+(CH_3)_2C$ H_2COOH
PFOAAmS	Perfluoroctaneamido ammonium iodide	$C_7F_{15}CONH(CH_2)_3N^+(CH_3)_3$
MPFBA	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid	$F(^{13}CF_2)_3^{13}COOH$
MPFHxA	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid	$F(CF_2)_4^{13}CF_2^{13}COOH$
MPFOA	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]octanoic acid	$F(CF_2)_4({}^{13}CF_2)_3{}^{13}COOH$
MPFNA	Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid	$F(CF_2)_4(^{13}CF_2)_4^{13}COOH$
MPFHxS	Perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate	$F(CF_2)_6SO^{16}O_2^{-1}$
MPFOS	Perfluoro-1-[1,2,3,4-13C4]octanesulfonate	$F(CF_2)_4(^{13}CF_2)_4SO_3^{-1}$

M6:2 FTSA	1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]- octane sulfonate	F(CF <sub>2</sub> ) <sub>6</sub> <sup>13</sup> CH <sub>2</sub> <sup>13</sup> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
M8:2 FTSA	1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]- decane sulfonate	$F(CF_2)_8^{13}CH_2^{13}CH_2SO_3^{-1}$
1240C	Coconuet shell based granular activated can	bon
AFFF	Aqueous film-forming foam	
ACF	Activated carbon fiber	
ACN	Acetonitrile	
AFFF	Aqueous film-forming foam	
Ambersorb	Carbonaceous resin/polymer	
AquaNC	Wood based carbon	
AT	Ammonium gas treatment	
ATRP	Atom transfer radical polymerization	
BioNC	Wood based powdered activated carbon	
BPL	Bituminous coal based powdered activated	carbon
CMC	Critical micelle concentration	
CNT	Carbon nanotube	
CSPC	Critical separate phase concentration	
F400	Bituminous coal based granular activated c	arbon
GAC	Granular activated carbon	
GC	Gas chromatography	
HAc	Acetic acid	
HT	High-temperature treatment	
IEP	Isoelectric point	
$K_d$	Solid-phase distribution coefficient	
$K_{oc}$	Soil organic carbon-water partitioning coef	ficient
LC-MS/MS	Liquid chromatography-mass spectrometry	I
МеОН	Methanol	
MRM	Multiple reaction monitoring	
NAPL	Non-aqueous phase liquid	
NOM	Natural organic matter	
PAC	Powdered activated carbon	
PCM	Pyrogenic carbonaceous material	
$pK_a$	Acid dissociation constant	
PZC	Point of zero charge	
SWCNTs	Single walled carbon nanotubes	
SOM	Soil organic matter	
MWCNTs	Multi-walled carbon nanotubes	
WVB	Wood based granular activated carbon	
XPS	X-ray photoelectron spectroscopy	

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After an intensive period of four years, today is the day: writing this note of thanks is the finishing touch on my doctoral thesis. It has been a journey which filled with joy, excitement, frustration, loss and hesitation. In the end, I feel a sense of accomplishment, not only in the scientific arena but also on a personal level. A lot of people have helped me and accompanied me throughout this four-year Ph.D. journey. I would like to thank them all sincerely.

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In the end, back in China, where the most basic source of my life energy resides: my family. I have an amazing family, unique in many ways, and the stereotype of a perfect family in many others. Their support has been unconditional all these years; they have given up many things for me to be at McGill; they have cherished with me every great moment and supported me whenever I needed it.

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Yue Zhi

March 20, 2017

## Preface

In accordance with the "Guidelines for Thesis Preparation", this thesis is presented in a manuscript-based format. Chapters 1 and 2 are introduction and literature review, followed by the results and discussions presented in a manuscript format in Chapters 3-6. In Chapter 7, conclusions and future works are presented. Supplementary information of each manuscript is provided at the end of the thesis as appendixes. At the time of thesis submission, Chapter 3 and 4 have been published, and Chapter 5 and 6 are to be submitted to journals. These publications are as follows:

1. Zhi, Yue, and Jinxia Liu. "Adsorption of Perfluoroalkyl Acids by Carbonaceous Adsorbents: Effect of Carbon Surface Chemistry." *Environmental Pollution* 202 (2015): 168-176.

2. Zhi, Yue, and Jinxia Liu. "Surface Modification of Activated Carbon for Enhanced Adsorption of Perfluoroalkyl Acids from Aqueous Solutions." *Chemosphere* 144 (2016): 1224-1232.

3. Zhi, Yue, and Jinxia Liu. "Sorption of Anionic and Zwitterionic Perfluoroalkyl and Polyfluoroalkyl Surfactants to Soil Organic Matter." In preparation for submission to a peer review journal.

4. Zhi, Yue, and Jinxia Liu. "Comparative Investigation of Sorption of Perfluoroalkyl and Polyfluoroalkyl Substances to Soil Organic Matter (SOM) and Pyrogenic Carbonaceous Materials (PCMs)." In preparation for submission to a peer review journal.

The Ph.D. candidate and author of this thesis, Yue Zhi, held primary responsibility for performing the literature review, designing and performing experiments, analyzing and interpreting experimental data, and preparing the manuscripts for publication and the doctoral dissertation.

Professor Jinxia Liu of the department of Civil Engineering & Applied Mechanics at McGill University was the sole supervisor of the candidate Yue Zhi over the course of the research. She participated in the research by assisting defining research scope and objectives, supervising the design of experiments, contributing to the interpretation of results, and revising the manuscripts of the articles listed above and the thesis.

## **CHAPTER 1**

Introduction

### 1.1 Background

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have attracted considerable attention as a major category of emerging contaminants because of their widespread detection in various environmental compartments, bioaccumulation potential, and health and ecological risks to humans and wild animals <sup>1-5</sup>. The unique properties imparted by the fluorocarbon chain in these molecules have resulted in their popular use in many industries (e.g., metal plating, photolithography, semiconductor and polymer industries) and products (e.g., hydraulic fluids, aqueous film-forming foams, varnishes, specialty lubricants, and water repellents for leather, paper, and textiles) for well over half a century <sup>6</sup>. The direct release of PFASs at any stage of their production life cycle, as well as the indirect release from degradation of related compounds, gives rise to a global distribution of these persistent pollutants <sup>7</sup>. Perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) are examples of PFASs currently subject to strict regulatory and scientific scrutiny, but there are many structurally similar substances with a long perfluoroalkyl chain that have been manufactured and released into the environment.

In North America, PFASs are frequently detected in wastewater influent and effluent, biosolids, as well as drinking water supplies <sup>8-10</sup>. Removal of PFAS during water and wastewater treatment processes has been found to be very challenging <sup>9, 11, 12</sup>. PFASs resist conventional chemical and biological degradation processes in natural and engineered treatment systems because of the stable perfluoroalkyl chains. PFAS also exhibit relatively high hydrophilicity <sup>9, 13</sup>. Although treatment technologies that can decompose PFASs have been reported <sup>14</sup>, they are still in early-stage development and are infeasible for practical applications. In real-world treatment scenarios targeting PFASs, adsorption by granular activated carbon (GAC) has been almost exclusively employed as the key process for drinking water treatment <sup>8, 15, 16</sup>, as well as groundwater remediation <sup>17</sup>. However, the theoretical limits and practical implications for the removal of PFASs using sorption processes are still poorly understood. For example, it was reported that newly packed GAC filters could achieve 69-100% removal of PFOS and PFOA at ng L<sup>-1</sup> level in five treatment plants in Osaka, Japan <sup>16</sup>. However, the early breakthrough of PFASs due to weak interactions with carbon and the high cost of frequent filter replacement have been identified to be the main issues <sup>8</sup>.

A number of studies have explored the potential for removal of PFAS using activated carbon and other sorbent materials <sup>18-24</sup>; many issues, however, have not been fully addressed for improving removal efficiency for real-world treatment scenarios <sup>8</sup>. Most studies have only focused on determining sorption isotherms, examining the impact of carbon physical properties (e.g., particle size, pore size and surface area), or evaluating the effect of solution chemistry (e.g., pH, ionic strength, and cation concentration). Those studies were largely performed at high PFAS concentrations that might be relevant for industrial wastewater from a PFAS plant, but not for drinking or groundwater treatment situations. None have focused on how activated carbon chemical properties, which have been found to play a dominant role in determining removal efficiency of many other organic compounds from water, affect PFAS removal. Therefore, to establish the theoretical bases that can be further applied to making more suitable carbon materials for PFASs, it is necessary to examine among commercial activated carbons how various carbon characteristics, especially carbon surface chemistry, might influence PFAS uptake from water. To date, no study has been conducted to address the fundamental question.

Recently, studies have revealed another major form of PFAS pollution that is not directly related to PFAS manufacturing or PFASs in consumer products. For decades, repeated deployment of PFAS-based aqueous film-forming foams (AFFFs) into soil and groundwater during firefighting training activities conducted at military bases, airports, and firefighting training schools has led to widespread PFAS contamination. It is at AFFF-impacted sites that the highest perfluoroalkyl acid (PFAA) levels (e.g. 15 mg L<sup>-1</sup>) among any aqueous samples have been detected <sup>25-27</sup>. PFASs in AFFF formulations act as active ingredients that help block oxygen, suppress solvent vapors and prevent burn back during a flammable liquid fire <sup>6</sup>. Those active ingredients are various types of anionic, cationic or zwitterionic fluorosurfactants, and for which more than 100 different species have been identified recently, especially during 2012-2014 <sup>26, 28, 29</sup>. In contrast to the "legacy" PFASs (largely anionic sulfonates or carboxylates such as PFOS and PFOA), the newly identified PFASs possess functional groups such as sulfonyl, thioether, amine, quaternary ammonium, carboxylate, sulfonate, amine oxide, and betaine. They are collectively called "precursors" to PFAAs (PrePFAAs), as they may eventually degrade biologically or chemically to result in PFAAs when the non-fluorinated functional groups are lost <sup>30, 31</sup>. Currently, the research addressing characterization, management, and remediation of soil and groundwater contaminated by AFFFs is still in its early stage. Whereas some of the attention has been paid to the transformation potential

of PrePFAAs, the potential of PrePFAAs to be transported offsite in leachate or runoff is largely unexplored.

Inadequate understanding of transport potential of various PFAS species in soil and groundwater is among many challenges that people face when trying to manage and remediate AFFF-impacted sites. Several early studies have examined sorption to soil and sediment of legacy PFASs, mainly anionic PFAAs <sup>32-39</sup>. It was concluded that PFAA sorption to environmental solid matrices (both organic matter and mineral components) is driven by a combination of electrostatic and hydrophobic interactions <sup>32, 33, 39</sup>. It has been shown that organic carbon content ( $f_{oc}$ ) is the most important soil or sediment parameter that determines the magnitude of solid-water distribution coefficients for PFAAs. The influence of compound-specific parameters including perfluoroalkyl chain-length and type of hydrophilic head group has been quantified <sup>39</sup>. Sorption has also been found to generally increase with increasing calcium ion concentration and decreasing solution pH <sup>39</sup>.

Although past research may serve as a starting point for predicting the transport behaviour of a number of anionic PFAS species in AFFF-impacted sites <sup>35</sup>, little is known about the interactions of PrePFAAs with their environment, which can vary substantially from one PFAS family to another. PFOS and PFOA with low  $pK_a$  values exist only in deprotonated (anionic) forms at all environmentally relevant pH <sup>40-42</sup>, but the  $pK_a$  values of many of the PrePFAAs lie within the normal environmental pH range, and therefore they may exist in protonated or deprotonated form, or a mixture of both, depending on pH. Given the fact that the charge of some PrePFAAs is sensitive to pH, their sorption behaviors are likely to strongly depend on the molecular charge, a fact that has been little considered and cannot be simply derived from the knowledge developed based on PFAAs.

Moreover, to accurately predict the behaviors of PFAS in various AFFF-impacted sites, it is simply not sufficient just to look at the total organic carbon content in soil or sediment, as these solid matrices contain organic components of distinct origins and properties <sup>43</sup>. Soil organic matter (SOM) formed from the decomposition of plant materials is a weaker sorbent material, on a mass basis, than the inert, condensed, and aromatic pyrogenic carbonaceous materials (PCMs) that are formed from combustion <sup>44, 45</sup>. Fire-impacted soils, such as in fire training areas where AFFFs are

applied, can have an abundance of PCMs (as high as 30-45%)<sup>46</sup>. Known for their extremely efficient sorption, PCMs can play a critical role in retaining PFASs and prevent their migration off site. Additionally, to delineate the transport behaviors of PFAS, another issue of great importance is the reversibility of sorption or the lack of it. Sorption can exhibit hysteresis, which is demonstrated as the non-singularity of the sorption and desorption branches of the isotherm <sup>45</sup>. Few studies have addressed desorption behaviour of PFASs, which may be especially prone to sorption hysteresis because their long tails may hinder diffusion in small pores.

To date, no study has been conducted to investigate the role of PCMs on PFAS transport potential, or to attempt to make a distinction between SOM and PCMs in their interactions with PFAAs and PrePFAAs. A study of sorption, as well as desorption, of major families of PFASs with key carbonaceous materials present in soil and sediment, will extend our understanding of PFAS behaviour at a high number of AFFF-impacted sites in North America as well as other regions of the world. As sorption is closely linked to bioavailability and biotransformation potential of organic pollutants, such a study will present a critical contribution to the knowledge base for supporting PFAS cleanup and mitigation decisions at AFFF-impacted sites.

## 1.2 Research Objectives

Given the research needs described above, the overarching goal of the research is to elucidate the interactions between several major families of PFASs and naturally occurring and engineered carbonaceous materials using laboratory-scale sorption and desorption experiments. Five specific objectives were further defined in the proposed research.

- **Objective 1** was to identify what the dominant properties are for major commercial carbonaceous adsorbents that control the extent of PFOS and PFOA uptake.
- **Objective 2** was to evaluate whether the dominant properties that have been identified to control PFOS and PFOA uptake can be further enhanced to improve the performance of commercial carbons regarding removal efficiency of PFOS and PFOA from water.
- **Objective 3** was to evaluate the differences in sorption bond strength as well as sorption mechanisms between PFAAs and PrePFAAs in their interactions with soil organic matter (SOM).

- **Objective 4** was to compare the differences in sorption of PFAAs and PrePFAAs to organic matter of distinct origins, namely pyrogenic carbonaceous materials (PCMs) versus SOM.
- **Objective 5** was to assess sorption reversibility of PFAAs and PrePFAAs in their interactions with PCMs and SOM.

### 1.3 Thesis Organization

**Chapter 1** provides the overview of the study background, objectives, and structure of the thesis as well as the contribution of authors.

**Chapter 2** provides a detailed literature review on the properties of the target PFASs and the sorption of PFASs to commercial carbonaceous materials, soil, and sediment. Detailed discussion on interactions between PFAS molecules and a large variety of sorbents under varying experimental conditions is also presented.

**Chapter 3** addresses Objective 1 and identifies the major sorbent-specific factors for commercial carbonaceous sorbents that control the uptake of PFOS and PFOA. Ten sorbents with a wide range of raw parent materials and properties were evaluated in single-solute batch adsorption experiments. The main carbon characteristics controlling the uptake of PFOS and PFOA were discussed on the basis of experimental observations and statistical analysis. This study aims to provide an improved understanding of sorption mechanism of PFOS and PFOA, the knowledge that can contribute to adsorbent manufacturing, selection, and application. This chapter has been published as: Zhi, Y.; Liu, J. "Adsorption of perfluoroalkyl acids by carbonaceous adsorbents: Effect of carbon surface chemistry". *Environmental Pollution* 2015, 202, 168-176.

**Chapter 4** addresses Objective 2 and presents a follow-up study of Chapter 3. Given that carbon surface basicity plays a major role in sorption, this study further evaluates the adsorption of PFOS and PFOA by surface-modified carbons. High-temperature and ammonia gas treatments were applied to carbons made of different raw materials, sorption before and after the modifications was compared. This study has provided critical data for supporting surface modification approaches that can be applied to improve the efficacy and efficiency of PFAS treatment by activated carbon and other carbonaceous sorbents. This chapter has been published as: Zhi, Y.; Liu, J. "Surface

modification of activated carbon for enhanced adsorption of perfluoroalkyl acids from aqueous solutions". *Chemosphere* 2016, 144, 1224-1232.

**Chapter 5** addresses Objective 3 and focuses on the interactions between model SOM (Pahokee peat) and fifteen anionic or zwitterionic PFAS species that have been identified as dominant species in AFFF-impacted groundwater. They include six perfluoroalkyl carboxylic acids (PFCAs), three perfluoroalkyl sulfonates (PFSAs), three fluorotelomer sulfonates (FTSAs), and three polyfluoroalkyl betaines. The sorption to SOM was examined using a newly developed dynamic HPLC-based column method. The organic carbon-water distribution coefficients (log  $K_{oc}$ ) for all the PFAS species were determined, as well as the influence of solution pH and divalent cation concentrations on  $K_{oc}$ . This study has clarified the transport potential of both legacy PFAAs and newly-identified PFASs, which is important for elucidating their environmental fate and for holistically addressing PFAS pollution in AFFF-impacted areas.

**Chapter 6** addresses Objectives 4 and 5 and compares the sorption behaviors, as well as sorption hysteresis, of a cationic PFAS (perfluoroctaneamido ammonium iodide, PFOAAmS), PFOA, PFOS and two polyfluoroalkyl betaines (6:2 fluorotelomer sulfonamide betaine, 6:2 FTAB; perfluorooctane amido betaine, PFOAB) in the presence of two types of PCMs (i.e., wood-derived biochar and chimney soot) and model SOM (Pahokee peat). In this study, sorbents were characterized, and sorption-desorption isotherms were then constructed using batch sorption experiments. A sorption hysteresis index for each PFAS was calculated at selected concentrations. The potential sinks of PFASs in the soil where PCMs and SOM coexist are tentatively identified. The role of PCMs in the sorption of PFASs in AFFF-impacted sites is emphasized for the first time, adding the knowledge of one important environmental process that needs to be considered for an understanding of the behaviors of PFAS in the environment.

**Chapter 7** presents a summary of the thesis and the general conclusions of this doctoral research, as well as suggestions for future work.

### 1.4 Original Contributions to New Knowledge

The thesis addresses sorption of PFAS, a major class of contaminants of emerging concern, to various natural and engineered carbonaceous sorbents. The specific contributions to new knowledge are highlighted below.

(1) **High carbon surface basicity is closely linked to high uptake of PFOS and PFOA for commercial carbonaceous sorbents.** In real-world treatment scenarios targeting PFASs, adsorption by GAC is employed as the major treatment process <sup>8, 17, 47, 48.</sup> Due to the lack of adsorbent selection criteria, weak interactions between PFAAs and GAC have been observed <sup>8</sup>. The research demonstrates that high carbon surface basicity, measured by total HCl uptake capacity, is closely linked to high PFOS and PFOA affinity. Improved understanding of the property-performance relationship of carbonaceous adsorbents with respect to PFAAs as unique amphiphilic molecules provides key information for adsorbent selection and application.

(2) Activated carbons that are surface-modified through ammonia gas treatment can show enhanced uptake of PFOS and PFOA. Early studies have reported that carbon surface basicity can be enhanced through surface modification techniques including high-temperature and ammonia gas treatments. This study demonstrated that the ammonia gas treatment is more effective than the high-temperature treatment in enhancing surface basicity, as well as in improving adsorption affinity for PFOS and PFOA. The research further shows that different carbon raw materials respond to surface modification differently. Wood-based carbons and phenolic-polymer-based activated carbon fibers showed enhancement by one to three orders of magnitude, whereas carbons made of coal and coconut shells experienced a reduction in adsorption towards either PFOS or PFOA.

(3) A novel HPLC-based method was developed for the determination of SOM-water distribution coefficients ( $K_{oc}$ ) for a range of PFASs. Early studies have demonstrated that the dynamic flow-through HPLC-based method could be used to investigate the sorption of anionic and non-ionic organic contaminants to SOM packed in an HPLC column. Though the method has a number of advantages (e.g., short equilibration time, minimal sorbent aging and degradation), it is only applicable to the organic compounds that are detectable by conventional HPLC detectors

(e.g., UV), but not to PFASs. The research further developed the method by coupling a fraction collector with HPLC to allow the eluent to be fractionally collected and then separately analyzed by LC-MS/MS with proper quality control. We demonstrated that this modified HPLC-based method could be applied to both PFAAs and PrePFAAs to generate  $K_{oc}$  values, which are in good agreement with the results from conventional batch sorption experiments. This improved method has the potential to be used for other LC-MS/MS amendable organic compounds aside from PFASs.

(4) Sorption behaviour of new amphoteric and cationic PFASs to SOM have been quantitatively determined for the first time. Previous work has focused on the sorption and mobility of anionic PFAS such as PFCAs and PFSAs in soil and sediment, yet little information is available concerning the mobility of newly-identified PFASs, which are directly released into soil and groundwater, and from which PFCAs and PFSAs are generated as degradation products. For instance, amphoteric polyfluoroalkyl betaines and cationic fluorosurfactants (e.g., perfluorooctaneamido ammonium iodide, PFOAAmS) are the major PrePFAAs that have been identified in contaminated sites, but their environmental behaviors is poorly understood. In this study, sorption of three polyfluoroalkyl betaines and PFOAAmS to SOM was examined under varying pH and calcium ion conditions, and corresponding distribution coefficients were determined. The PrePFAAs exhibited stronger sorption than PFCAs with the same number of perfluoroalkyl chains, and the underlying causes were tentatively identified based on their chemical speciation and molecular charges. Increasing calcium ion concentration reduced sorption of the betaines to SOM, a trend opposite to the impact of calcium on PFCAs or PFSAs.

(5) **Sorption of anionic, cationic and amphoteric PFASs, including PFCA, PFSA, betaines and PFOAAmS, to PCMs has been quantitatively determined for the first time**. The role of PCMs in the sorption of PFASs has not been sufficiently addressed in the literature, despite the fact that PCM is black carbon and is known to play a critical role in the sorption of organic pollutants in the environment. The research evaluated sorption and desorption behaviour of both the legacy PFASs (e.g., PFCAs and PFSAs), as well as those of the newly identified PrePFAAs. Sorption of PFASs to PCMs has been found to surpass that to SOM by one to two orders of magnitude, suggesting that PCMs can be a major sink of PFAS in the AFFF-impacted soil where PCMs are present. Sorption isotherm nonlinearity also indicates that the role of PCMs is particularly profound at low PFAS aqueous concentrations.

(6) Sorption reversibility or hysteresis of major PFAS compounds was quantitatively determined for the first time. The phenomenon of sorption hysteresis is widely encountered with sorption to PCMs and SOM, and it has important implication for contaminant transport, natural attenuation, and bioavailability <sup>45</sup>. If contaminant transport and bioavailability models rest on the assumption of sorption reversibility, sorption coefficients applied in such models are normally derived from an adsorption isotherm, yet the prediction might not be accurate due to sorption hysteresis <sup>49</sup>. For the first time, the research has assessed sorption hysteresis of five PFASs: one cationic, two anionic, and two zwitterionic, in the presence of three types of PCMs and one model SOM. Apparent sorption-desorption hysteresis exhibited by biochar (a type of PCM) was sorbate-specific and the most significant among all the sorbents. The magnitude of hysteresis shows dependence on the stiffness of the sorbent matrix. *Log K<sub>d</sub>* values derived from the desorption process were reported for the first time.

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# CHAPTER 2

Literature Review

## 2.1 Introduction

### 2.1.1 Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) and Applications

PFASs contain multiple alkyl carbon atoms, on which all the hydrogen substituents that would normally be present in the non-fluorinated analogs are replaced by fluorine atoms <sup>1</sup>. Many of these substances are surfactants, generally consisting of a perfluoroalkyl tail ( $C_nF_{2n+1}-$ ) and a hydrophilic hydrocarbon-based head group. The perfluoroalkyl tail repels water as well as oil and fat, rendering the whole molecule both water and oil repellent. Depending on the type of functional group in the head group, fluorosurfactants can be anionic (e.g., carboxylate, sulfonate, sulfate, phosphonate), cationic (e.g., protonated amino, quaternary ammonium) or amphoteric (e.g., amine oxide, betaine). It is noted that PFASs in the thesis are characterized by their functional groups, and the terminology is consistent with Buck et al. (2011)<sup>1</sup>. The same acronyms apply to acids and their corresponding deprotonated forms for simplicity.

As surfactants, PFASs can act as wetting agents, foaming agents, dispersants, and detergents. PFASs possess higher thermal and chemical stability than non-fluorinated counterparts because of the highly fluorinated segments<sup>2</sup>. Unique structure and properties have resulted in popular use of PFSAs over the past six decades in many industries (e.g., metal plating, photolithography, semiconductor, and polymer industries) and products (e.g., hydraulic fluids, aqueous film forming foams, varnishes, specialty lubricants, and water repellents for leather, paper, and textiles)<sup>2</sup>. Aqueous film-forming form (AFFF) is one of the most important products containing PFASs. AFFFs were developed in the 1960s as key tools for extinguishing fires involving flammable liquid fuels (i.e., gasoline and kerosene)<sup>3</sup>. AFFF, which mainly contains organic solvents, perfluorinated or partially fluorinated and hydrocarbon surfactants<sup>4</sup>, can quickly form a film on the fuel surface to prevent re-ignition of fuels<sup>2,4</sup>. Mixtures of anionic, nonionic or cationic, amphoteric, and nonionic PFASs have been shown to enhance the performance of AFFF<sup>2</sup>. A percentage breakdown of United States consumers of AFFF products (1986) indicated that the military comprises 75% of the total market, whereas municipal entities and the hydrocarbon-processing industry represent 13% and 5%, respectively <sup>4</sup>. The U.S. market for AFFF products (i.e., 3% and 6% concentrates) was 6.8 million liters in the year 1985<sup>4</sup>.

Limited toxicological studies on AFFF formulations have shown that AFFF formulations have mild to high toxicity <sup>4</sup>. However, selected PFAS ingredients, in particular, perfluoroalkyl acids (PFAAs), have been widely investigated for a potential threat to human health and wildlife <sup>5, 6</sup>. Perfluorooctane sulfonic acid [PFOS, C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>H] and carboxylic acid [PFOA, C<sub>7</sub>F<sub>15</sub>COOH] are not readily eliminated from humans, and the half-life values in humans range from 2.3 to 5.4 years<sup>7</sup>. Epidemiology studies have shown that PFOS is strongly associated with high cholesterol, decreased female fecundity and fertility, developmental issues in infants, and implicated in bladder, colon and prostate cancer <sup>7</sup>. Exposure to PFOA is probably linked to high incidence of six diseases (high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension) <sup>7</sup>. It is noteworthy that PFAAs come from other sources as well, but AFFFs generally cause the most severe pollution because of the repeated applications over a long period time in dedicated firefighting training sites. Increasing environmental and human health concerns have shifted the types of PFASs incorporated in AFFF formulations in recent years and curbed the use of PFASs in firefighting training activities <sup>2</sup>.

Regulatory efforts have been largely focused on long-chained PFAA homologues and their chemical precursors. For perfluoroalkyl carboxylic acids [PFCAs,  $C_nF_{2n+1}COOH$ ],  $n \ge 7$  is considered long chain while  $n \ge 6$  is defined as long-chain for perfluoroalkyl sulfonic acids [PFSAs,  $C_nF_{2n+1}SO_3H$ ]. With PFOS and PFOA phaseout, shorter-chained PFASs are used instead because of lower bioaccumulation potential and toxicity <sup>8</sup>. As a result, rising environmental occurrence of shorter-chained PFAAs is expected. The U.S. Environmental Protection Agency (EPA) has proposed provisional health advisory of 0.07 µg L<sup>-1</sup> for PFOS, PFOA, or combined in drinking water in 2016 <sup>9</sup>. A stringent guideline of 0.04 µg L<sup>-1</sup> for PFOA has been put forward in New Jersey, USA in the year of 2007 <sup>10</sup>. New rules regarding a wider range of PFAAs and for protecting aquatic life are expected.

### 2.1.2 PFASs Contamination in AFFF-Impacted Sites

The past common practice of uncontrolled release of PFAS-based AFFF is associated with elevated PFAS concentrations in soil <sup>11-13</sup>, sediments <sup>12, 14</sup>, and groundwater <sup>11, 15, 16</sup>. Apart from intensively studied persistent PFAAs, more than 100 new types fluorosurfactants (so-called precursors to PFAAs, or PrePFAAs) have been identified in AFFF formulations and in AFFF-

impacted environments <sup>13, 15, 17</sup>. Following the train derailment accident in Lac-Mégantic (Quebec, Canada) in 2013, betaine-type PrePFAAs were found to dominate PFAS composition profiles (~94%) in sediments while PFAAs concentrations appeared to be relatively insignificant (~3%) <sup>18</sup>. Similarly, a new betaine-type PrePFAA (6:2 fluorotelomer sulfonamide betaine, 6:2 FTAB) was prominently detected in the soils near a Norwegian airport where AFFFs were used <sup>9</sup>. Moreover, large amounts of FTSAs were detected in AFFF-impacted sites, especially the 6:2 FTSA <sup>3, 15</sup>.

It is reported that only a small portion of the total organic fluorine is known PFASs, and the rest may be attributed to PrePFAAs, for which only a very small number of chemical standards are available <sup>19</sup>. These PrePFAAs have different chemical properties from their PFAA counterparts and may exhibit vastly different environmental behaviors <sup>3, 15, 17, 20</sup>. PrePFAAs may have a strong affinity for soil and aquifer solids due to their anionic, cationic, and zwitterionic moieties. They may also substantially partition to soil organic matter, especially for those with a perfluoroalkyl group containing more than seven carbon atoms <sup>21</sup>. Therefore, remediation of are AFFF-impacted site is challenging due to the abundance of PFASs and complexity of chemical properties and behaviors.

#### 2.1.3 Treatment of PFASs

PFAAs are highly persistent in the environment. Therefore they resist typical degradation processes in engineered treatment systems <sup>22, 23</sup>. Treatment technologies that can decompose PFASs have been reported <sup>24</sup>, but they are in early-stage development and infeasible for practical applications. Thus in real-world treatment scenarios targeting PFASs, adsorption by granular activated carbon (GAC) has been employed as the major treatment process for wastewater <sup>25, 26</sup> and drinking water treatment <sup>27</sup>, as well as for groundwater remediation <sup>28</sup>. However, varying performance has been observed in laboratory studies and treatment systems of various scales <sup>27</sup>. Early breakthrough of PFAAs, especially increasingly used shorter chained PFAS in GAC filter beds, and short service life of GAC in full-scale treatment systems have been documented <sup>27</sup>. The major causes are slow adsorption kinetics and weak interactions between PFAAs and sorbents <sup>27</sup>. <sup>29</sup>. As many water treatment and remediation facilities already have GAC filtration systems in place to remove trace organic compounds, adsorption has the greatest potential for practical applications if improvement could be made to enhance interactions between PFAAs and sorbents.

Adsorption can also be used in a treatment train to concentrate PFAAs before other chemical destruction technologies (e.g., advanced chemical oxidation) can be applied.

## 2.2 Physical and Chemical Properties of PFASs

The unique properties of PFAS are owing to the C-F bond that is resistant to acids, alkali, oxidation, and reduction, even at relatively high temperature <sup>2</sup>. The perfluoroalkyl tail is rigid and subject to little conformational changes and engages weak van der Waal interactions. Understanding the influence of the perfluoroalkyl chain is the key to appreciating properties and sorption or partitioning behavior of PFASs.

The solubility of PFAAs spans a wide range and decreases with increasing perfluoroalkyl chain length <sup>2</sup>, while PFOA and perfluorodecanoic acid (PFDA) have an aqueous solubility of 0.023 M and 0.01 M, respectively <sup>30</sup>. Similarly, C2 and C3 acids of PFSAs are miscible in water whereas C7 and C8 acids are only moderately soluble <sup>2</sup>. It is also important to consider the influence of counterion and ionic strength on the solubility of PFAAs <sup>2, 31</sup>. The solubility of the potassium salt of PFOS is reported to be 519 - 680 mg L<sup>-1</sup>, 20 mg L<sup>-1</sup>, and 12.4 mg L<sup>-1</sup> in pure water, 3.55 M NaCl solution, and natural sea water, respectively <sup>32</sup>.

PFAAs exhibit lower critical micelle concentration (CMC) values than those of their hydrocarbon counterparts of equal chain length <sup>2</sup>. Within the same chemical class, PFAAs or salts of PFAAs with shorter carbon chain length have higher CMC values. For instance, CMCs for sodium salts of perfluoroheptane sulfonic acid (PFHxS), PFOS, and perfluorododecane sulfonic acid (PFDoS) are 17.5, 8.5 and 8.1 mM, respectively <sup>2, 31</sup>. Similarly, CMC for perfluoroheptane carboxylic acid (PFHpA) was reportedly 25 - 32 mM, higher than 9 - 30 mM for PFOA <sup>33</sup>. Though most studies and treatment scenarios deal with concentrations much lower than CMCs, Lopez-Fontan et al. (2005) suggest that PFOA micelle formation is a gradual process: PFOA anions start forming dimers and trimers at  $4.6 \pm 1.4$  pM and pre-micelles at 0.01 M <sup>34</sup>.

There has been much debate about the accurate values of  $pK_a$  as detailed by Rayne et al. (2009), Goss (2008) and Burns et al. (2008), and a broad range of experimental and simulation data can be found in those studies <sup>35-37</sup>. Nevertheless, all studies have shown that because the  $pK_a$  values of PFAAs are lower than environmentally relevant pH values of 6 - 9, PFAAs are predominantly

present as anions in most experiments and treatment scenarios. For PFOA, concentration– dependent aggregation behavior has been suggested to lead to decreasing  $pK_a$  with increasing concentrations <sup>34, 38</sup>. The most widely cited  $pK_a$  value of 2.8 <sup>39</sup> is suggested for partially aggregated PFOA, while 1.01 is for completely aggregated PFOA <sup>34</sup>. Estimated  $pK_a$  values in the range of 0 to 3.8 have been used in various studies for PFOA <sup>40, 41</sup>. Similarly, a reliably measured  $pK_a$  value for PFSA is also lacking. For PFOS as a strong acid, a calculated value (through ACD Lab Service) of -3.27 has been widely cited <sup>42</sup>. In addition, a  $pK_a$  value of 0.14, which was estimated by SPARC, has been widely used for perfluorobutane sulfonic acid (PFBS) and PFDS <sup>43, 44</sup>.

## 2.3 PFAS Sorption Mechanisms

The sorption literature on PFASs is largely limited to PFAAs. Sorption of PFASs at the solidliquid interface depends on several factors:

- The molecular structure of PFASs. Interactions of sorbent-PFAS depend on the structure of the hydrophobic and hydrophilic groups of fluorosurfactants.
- The nature of the sorbents. Sorbent chemistry and physical properties such as surface polarity, chemical composition, surface functional groups, surface geometry (porosity) and probably anion exchange capacity should be considered for their effect on sorption.
- The composition of the liquid phase. Nature of the liquid phase, pH, and background electrolyte or other additives can impact sorption.
- The physical conditions, such as temperature, pressure, and agitation.

### 2.3.1 Major Sorption Mechanisms

It is often suggested that the "hydrophobic effect" plays a dominant role for PFAA sorption in many instances despite the ionizable functional groups. Schwarzenbach et al. (1993) point out that the hydrophobicity effect does not specifically refer to intermolecular interactions, rather it is the result of attractive interactions between water and molecules of interest being less than water–water interactions <sup>45</sup>. Due to the high free energy cost for cavity formation in the bulk water phase, partitioning of "hydrophobic" molecules into the water phase is unfavorable, because the energy

gain cannot compensate for the energy cost of the disturbed H-bonding structure between water molecules.

The hydrophobic effect has been suggested in multiple studies to play an important role for PFAA sorption. Sorption of PFAAs is found to increase with increasing carbon chain-length of the molecules when the carbon chain-length is more than six <sup>21, 46, 47</sup> or when hydrophobicity of a sorbent is enhanced <sup>48, 49</sup>. Deprotonated PFAAs are shown to sorb to a negatively charged surface despite the unfavorable electrostatic repulsion, owing to the dominating hydrophobic effect <sup>44,50-57</sup>.

Electrostatic interactions between PFAAs and the charged sorbent surface also play a critical role. Because of low  $pK_a$  values (< 1- 3.5), PFAAs are mostly present as anions at environmentally relevant pH (6-9) and pose negative charges on the head group. Electrostatic interactions seem to dominate for short-chain PFAAs (n < 6) <sup>58</sup>. Some have also suggested that the negative charge on a PFAA molecule is also from the perfluoroalkyl tail <sup>59, 60</sup>. A negative shell around a positively charged core of a PFAA molecule can originate from the high electronegativity of fluorine atoms <sup>59</sup>. Sorption of amphoteric PFAS molecules (e.g., polyfluoroalkyl betaines) presents a much more complex situation depending on how the molecule dissociates. Moreover, the cationic and anionic groups on an amphoteric compound may also interact with one another. Lomax (1996) suggested that the cationic group, under conditions where it dominates, can act to decrease repulsion between anionic negatively charged groups, promoting closer packing of the surfactant molecules along the interface <sup>61</sup>. As of today, little attention has been paid to the sorption of these compounds despite their high concentrations in AFFF formulations and detection in AFFF-impacted environments.

Other specific interactions such as hydrogen bonding and covalent bonding have been observed, but they seem to play a less important role, though each specific situation needs to be evaluated case by case. Organofluorine can behave as a hydrogen-bonding acceptor and can form a very weak H-bond, as in O-H…F-C and C-H…F-C systems <sup>62</sup>. The very low bond energy (< 4 kcal mol<sup>-1</sup>) suggests that such interaction would not play a significant role in PFAS sorption. In addition, the oxygen or sulfur atoms on PFAA's acid functional groups can also behave as a hydrogen-bonding acceptor. Covalent bond formation for PFOA has been suggested in one study for interactions with inorganic surfaces <sup>63</sup>.

A recent study has proposed that air bubbles on the surface of hydrophobic carbonaceous adsorbents can contribute to PFOS adsorption. Because of the amphiphilic nature, PFOS tends to accumulate at interfaces, including the additional interfaces created by the air bubbles building on adsorbent surface. The study supported the mechanisms by showing the decrease in PFOS sorption on carbon nanotubes and graphene by 79% and 74%, respectively, after vacuum degassing <sup>64</sup>.

PFAA sorption to porous sorbents is also controlled by physical interactions, in particular through size exclusion and microporosity effects. Size exclusion, which is primarily a function of accessible adsorbent surface area, controls the access of a particular adsorbate to the finer carbon pores that often account for a higher fraction of total internal surface area <sup>65</sup>. The steric effect, which is in nature a size exclusion phenomenon, was suggested in the adsorption of PFASs to activated carbon, as well as to whole soils, to explain the high sorption of shorter-chained PFAA <sup>58, 66</sup>. The microporosity effect refers to the observation that higher microporosity (micropores < 2 nm, IUPAC definition) corresponds to increased sorption of low-molecular-weight molecules, because of greater sorption energy in micropores with all other factors being equal <sup>65</sup>. ChemBio3D software predicts the molecular length and diameter of a single anionic PFOA molecule to be approximately 1.2 nm and 0.4 nm, respectively, and 1.3 nm and 0.4 nm for PFOS. To put it simplistically, the micropores with dimensions larger than PFOA as well as macropores (> 50 nm) and mesopores (2 - 50 nm) are theoretically all accessible to PFOA.

#### 2.3.2 Impact of Solution Chemistry

The impact of solution chemistry is partly the result of electrostatic interactions, which are most notably expressed during changes in pH or cation concentrations of the aqueous solution. Because of relatively low  $pK_a$  values for PFAAs, any pH effects observed are likely due to pH-dependent changes for most sorbents, rather than protonation/deprotonation of the sorbates. Sorption of PFAAs to most sorbents generally decreases with increasing solution pH <sup>21, 50-52, 66-70</sup>. Larger sorption capacities exhibited by activated carbon, as well as faster initial sorption rates, have also been observed at lower pH <sup>66</sup>. Though sorption of amphoteric PFASs is yet to be examined, solution pH impacts speciation of hydrocarbon-based amphoteric surfactants and consequently solubility and interactions with sorbent surfaces. A general solubility diagram shows a minimum solubility in the isoelectric point of a betaine-type molecule <sup>61</sup>, and the sorption could, therefore,

reach the maximum at this point. Nevertheless, it is found that the adsorption of betaine on the surface of quartz decreases with increasing pH. It was proposed that the hydrated OH<sup>-</sup> ion had a strong ability to bind with positive sites in the betaine molecule at high pH, which weakened the electrostatic interactions between betaine and the solid surface <sup>71</sup>.

The impact of divalent cations, in particular Ca<sup>2+</sup>, has been noted for PFAA sorption. Sorption in general increases with increasing Ca<sup>2+</sup> concentrations, as shown in a variety of sorbent materials, such as e.g. sediments <sup>21, 54, 68, 72, 73</sup>, mineral materials <sup>67, 74</sup>, multi-walled carbon nanotubes <sup>75</sup>, black carbon <sup>76</sup>, polyamide films <sup>77</sup>, and modified mesoporous SiO<sub>2</sub> hollow nanoparticles <sup>78</sup>. The possible interactions with calcium, which probably would be absent using monovalent cations (Na<sup>+</sup> or K<sup>+</sup>), are proposed as follows. (i) Ca<sup>2+</sup> could be adsorbed on a sorbent surface and neutralize negative charges of surface functional groups <sup>68, 79</sup>. (ii) Ca<sup>2+</sup> could bridge ion pair formation between anionic PFAAs, and thus could change the apparent solubility of PFAAs and may even cause precipitation <sup>68, 80</sup>, depending on the ratio of calcium to anion equivalents <sup>51</sup>. (iii) Divalent cations like Ca<sup>2+</sup> could bridge the negatively charged groups (e.g., carboxyl, phenolic or hydroxyl groups) on the sorbents and PFASs anions via cation-bridging. (iv) The addition of electrolytes, in general, is known to compress the electrical double layer of the sorbents and thus alter their affinity to PFAAs <sup>51, 52, 59, 63, 69, 77, 81</sup>.

## 2.4 Sorbent Literature

To facilitate discussion, sorbents are divided into two major categories: synthesized adsorbents and naturally occurring sorbents. Adsorption of PFOS and PFOA onto different adsorbents is summarized in Table 2.1 while the partitioning parameters/absorption of PFOS and PFOA by naturally occurring sorbents, such as soil and sediments are listed in Table 2.2.

### 2.4.1 Carbon-Based Sorbents

#### Activated Carbon

GAC has been used to treat PFAAs in a few full-scale installations <sup>27</sup>. Overall weak interactions between PFAA and activated carbon, limited sorption capacity, the early breakthrough of short-chained PFAAs (e.g., PFBA) and therefore frequent replacement of GAC filters have been identified to be the major issues <sup>82-84</sup>. A survey of five treatment plants in Japan showed that 69-

100% removal of trace-level PFOS or PFOA could be achieved when the GAC filter was newly installed or used within nine months <sup>84</sup>. In a separate study in the Netherlands, filtration by GAC, rather than by other preceding processes, was found to be the only process that achieved 100% removal of PFNA, PFOS and PFHxS and 50% removal of PFOA (~50%) in a treatment plant <sup>85</sup>. However, the GAC filter failed to remove other short-chained PFAAs including C3-C6 PFCAs and PFBS <sup>85</sup>. Partial removal of trace-level PFOA (~41%) and PFOS (~63%) by GAC adsorption was reported in a drinking water treatment plant in Spain <sup>86</sup>. It was also noticed that branched PFAAs were less sorbed than the linear isomers <sup>85</sup>.

Competitive adsorption by natural organic matter (NOM) also greatly reduces sorption capacity towards PFAAs <sup>85</sup>. Accelerated breakthrough in a GAC-packed column of C3-C5 and C7-C8 PFCAs and C4, C6 and C8 PFSAs was observed when NOM was added to feed water<sup>29</sup>. Furthermore, Yu et al. (2012) observed that the low molecular weight fraction of organic matter (<1 kDa) present in wastewater effluent had a greater impact than the high molecular weight fraction (> 30 kDa) in reducing adsorption capacity for the PFAAs, probably through competition for sorption sites in microspores <sup>87</sup>. In the study, adsorption of NOM also lowered the point of zero charge (PZC) of the carbon surface, resulting in stronger electrostatic repulsion and reduced adsorption of PFOS and PFOA <sup>87</sup>.

#### **Carbon** Nanotubes

Carbon nanotubes (CNTs) have a large specific surface area (as high as  $1300 \text{ m}^2 \text{ g}^{-1}$  for single-wall CNTs) as a result of nanoscale dimensions (e.g., 1-20 nm in diameter), therefore have been proposed for water treatment <sup>88</sup>. High electrical conductivity can also be employed to enhance electrostatic attraction or create electrochemical reactions <sup>89</sup>. In contrast to activated carbon, CNTs provide adsorption sites mainly on the external surface to allow fast adsorption kinetics and probably easier regeneration. For instance, an equilibrium time of 2 h was observed for PFOS sorption to non-functionalized CNTs as opposed to 4 h for sorption to powdered activated carbon (PAC) <sup>66, 90</sup> or 168 h for GAC <sup>66</sup>.

The dominant mechanisms for adsorption of PFAAs are van der Waals interactions (or the hydrophobic effect) for non-functionalized CNTs and, additionally, electrostatic interactions for functionalized CNTs. Deng et al. (2012) have shown a linear increase of the amount of sorbed

PFAAs onto pristine single-walled carbon nanotubes (SWCNTs) with increasing carbon chainlength for three C3, C5 and C7 PFCAs and three C4, C6 and C8 PFSAs <sup>50</sup>. Very low adsorption of PFOA onto hydroxyl- and carboxyl-functionalized multi-walled carbon nanotubes (MWCNTs) was a result of strong electrostatic repulsion, as well as competitive sorption from water molecules <sup>50</sup>.

The influence of morphology on the adsorption capacity of CNTs for PFAAs has been noted. Similar sorption capacities per sorbent mass (712, 656, and 514 mg g<sup>-1</sup>, respectively, Table 2.1) were noticed by sorption of PFOS to one SWCNT (outer diameter, OD = 2 nm; surface area = 547 m<sup>2</sup> g<sup>-1</sup>) and two MWCNTs (OD = 10 and 50 nm, respectively; surface area = 292.4 and 92 m<sup>2</sup> g<sup>-1</sup>, respectively) <sup>90</sup>. When the sorption capacity was normalized by surface area, the MWCNTs with the largest OD and smallest surface area showed the highest PFOS uptake. It is probably related to CNT surface curvature. A PFOS molecule with a rigid perfluoroalkyl tail that is subject to little conformation change probably can engage strong van der Waals interactions with relatively "flat" surfaces of CNTs of large diameters because of the large surface contact area.

#### 2.4.2 Resins and Polymers

#### Synthetic Polymeric Resins

Studies have shown that compared to GAC, commercial anion-exchange and non ion-exchange polymers generally have comparable or higher sorption capacity for PFOS and PFOA (Table 2.1) <sup>66, 91-93</sup>. For anion-exchange resins, polymer material appeared to be the critical factor, more than resin porosity or type of functional groups (e.g., amine or quaternary ammonium), in determining sorption capacity of anion-exchange resins <sup>91</sup>. Polyacrylic anion-exchange resins showed higher sorption capacity and faster kinetics than polystyrene with a more hydrophobic surface. Anion exchange was suggested to be the dominant adsorption mechanism; formation of PFOS hemimicelles in intraparticle pores was suspected to have caused larger than unity ion exchange stoichiometry <sup>91</sup>. Senevirathna et al. (2012) have also demonstrated that non-ion-exchange polymers made of polystyrene divinylbenzene and macroreticular crosslinked aromatic polymer are effective in removing PFOS, particularly at low concentrations <sup>92</sup>.

Compared to GAC, significant sorption of short-chained PFAAs was observed with a strong base anion resin <sup>27</sup>. Polystyrene anion-exchange resins had higher sorption capacity for PFBS than for PFOS <sup>91</sup> while anion-exchange resin AI400 (polystyrene divinylbenzene) had larger sorption capacity for PFOA than for PFOS <sup>66</sup>. In the real world treatment scenario, porous anion exchange resin (Purolite FerrIX A33<sup>®</sup>) impregnated with iron oxide achieved good removal efficiency for PFCAs (54% for C6 and 76% for C7), and PFSAs (83%, >97% and >90% for C4, C6 and C8, respectively) <sup>29</sup>. However, the resin failed to remove shorter chain PFCAs (chain length < 5). Magnetic ion exchange (MIEX<sup>®</sup>) which is predominantly used for natural organic matter removal was unable to remove PFAAs at a plant in Alabama <sup>29</sup>.

#### Natural Biopolymers

Chitosan is an alkaline deacetylated product of chitin, and it has been employed to remove organic contaminants and heavy metals from water <sup>94-98</sup>. Chitosan has a linear polysaccharide structure with a large number of hydroxyl and amino groups on the poly-(D) glucosamine. Chitosan and its derivatives are nontoxic, biocompatible, and biodegradable <sup>96</sup>.

Several studies have demonstrated the ability of chitosan biopolymers for removal of PFAAs in aqueous solution, particularly at high PFAA concentrations <sup>69, 99, 100</sup>. The amino groups in chitosan polymers, when pronated, can attract anionic PFAAs via electrostatic interaction while the hydrophobic  $\beta$ -D-pyranoid functional group allows PFAA sorption due to the hydrophobic effect <sup>69, 99, 100</sup>. Higher sorption capacity was observed at lower pH range (i.e, pH = 3) due to the strong electronic attraction between pronated amino groups on chitosan and anionic PFOS. Experimental data have also shown the significant hydrophobic effect: sorption capacity increases with increasing perfluoroalkyl tail size from C4, C6 to C8 PFSAs, and the sorption was little influenced by the competing metal anions (e.g., sulfate or chromium<sup>VI</sup>).

#### Novel Polymer-modified Adsorbents

A novel polymerization technology, atom transfer radical polymerization (ATRP), was applied for preparing functionalized adsorbents for PFAA removal <sup>101, 102</sup>. Polymer brushes of poly (2-dimethylamino) ethyl methacrylate and poly-glycidyl methacrylate were grafted onto the surface

of fibrous cotton and rice husk, respectively, by ATRP. Both adsorbents showed high sorption capacities for PFOS and PFOA. The quaternized cotton functionalized with poly (2-dimethylamino) ethyl methacrylate gave a stable sorption behavior over a wide pH range of 3-10. At low pH (< 6), PFAAs were sorbed via electrostatic interaction with protonated quaternary ammonium groups <sup>101</sup>. In contrast, the aminated rice husk removed PFOS from solution via electrostatic attraction and van der Waals interactions, and the sorption capacity was subject to change with solution pH.<sup>102</sup> Short equilibrium times (Table 2.1) were observed, attributed to the positioning of the grafted polymer brushes on the outer layer of adsorbents to allow a short diffusion path into intraparticle pores.

Adsorbent	Surface area (m <sup>2</sup> g <sup>-1</sup> )	PZC	Adsorbate	Sorption capacity (mg g <sup>-1</sup> )	Sorption capacity (mg m <sup>-2</sup> )	Ref.
Activated carbon						
GAC CALGON F400 (coal based)	900-1100	9.2	PFOS	236 ª	0.25	48, 92
GAC CALGON F400	900-1100	9.2	PFOA	112 a	0.12	48, 92
GAC CALGON F300	-	-	PFOS	196 <sup>a</sup>	0.21	48
GAC CALGON URV-MOD1	-	-	PFOS	212 a	0.22	48
PAC (coal based, $\leq 0.1$ mm)	812	7.5	PFOS	560 <sup>a</sup>	0.69	66
PAC (coal based, $\leq 0.1$ mm)	812	7.5	PFOA	292 <sup>a</sup>	0.36	66
GAC (coal based)	712	7.5	PFOS	199 <sup>a</sup>	0.28	66
GAC (coal based)	712	7.5	PFOA	170 a	0.24	66
PAC	-	-	PFOS	473		103
PAC	-	-	PFOA	449		103
GAC (bamboo-based)	2450	3.2	PFOS	1184	0.48	104
GAC (bamboo-based)	2450	3.2	PFOA	449	0.18	104
Pyrogenic carbonaceous materials						
Biochar (wood-based)	404	-	PFOS	0.04 <sup>b</sup>		105
Biochar (wood-based)	404	-	PFOA	0.01 <sup>b</sup>		105
Biochar (paper mill waste-based)	13.2	-	PFOS	0.03 <sup>b</sup>		105
Biochar (paper mill waste-based)	13.2	-	PFOA	0.01 <sup>b</sup>		105
Soot	-	-	PFOS	0.06 <sup>b</sup>		76
Carbon nanotubes						
SWCNT	547	3.9	PFOS	712 <sup>a</sup>	1.30	90
MWCNT10	325	3.2	PFOS	656 <sup>a</sup>	2.02	90

**Table 2.1** Comparison of adsorption capacities of PFOS and PFOA on different adsorbents

MWCNT50	07.2	2.5	DEOG	<b>51</b> 4 a	5 20	00
MWCN150	97.2	3.5	PFOS	514 "	5.29	90
MWCNT	149.3	4.0	PFOS	138 <sup>b</sup>	0.92	75
Oxidative-MWCNT	185.2	1.0	PFOS	84 <sup>b</sup>	0.45	75
Resins and polymers						
Ion-exchange polymers (DowMarathonA)			PFOS	0.054 <sup>b</sup>		92, 93
Ion-exchange polymers (AmbIRA400)			PFOS	0.108 <sup>b</sup>		92, 93
Non-ion-exchange polymers (Amb	>750		PFOS	0.08 <sup>b</sup>		92, 93
XAD4)						
Non-ion-exchange polymers	1025		PFOS	0.08 <sup>b</sup>		92, 93
(DowV493)						
Anion-exchange resin IRA67			PFOS	3013		91
Anion-exchange resin IRA958			PFOS	1990		91
Anion-exchange resin AI400			PFOS	225 a		66
Anion-exchange resin AI400			PFOA	1273 <sup>a</sup>		66
Chitosan-based molecularly imprinted polymer			PFOS	2745 <sup>a</sup>		99
Chitosan derivatives (chitosan-based mo polymer)	lecularly imp	orinted	PFOS	1452 <sup>a</sup>		69
Quaternized cotton functionalized with p ethyl methacrylate	oly (2-dimet	hylamino)	PFOS	1775		101
Quaternized cotton functionalized with p ethyl methacrylate	oly (2-dimet	hylamino)	PFOA	1351		101
Aminated rice husk			PFOS	1322 <sup>a</sup>		102
Aminated rice husk			PFOA	1028 <sup>a</sup>		102

<sup>a</sup> Maximum adsorbed or adsorption capacity predicted by Langmuir model.

<sup>b</sup> Adsorbed or adsorption capacity predicted at an aqueous equilibrium concentration of 1 µg L<sup>-1</sup>.

### 2.4.3 Soil, Sediment and Sludge

#### Soil and Sediment

Sorption of PFAAs to soil and sediment has been studied in order to elucidate the fate, transport and distribution of PFAAs in soil or sediment where PFAAs are detected, e.g., agricultural lands applied with biosolids, AFFF-impacted sites, landfills, etc. Solid-water partitioning coefficients ( $K_d$ ) and organic carbon normalized partition coefficients ( $K_{oc}$ ) for a range of PFCAs and PFSAs have been reported from batch, saturated soil columns, and field systems <sup>21, 58, 106-109</sup>. Most studies allude to the hydrophobic effect and organic carbon content strongly dictating the magnitude of sorption to soil and sediment. Changes of  $K_d$  with solution pH and concentrations of divalent inorganic ions suggest that electrostatic interactions play an important role, especially for shortchain PFAAs <sup>21, 51, 54, 58, 67, 68, 72, 73</sup>. Furthermore, it was found that the hydrophobic effect diminishes as the perfluoroalkyl chain-length decreases, and it has been suggested that anion exchange dominates the sorption of C3 and C4 PFCAs to soil <sup>58</sup>. The steric effect was also suggested for short-chain PFAAs <sup>58</sup>.

Previous studies have shown that interactions with soil or sediment organic matter are likely the primary process impacting PFAA transport in soils and aquifers <sup>21, 58</sup>. The historic paradigm for sorption to organic matter is the solid-phase dissolution or partitioning, and the process under the diluted condition is supposed to generate linear isotherms <sup>110</sup>. However, the nonlinearity of sorption isotherms exhibited in batch studies <sup>21, 58</sup>, might be due to the heterogeneity of soil organic matter (SOM), which is consistent with the new theory that SOM is a heterogeneous mixture of physical states that provides a hierarchy of sites with varying sorption capacity <sup>110</sup>.

Delineation of soil transport of PFAAs in AFFF-impacted sites has proven to be challenging due to the presence of various co-contaminants (e.g., TCE as nonaqueous phase liquids and non-fluorinated surfactants) <sup>58, 76, 111</sup>. The impact of co-contaminants on sorption or partitioning behaviors of PFAAs depends on a myriad of factors, such as solid phase characteristics, PFAA concentration, head group and size, as well as the co-contaminant concentration and types. Data generated in laboratory studies have shown that in general the presence of co-contaminants increased the sorption of PFAAs to soils, thus might prevent further spreading of PFAAs from source zones. However, some non-fluorinated surfactants were found to reduce sorption of PFAAs by increasing aqueous solubility of PFAAs <sup>58, 111</sup>

#### Sewage or Activated Sludge

PFAAs are ubiquitously detected wastewater influents, mixed liquors and effluents in the range of ng L<sup>-1</sup> to µg L<sup>-1</sup> <sup>112, 113</sup>. As PFAAs are resistant to biodegradation, partitioning into the solid phase is an important route for PFAA elimination from liquid waste streams. The hydrophobic effect appears to play a major role for adsorption of PFOS and PFOA to activated sludge of different origins, as solid-liquid partitioning coefficients positively correlated with the perfluoroalkyl chain length <sup>44</sup>. Because the activated sludge surface is negatively charged at environmentally relevant pH values, reduced sorption of anionic PFAAs occurred at higher pH due to electrostatic repulsion

<sup>55</sup>. It was also suggested that proteins of extracellular polymeric substances in activated sludge was the key factor affecting adsorption, as demonstrated by the positive correlation of the values of  $logK_F$  with protein contents of sludge <sup>55</sup>.

#### **Pyrogenic Materials**

Ashes and chars generated from burning crop residues, a common agricultural practice in many parts of the world, are potential low-cost adsorbents for removal of PFAAs. Burning produces a significant amount of ashes and black carbon via the combustive carbonization process <sup>114, 115</sup>. Multiple studies have suggested that black carbon content is crucial in evaluating adsorption behavior of organic contaminants in ashes, soils and sediments <sup>116, 117</sup>. In addition, dedicated firefighting training areas often have elevated levels of pyrogenic materials compared to background soil or sediment <sup>118</sup>, so understanding sorption of PFASs to such materials is important for site characterization.

Maize straw-origin ashes (surface area =  $38.3 \text{ m}^2 \text{ g}^{-1}$ , PZC = 10.5) exhibited very high adsorption capacity for PFOS ( $811 \text{ mg g}^{-1}$ ), even higher than that of CNTs or activated carbon of larger surface areas  $^{90}$  (Table 2.2). In comparison, the PFOS sorption capacity by maize straw- and willow-derived chars (surface area =  $11.6 \text{ and } 7.21 \text{ m}^2 \text{ g}^{-1}$ ; PZC = 2.2 and 2.0) was much lower ( $164 \text{ and } 91.6 \text{ mg g}^{-1}$ , respectively). In addition to the strong hydrophobic effect and electrostatic attraction between anionic PFOS and positively charged maize straw-origin ashes, strong adsorption to black carbon was proposed to contribute to the high sorption capacity of the ashes. However, a separate study, Chen et al. (2009) did not find a model black carbon derived from diesel oil (SRM 2975, PZC = 2.04) to exhibit higher affinity for PFOS than average organic matter found in sediments  $^{76}$ . Kupryianchyk et al. (2016) recently studied the sorption of PFOS, PFOA, and C6 PFSA to two biochars derived from mixed wood and paper mill waste  $^{105}$ . The sorption capacity of the materials was relatively lower than GAC  $^{105}$ . In a separate study, sorption of PFOS by oil-derived soot was found to be weaker than activated carbon  $^{76}$ .

Sorbent	Sorbate	log Kd	$f_{\rm oc}$ of sorbents (%)	log Koc	Ref.
		(L kg <sup>-1</sup> )		(L kg <sub>oc</sub> <sup>-1</sup> )	
Activated sludge					
Activated sludge	PFOS				55
Activated sludge	PFOA				55
Aerobic activated sludge	PFOS	2.30-3.61			44
Aerobic activated sludge	PFOA	2.18-2.54			44
Anaerobic granular sludge	PFOS	2.16-2.32			48
Anaerobically digested sewage sludge	PFOS	1.89-2.44			48
Primary sludge	PFOS	2.95-3.35			119
Primary sludge	PFOA	2.27-2.78			119
Activated sludge	PFOS	2.86-3.37		2.98-3.49	119
Activated sludge	PFOA	2.30-2.71		2.43-2.83	119
Sodiments and soil					
Freshwater acdimenta	DEOS	2 04 4 26	0.75	2 04 2 25	111
Freshwater sediments	PEOS	3.94-4.20	0.75	2.94-3.23	21
Freshwater addiments	PFOS	1.11	0.56 0.66	2.08	21
Freshwater sediments	PFUA	0.07.1.07	0.56-9.66	2.11	21
Freshwater sediments	PFOS	0.27-1.37	0.16-1.49	2.97-3.20	68
Freshwater sediments	PFOS	2.40	4.80	3.70	120
Loam	PFOS	2.62-15.61	0.80-1.70	2.80	58
Loam	PFOA	0.63-3.50	0.80-1.70	1.89	58

Table 2.2 Comparison of adsorption capacities of PFOS and PFOA on soil, sediment and sludge

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## **CHAPTER 3**

## Adsorption of Perfluoroalkyl Acids by Carbonaceous Adsorbents: Effect of Carbon Surface Chemistry

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## Abstract

Adsorption by carbonaceous sorbents is among the most feasible processes to remove perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) from drinking and ground waters. However, carbon surface chemistry, which has long been recognized essential for dictating the performance of such sorbents, has never been considered for PFOS and PFOA adsorption. Thus, the role of surface chemistry was systematically investigated using sorbents with a wide range of precursor material, pore structure, and surface chemistry. Sorbent surface chemistry overwhelmed physical properties in controlling the extent of uptake. The adsorption affinity was positively correlated carbon surface basicity, suggesting that high acid-neutralizing or anion exchange capacity was critical for substantial uptake of PFOS and PFOA. Carbon polarity or hydrophobicity had an insignificant impact on the extent of adsorption. Synthetic polymer-based Ambersorb and activated carbon fibers were more effective than activated carbon made of natural materials in removing PFOS and PFOA from aqueous solutions.

**Keywords:** PFOS; PFOA; Activated carbon fibers; Carbonaceous sorbents; Surface chemistry; Basicity

# Graphical Abstract



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### 3.1 Introduction

Perfluoroalkyl acids (PFAAs) and their derivatives have been used over half a century as highperformance surface-active agents in a variety of products <sup>1</sup>. However, their use and release have given rise to a global distribution of PFAAs in various environmental compartments <sup>2</sup>. Their presence in humans and wildlife poses great health and ecological risks <sup>3 4</sup>. PFAAs in surface water are generally around low ng L<sup>-1</sup> levels, but levels as high as mg L<sup>-1</sup> close to point sources have been reported <sup>5, 6</sup>. U.S. Environmental Protection Agency (EPA) has proposed provisional health advisory for two most prominent PFAA species: 0.2  $\mu$ g L<sup>-1</sup> for perfluorooctane sulfonic acid (PFOS) and 0.4  $\mu$ g L<sup>-1</sup> for perfluorooctanoic acid (PFOA) in drinking water <sup>7</sup>. For the protection of groundwater in the areas impacted by aqueous film-forming foams, which may contain PFAAs and other fluorinated surfactants, Environment Canada (2013) has proposed 50  $\mu$ g L<sup>-1</sup> for PFOS in its Federal Environmental Quality Guidelines <sup>8</sup>. Current and upcoming regulations are among the major driving forces to investigate treatment technologies and options for PFAAs.

PFAAs are chemically and biologically stable and extremely persistent. They resist typical degradation processes in natural and engineered treatment systems <sup>9, 10</sup>. Treatment technologies that can decompose PFAAs have been reported <sup>11</sup>, but they are in early-stage development and infeasible for practical applications. Another primary concern is a potential generation of degradation by-products of unknown toxicity due to incomplete reactions. In real-world treatment scenarios targeting PFAAs, adsorption by granular activated carbon (GAC) has been employed as the major process for wastewater <sup>12, 13</sup> and drinking water treatment <sup>14</sup>, as well as groundwater remediation <sup>15</sup>. Uptake of PFAAs by activated carbon from aqueous solutions has also been investigated in laboratory-scale studies <sup>16-20</sup>. However, varying performance observed in those studies and sorbent-specific parameters influencing PFAA adsorption by carbonaceous sorbents have not been explored.

PFOS and PFOA are amphiphilic molecules containing a perfluoroalkyl carbon chain and a hydrophilic head group. Because of low *pKa* values, PFOS and PFOA predominantly exist as anions in environmentally relevant scenarios (pH of 5–8)  $^{21, 22}$ . Past studies on sorption by natural sorbents (e.g., sediment, soil, iron oxide, clay and sand) have interpreted sorption of PFOS and PFOA mainly through hydrophobic effect and Coulombic effect (or electrostatic interactions)  $^{23,24}$ .

The hydrophobic effect appears to be the driving force for sorption by sediment and soil as shown by the strong influence of sorbent organic carbon content. Electrostatic interactions are influenced by sorbent surface charge at a given pH, but none of the sorbent-specific parameters (e.g., anion exchange capacity or iron oxide content) has been found to correlate with the extent of PFAA sorption<sup>23</sup>. Instead, the role of electrostatic interactions is exhibited through varying solution chemistry (e.g., solution pH, [Ca<sup>2+</sup>] and ionic strength) <sup>23, 25</sup>. Other mechanisms such as repulsive forces between PFOS–PFOS molecules and hemimicelle formation at sorbent–solution interface have been proposed <sup>19, 25</sup>.

Adsorption of organic contaminants by carbonaceous sorbents are influenced by many factors, and sorbent-specific factors including sorbent surface chemistry (e.g., elemental compositions, surface acidity and basicity, and point of zero charge) and physical properties (e.g., pore size distribution, pore volume, and shape) are often examined and used for selecting proper sorbents for a specific application. Among the chemical factors, heteroatoms (e.g., O, H and N) that are interspersed within fullerene-like carbon network or carbon basal plane and in the form of various functional groups strongly influence surface chemistry. Speciation of these surface functionalities in particular oxygen-containing groups often controls the extent of uptake of organic contamination from aqueous solutions <sup>26</sup>. For instance, less hydrophobic activated carbon with higher oxygen and nitrogen contents <sup>27</sup>, or activated carbon with higher surface acidity imparted by surface oxygen groups have been reported less effectively in taking up organic contaminants such as trichloroethylene<sup>28</sup>. For adsorption of non-fluorinated anionic surfactants, Pendleton et al. (2002) reported higher oxygen content of GAC lowered the adsorbed amount, though only three GAC was examined <sup>29</sup>. Past studies also suggest the important role of physical interactions between sorbate molecules and activated carbon, in particular, microporosity effect and size exclusion <sup>28</sup>. Microporosity effect refers to the presence of high sorption energy sites within micropores (< 20Å, IUPAC definition) and these sites have pore sizes only slightly larger than sorbate molecules<sup>28</sup>. Size exclusion refers to the phenomenon that the accessible adsorbent surface area (or pore volume) controls the access of a particular adsorbate to finer carbon pores. The importance of size exclusion is apparent when sorbates of different sizes co-exist. Previously, Yu et al. (2009) suggested the adsorption of PFOS and PFOA by activated carbon is also mainly due to hydrophobic effect and electrostatic interactions <sup>19</sup>. However, no study has explored what sorbentspecific factors play a dominant role in determining the extent of PFAA adsorption by activated
carbon or other types of carbonaceous sorbents, and how those factors affect the relative significance of mechanisms of interactions. Understanding property–performance relationship is critical for selecting proper sorbents for removing target compounds <sup>27</sup>, and such knowledge can contribute to devising approaches to improve process efficiency or reduce competitive sorption <sup>28</sup>; competitive sorption by dissolved organic matter is known to adversely affect PFAA uptake <sup>14</sup>.

Thus this study aimed to identify the most significant sorbent-specific factors for carbonaceous sorbents that control the uptake of PFOS and PFOA. Ten sorbents with a wide range in raw materials and properties were evaluated in single-solute batch adsorption experiments. Main carbon characters controlling the uptake of PFOS and PFOA were discussed on the basis of experimental observations and statistical analysis. Particularly, sorption of PFOS and PFOA by polymer-based carbonaceous sorbents has been reported for the first time.

## 3.2 Materials and Methods

### 3.2.1 Chemicals

Perfluorooctanoic acid (PFOA, 96%) and sodium perfluorooctane sulfonate (Na–PFOS,  $\geq$ 98.0%) were purchased from Sigma–Aldrich (Oakville, ON, Canada). Isotope-labeled sodium perfluoron-[1,2,3,4–<sup>13</sup>C<sub>4</sub>]-octanesulfonate (MPFOS) and perfluoro-n-[1,2–<sup>13</sup>C<sub>2</sub>] octanoic acid (MPFOA) were obtained from Wellington Laboratories (Guelph, ON, Canada) and DuPont USA (Wilmington, DE, USA), respectively. They were used as internal standards for chemical analysis of PFOS and PFOA. The information on other chemicals and reagents is included in Appendix A.

### 3.2.2 Sorbents and Adsorbent Characterization

Ten carbonaceous sorbents (Table 3.1) were examined: bituminous coal-based GAC Filtrasorb 400 (F400) and powered activated carbon (PAC) BPL from Calgon Inc. (USA), wood-based GAC WVB 14×35 (WVB) and BioNuchar (BioNC) from MeadWestvaco Co. (USA), wood-based PAC AquaNuchar (AquaNC) from MeadWestvaco, coconut shell-based GAC AquaCarb 1240C (1240C) from Siemens Inc. (USA), and three activated carbon fibers (ACF15, ACF20 and ACF25) from Kynol Inc. (Japan). The ACFs are carbonaceous fibers made via pyrolysis of phenolic formaldehyde fibrous resin. The study also included Ambersorb 563 (Ambersorb, Supelco Inc.

USA), which is a carbonaceous resin produced via controlled pyrolysis of a highly sulfonated styrene/divinylbenzene ion-exchange resin. Ionic functional groups on the resin are lost during carbonization process. The sorbents (except for Ambersorb) were first washed in deionized water under sonication for 3 h, and then dried at 103 °C for 24 h. Subsequently, all the granular sorbents (except for Ambersorb) were sieved and particles retained between sieves 0.85 and 1.00 mm were used for the study.

Nitrogen adsorption isotherms measured at 77 K with an Autosorb-1 analyzer (Quantachrome Co., USA) were used to determine physical characteristics. Specific surface area was computed by using a Multi-BET equation. Pore volume and distribution were generated by applying density-functional theory and Monte Carlo simulation <sup>30, 31</sup>. The point of zero charge (PZC), the pH at which the total net surface charge is zero, was measured by mass titration/pH equilibration method <sup>32</sup>. Total surface acidity (NaOH uptake) and basicity (HCl uptake) were measured by titration using CO<sub>2</sub>-free water and under nitrogen atmosphere <sup>33</sup>. Elemental compositions of the sorbents were analyzed using a PerkinElmer 2400 series elemental analyzer by a certified commercial laboratory.

### 3.2.3 Adsorption Experiments

Uptake kinetics and equilibrium adsorption isotherms were determined using single-solute batch adsorption experiments. Prior to the experiments, plastic vessels made of different materials were tested for PFOS recovery and polypropylene (PP) bottles showing negligible adsorption of PFOS at current experimental conditions were chosen as test vessels. Aqueous PFOS and PFOA concentrations ( $C_e$ ) were measured using liquid chromatography tandem mass spectrometry (LC-MS/MS), and the corresponding adsorbent concentrations ( $C_s$ ) were calculated via an aqueous mass loss method. The experiments were conducted such that the equilibrium aqueous concentrations spanned from below the US EPA health advisory levels for drinking water <sup>7</sup> to at least three orders of magnitude higher. Further details regarding batch sorption experiments, chemical recovery from test vessels, LC-MS/MS condition, detection limits, and quantitation methods can be found in Appendix A.

Filtration was initially evaluated as a possible method for solid–liquid separation during sample preparation. However, significant PFOS mass loss occurred to all filters, which would lead to potential underestimation of aqueous concentrations. Similar findings on substantial sorption of

aqueous-phase PFAAs to filtration media have been recently reported by Chandramouli et al. (2015)<sup>34</sup>. Therefore, centrifugation was used for solid–liquid separation during sample preparation and more details describing the above testing and sample preparation are provided in Appendix A.

#### 3.2.4 Data analysis

Adsorption uptake rate data were modeled with a pseudo-second-order kinetic model. Equilibrium adsorption data were found to be best modeled with the Freundlich isotherm equation (listed in Appendix A) <sup>35</sup>. Possible correlations between the adsorption affinity, which was described by adsorption distribution coefficient ( $K_d = C_s/C_e$ ) calculated at a low aqueous concentration, and sorbent properties were examined based on Spearman rank correlation method using SPSS (Version 19.0, IBM). The method results in a Spearman rank coefficient ( $r_s$ ), which is a statistical measure of the strength of a monotonic relationship between paired data. The closer  $r_s$  is to ±1, the stronger the monotonic relationship. The absolute value of  $r_s$  0.60–0.79 means "strong correlation" and 0.80–1.0 "very strong correlation". A significance value (sig.) less than 0.05 is considered statistically significant (95% confidence level).

Table 3.1	Adsorbent	Characteristics
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Adsorbent	Physical state/raw material	sical state/raw Surface erial area,			Pore	e volume distri	bution, ml g <sup>-1</sup>		PZC	Total acidity,	Total basicity,	Elemental compositions, wt%			
		m <sup>2</sup> g <sup>-1</sup>	ml g-1	<8 Å	8-20 Å	20-100 Å	100-200 Å	>200 Å		µeq m <sup>-2</sup>	µeq m²	0	Ν	С	Н
F400	GAC/Bituminous coal	947.8	0.58	0.15	0.14	0.29	0	0	8.29	0.401	0.443	1.00	0.11	86.75	<0.1
BPL	PAC/Bituminous coal	1387	0.72	0.23	0.23	0.19	0.02	0.05	8.35	0.230	0.238	0.43	< 0.05	87.16	<0.1
1240C	GAC/Coconuet shell	1428	0.64	0.30	0.24	0.1	0	0	9.27	0.085	0.407	1.25	< 0.05	93.45	0.13
WVB	GAC/Wood	1558	1.53	0.09	0.29	0.74	0.25	0.16	4.50	0.077	0.163	3.40	< 0.05	66.30	3.04
BioNC	GAC/Wood	2341	3.79	0	0.14	3.14	0.39	0.11	4.07	0.383	0.103	3.18	< 0.05	85.18	1.06
AquaNC	PAC/Wood	1860	1.29	0.09	0.38	0.65	0.09	0.08	4.75	0.244	0.152	3.47	1.06	76.70	< 0.1
Ambersorb	Carbonaceous resin/Poymer	902.6	0.82	0.26	0.07	0.07	0.05	0.37	8.78	0.143	0.540	<0.3	< 0.05	91.17	<0.1
ACF15	ACF/Polymer	1248	0.84	0.25	0.18	0.4	0	0	7.58	0.306	0.433	1.15	< 0.05	92.91	< 0.1
ACF20	ACF/Polymer	2055	1.15	0.39	0.37	0.32	0.09	0.04	7.28	0.170	0.209	3.50	< 0.05	93.20	<0.1
ACF25	ACF/Polymer	1797	0.83	0.23	0.37	0.21	0.01	0	7.70	0.307	0.298	1.33	< 0.05	93.47	< 0.1



**Figure 3.1** Uptake kinetics of (a) PFOS and (b) PFOA by carbonaceous adsorbents. Error bars indicate standard deviations for each time point (N = 3). Lines are the pseudo-second-order rate model fits

## 3.3 Results and discussion

### 3.3.1 Adsorption kinetics

As demonstrated in Figure 3.1, all sorbent concentrations experienced dramatic increase at the beginning and then slow increase and the kinetics was well described by a pseudo-second-order kinetic model ( $r^2 \ge 0.990$ , Table 3.2). While previous studies reported higher rate constants (values of  $v_0$  or k, Table 3.2) for PFOS than PFOA without an explanation being provided <sup>17 36</sup>, PFOS did not always show higher rates than PFOA in the study. Throughout the discussion, anions of PFOS

and PFOA were still referred as PFOS or PFOA, although recognizing that the deprotonated forms were dominant under the experimental conditions. As illustrated in Figure 3.1, the relative order of the adsorption rates for either PFOS or PFOA was: ACF20 > AquaNC > BPL > Ambersorb > F400 or 1240C > WVB or BioNC. The observation confirmed that macroscopic particle size is one of the major factors controlling adsorption uptake rate of the PFAAs. Uptake rates are directly related to a diffusion time constant,  $D/R^2$ , where D is diffusivity of an adsorbate and R radius of a spherical particle <sup>37</sup>. Thus, the uptake rates of PFOS and PFOA were expected to increase rapidly with decreasing particle radius. Two PAC with fine particles (~44 µm in diameter for BPL and 45–150 µm in diameter for AquaNC) and ACF20 (~9 µm in diameter) reached equilibrium within 2 h. ACF20 had high microporosity (<20 Å) and its spores were slit-shaped, uniform, and oriented along the fiber axis and open to the outside of the fibers. Such pore structure with diffusion length less than a few microns is conducive to fast uptake of sorbates from aqueous solutions <sup>37</sup>. The granular Ambersorb with sizes of 0.30–0.84 mm reached equilibrium about 17 h (95% of maximum possible uptake) for both PFOS and PFOA. For the rest of four GAC (F400, 1240C, WVB, and BioNC) with larger particle sizes (0.85–1.0 mm), equilibration time ranged from 48 h to 240 h for 95% of uptake (Figure 3.1). As their particle sizes were identical, the wide variation in uptake rates was partly due to their differences in pore size distribution and carbon surface chemistry.

		PFO	S		PFOA					
Adsorbent	$C_s$	$C_s$ k $v_0$		$r^2$	$C_s$	k	$\mathcal{V}_{0}$	$r^2$		
	$\mu g m g^{-1}$	mg $\mu$ g <sup>-1</sup> h <sup>-1</sup>	$\mu g m g^{-1} h^{-1}$		$\mu g m g^{-1}$	mg $\mu g^{-1}$ h <sup>-1</sup>	$\mu g m g^{-1} h^{-1}$			
F400	2.59	0.064	0.43	0.999	2.52	0.36	2.31	0.999		
BPL	2.48	12.9	79.4	0.999	2.49	3.63	22.4	0.999		
1240C	2.53	0.18	1.13	0.999	2.58	0.080	0.60	0.999		
WVB	2.44	0.041	0.24	0.999	2.34	0.080	0.60	0.999		
BioNC	2.57	0.041	0.28	0.999	2.21	0.040	0.10	0.999		
AquaNC	2.48	101	625	0.999	2.46	16.2	98.0	0.999		
Ambersorb	2.50	0.45	2.84	0.999	2.50	0.45	2.89	0.990		
ACF 20	2.50	123	769	0.999	2.50	54.3	339	0.999		

**Table 3.2** Kinetic parameters of the pseudo-second-order model for adsorption of PFOS and PFOA

The two wood-based GAC (BioNC and WVB) with the lowest adsorption uptake rates had the lowest microporosity (<20 Å), 3.7% (percentage of micropore volume) for BioNC and 25% for WVB, while the other three granular sorbents (F400, 1240C and Ambersorb) had microporosity in the range of 40–84%. As pore diffusion is among rate limiting steps for uptake, larger pores pose larger diffusion distance, thus contributing to slower uptake by BioNC and WVB. Furthermore, as illustrated in Figure A.2 in Appendix A, carbon surface chemistry in particular PZC and total basicity appeared to affect the initial adsorption rate  $(v_0)$ , while total acidity and oxygen content did not. Figure A.2 suggested that electrostatic repulsion between negatively charged sorbent surface (PZC < pHsolution  $\approx$  7) and PFOS and PFOA always resulted in low adsorption rates, but other factors could contribute to low rates for positively charged surface (PZC > pHsolution  $\approx$  7). Yu et al. (2009) observed that adsorption uptake rates decreased with increasing solution pH (more negatively charged sorbent surface) for adsorption of PFOS and PFOA by activated carbon, which agreed with our finding that electrostatic repulsion could reduce adsorption rates <sup>19</sup>. The fact that both PZC and total basicity affected kinetics in a similar way (Figure A.2) might be due to the correlation between the two parameters. The ratio of basicity and acidity determined PZC to some extent as illustrated in Figure A.3, which has been previously reported by Faria et al. (2004)<sup>38</sup>. However, one must be careful in drawing a definitive conclusion from these observations, as relationships between adsorption kinetics and sorbent surface chemistry are not very straightforward. High sorbent surface affinity for target sorbates does not necessarily result in faster kinetics. The literature is sparse on the topic, especially involving adsorption from aqueous phase across a diverse range of sorbents. Further study on how carbon surface chemistry influences adsorption kinetics is needed.

### 3.3.2 Adsorption isotherms

Freundlich isotherm provided good fits to the experimental data as demonstrated by the high correlation coefficients ( $r^2$ ) in Table 3.3, while Langmuir isotherm equation did not fit the experimental data as well for most of the sorbents. The exponential term in Freundlich isotherms, n, was no more than 1 for PFOS, but spanned from 0.66 to 3.86 for PFOA (Table 3.3), suggesting the wider distribution of sorbent-sorbate bonding energy for PFOA. Isotherms of PFOS (Figure 3.2) and PFOA (Figure A.4) showed noticeable curvature on log–log coordinates for some adsorbents with high  $K_F$  (e.g., Ambersorb and ACFs), which was partly due to the wide

concentration range examined in the study. The data scattering occurring to ACFs might be linked to the difficulty of handling the fibrous materials and their high adsorption, yet no improvement was found when adsorption experiments were repeated. Adsorption isotherms of ACF20 deviated significantly from ACF15 and ACF25 (Figure 3.2 and Figure A.4). The major differences between ACF20 and the other ACFs were oxygen content and total basicity (Table 3.1), which however could not fully explain such deviation as discussed in later sections. There is a lack of data in the literature regarding adsorption of PFAAs by ACFs to allow further comparison.

		PFOS			PFOA					
Adsorbents	<i>K<sub>F</sub></i> (μg /mg)( μg /L) <sup>-n</sup>	<i>K<sub>F</sub></i> (μg /m <sup>2</sup> )( μg /L) <sup>-n</sup>	n	$r^2$	<i>K<sub>F</sub></i> (μg /mg)( μg /L) <sup>-n</sup>	<i>K<sub>F</sub></i> (μg /m <sup>2</sup> )( μg /L) <sup>-n</sup>	n	$r^2$		
F400	1.72	1.82	0.61	0.93	3.26	3.44	1.96	0.94		
BPL	0.09	0.06	1.00	0.96	0.13	0.09	1.29	0.97		
1240C	1.11	0.78	0.68	0.88	1.92	1.34	1.13	0.88		
WVB	1.27	0.81	0.54	0.98	0.14	0.09	0.75	0.99		
BioNC	0.97	0.41	0.59	0.99	0.18	0.08	0.71	0.99		
AquaNC	2.53	1.36	0.60	0.98	0.72	0.39	0.66	0.97		
Ambersorb	6.18	6.85	0.51	0.90	4.31	4.77	1.14	0.80		
ACF15	4.25	3.40	0.63	0.78	5.13	4.11	0.70	0.78		
ACF20	3.54	1.72	0.70	0.86	0.51	0.25	3.86	0.88		
ACF25	4.51	2.51	0.68	0.89	4.98	2.77	0.68	0.87		

Table 3.3 Freundlich isotherm constants at 25 °C for PFOS and PFOA

Adsorption distribution coefficient ( $K_d = C_s/C_e$ ) was calculated for each sorbent at  $C_e = 0.3 \ \mu g \ L^{-1}$  (Table A.1) to indicate adsorption affinity and to allow identifying the influence of sorbent-specific factors, as discussed later. The concentration is the average EPA drinking water guideline value for PFOS (0.2  $\mu g \ L^{-1}$ ) and PFOA (0.4  $\mu g \ L^{-1}$ ). The PFOS adsorption affinity or the extent of adsorption based on  $K_d$  (Table A.1) followed the order: Ambersorb > ACF15 > ACF20 > ACF25 > F400 > AquaNC > WVB > 1240C > BioNC > BPL. The PFOA adsorption affinity followed: ACF15 > Ambersorb/ACF25 > 1240C > F400 > AquaNC > WVB > BioNC > BPL > ACF20. Polymer-based sorbents Ambersorb and ACFs generally showed higher uptake for PFOS and PFOA than other sorbents made of natural materials (e.g., F400 and 1240C).



Figure 3.2 Adsorption isotherms (at 25 °C) of PFOS onto the ten carbonaceous adsorbents

### 3.3.3. Effect of adsorbent surface chemistry

If the hydrophobic effect and electrostatic interactions were dominant, then the sorbent surface that favored high uptake of PFOS and PFOA should be hydrophobic (low oxygen content and low acidity) and positively charged (high PZC). Though carbon surface basicity has been less studied regarding its role in the uptake of organic contaminants from aqueous solutions, it was reasonable to assume that high basicity, an indicator of acid neutralizing ability or anion exchange capacity, also favored uptake of the organic anions. Figure 3.3 and Figure A.5 illustrated the influence (or the lack of influence) of sorbent chemical characteristics on sorption affinity ( $K_d$ ) for PFOS and PFOA, respectively. The general lack of clear trends in the figures showed sorbent-PFAA interactions were complicated. Ambersorb with the highest  $K_d$  values (Table A.1) possessed some of the key chemical characteristics that favored significant uptake of PFOS and PFOA. The sorbent was positively charged in circumneutral solutions with PZC of 8.78 and had the highest surface basicity and the lowest oxygen content. Its  $K_d$  values for PFOS and PFOA were about 4 times of those of F400; previously, Ambersorb was found to have 2–5 times of the capacity of F400 in taking up volatile organics in groundwater <sup>39</sup>. ACFs overall were the second best-performing

sorbents evaluated based on  $K_d$  values. ACFs with PZC close to 7 were only slightly positively charged under the current experimental conditions, thus electrostatic attraction of negatively charged PFOS and PFOA to ACF surface was not significant. Physical characteristics of ACFs probably played an important role in their high affinity for PFOS and PFOA. As a direct consequence of unique pore size distribution, ACFs generally can engage stronger interactions with sorbate molecules than activated carbon with similar surface areas, because their smaller pores give rise to the stronger overlap of sorption potentials from surrounding surfaces <sup>37</sup>. F400 and 1240C, which are among the most widely used GAC for water treatment, had high PZC, medium to high basicity, and low oxygen content among the ten sorbents, though F400 had higher acidity. F400 showed higher affinity for PFOS, while 1240C showed a slightly higher affinity for PFOA. Wood-based AquaNC, despite its overall seemingly unfavorable surface chemistry including low PZC (4.75), high oxygen content, and low basicity, showed higher affinity for PFOS than 1240C. Coal-based BPL and wood-based BioNC were overall least effective in PFOS and PFOA removal. The fact that BioNC had the largest surface area showed that surface area alone was not a useful predictor of adsorption, which was confirmed by a comparison of the high PFAA uptake by Ambersorb with the smallest BET surface area. The chemical characteristics of BioNC could explain to some extent its low PFAA uptake - high oxygen content and low basicity. BPL was expected to have a great affinity for the PFAAs due to its moderately basic surface and high PZC. Its  $K_d$  values, however, were more than one order of magnitude lower than those for F400 made of the same raw material of bituminous coal.

The complexity of the sorbent-sorbate interactions was also shown by the relative affinity for PFOS and PFOA by the sorbents. PFOS sometimes, but not always, showed higher  $K_d$  than PFOA in the study (Table A.1), while past studies have generally shown higher adsorption for PFOS than PFOA to natural sorbents, activated carbon, or carbon nanotubes <sup>23, 40</sup>. PFOS is a larger molecule with eight fluorinated carbons while PFOA has seven. The van der Waals interactions with sorbent surface induced by PFOS are expected to be stronger than those induced by PFOA because of the higher polarizability of PFOS molecules (19.12 Å<sup>3</sup>·molecule<sup>-1</sup> for PFOS and 16.26 Å<sup>3</sup>·molecule<sup>-1</sup> for PFOA, calculated using SPARC). In addition, the electrostatic forces with the charged surface functionalities induced by PFOS are also expected to be much stronger because of the higher charge on the PFOS molecule. Though F400 and Ambersorb of high PZC showed higher  $K_d$  for PFOS than for PFOA, the three carbons (WVB, BioNC and AquaNC) with low PZC and thus

likely high electrostatic repulsion to PFOS molecules had higher  $K_d$  for PFOS than PFOA, suggesting the likely dominance of the hydrophobic effect.



**Figure 3.3** Correlation between adsorption distribution coefficient  $K_d$  (L m<sup>-2</sup>) and carbon surface basicity, PZC, or oxygen content for the ten carbonaceous adsorbents

Considering such complexity, statistical analysis based on Spearman rank correlation method was conducted to identify dominant sorbent-specific factors influencing adsorption of PFOS and PFOA, and the results were shown in Table 3.4. Statistical analysis can provide insights into adsorption mechanisms, but must be interpreted with great caution. Chemical characteristics were correlated with  $K_d$  expressed on a surface area basis (L·m<sup>-2</sup>) to eliminate the effect of varying BET surface area. The closer the Spearman rank coefficient ( $r_s$ ) is to  $\pm 1$ , the stronger effect the sorbent

characteristics has on  $K_d$ . As shown in Table 3.4, the only statistically significant correlation ( $\geq$ 95% confidence level) was observed between  $K_d$  and total basicity for both PFOS ( $r_s = 0.66$ , sig. = 0.04) and PFOA ( $r_s = 0.65$ , sig. = 0.04), while other chemical characteristics showed much less influence on adsorption affinity. Total acidity with  $r_s$  values closest to zero showed the least influence.

T	Table 3.4	Results	of Spearman	rank corr	elation b	etween	the a	adsorption	distribution	coeffic	ient
()	$K_d$ ) of Pl	FOS or Pl	FOA and ads	orbent ch	aracteris	tics.					

	$K_d^{a}$ of I	PFOS	$K_d^{a}$ of	PFOA
	$r_s$	Sig.	$r_s$	Sig.
Total acidity	-0.14	0.70	-0.15	0.68
Total basicity	0.66*	0.04	0.65*	0.04
Oxygen %	-0.24	0.51	-0.43	0.21
PZC	0.20	0.58	0.38	0.28
Physical properties				
	$K_F$ <sup>b</sup> of I	PFOS	$K_F$ <sup>b</sup> of	PFOA
	$r_s$	Sig.	$\Gamma_{S}$	Sig.
Surface Area	-0.29	0.42	-0.41	0.24
<8 Å <sup>c</sup>	0.41	0.24	0.14	0.70
8-20 Å <sup>c</sup>	0.02	0.95	-0.17	0.64
<20 Å <sup>c</sup>	-0.23	0.52	-0.27	0.45
20-100 Å <sup>c</sup>	-0.21	0.56	-0.55	0.10
100-200 Å <sup>c</sup>	-0.063	0.86	-0.34	0.34
>200 Å <sup>c</sup>	0.41	0 24	0.14	0.70

<sup>a</sup> L/m<sup>2</sup>; <sup>b</sup> L/g; <sup>c</sup> Pore volumes in the corresponding range of pore width (mL g<sup>-1</sup>)

\* Sig.  $\leq 0.05$ , statistically significant with  $\geq 95\%$  confidence level

Though carbon surface basicity exhibited the strongest influence on adsorption affinity for PFOS and PFOA across all the sorbents, the origin of basicity in activated carbon is not yet well elucidated. For carbons with high oxygen content, basicity can be attributed to oxygen-containing groups of pyrone and chromene <sup>37, 41-43</sup>. These groups when protonated attract anions electrostatically <sup>38</sup>. Basicity also comes from the  $\pi$ -electron basicity of exposed graphene layers, which is likely significant for the carbonaceous sorbents with low oxygen content, such as Ambersorb <sup>42,43</sup> (Table 3.1). These oxygen-free basic sites may attract protons to become positively

charged and further attract anions <sup>43</sup>. In addition, Boehm (2008) has suggested that dispersive interactions can be large in the case of "soft"  $\pi$ -electrons (Lewis base, electron pair donor) from carbon graphene plane with "soft" organic carboxylic or sulfonic acids (Lewis acid, electron pair acceptor), to result in substantial sorption of such acids. The adsorption of organic acids, because of strong van der Waals interactions, could be more substantial than inorganic acid counterparts for the same adsorbent. The basic sites imparted by  $\pi$ -electrons were also suggested to behave as a  $\pi$ -bond donor to engage electron donor-acceptor types of interactions with adsorbates with free electrons or  $\pi$ -bond donor/acceptor (i.e., aromatic organics) <sup>44</sup>. Since PFOS and PFOA are not strong  $\pi$ -bond donor or acceptor, such types of interactions were not expected. In addition, nitrogen content was very low for most sorbents (<0.05%, except for AquaNC) and therefore was unlikely to contribute to surface basicity.

Though Spearman rank correlation showed a lack of statistically significant correlation between  $K_d$  and sorbent PZC or oxygen content, the possible role of the two chemical characters cannot be totally ignored. Figure 3.3 showed that negatively charged sorbent surface (PZC < pHsolution  $\approx$ 7) was associated with low uptake owing to electrostatic repulsion to the anionic sorbates, whereas other factors may also contribute to low uptake when the adsorbent surface was positively charged (PZC > pHsolution  $\approx$  7). Previously, Al-Degs et al. (2000) reported high adsorption capacity for anionic dyes by activated carbon with high PZC<sup>41</sup>. Similarly, Figure 3.3 showed that high oxygen content was associated with low uptake, but other factors may also contribute to low uptake when oxygen content was low. The high oxygen content of activated carbon imparts higher polarity and may lead to high affinity to water molecules, thereby reducing uptake of hydrophobic organics <sup>28</sup>, <sup>45</sup>. Overall, the present study showed that sorbent PZC and oxygen content had some effect on adsorption of PFOS and PFOA, but they were not strong predictors of sorbent affinity for the target sorbates. Carbon surface acidity, which originates from the oxygen-containing groups such as hydroxyl, lactone, lactol, and carboxyl groups <sup>37</sup>, had little impact as shown in Fig. A.5 and Table 3.4, though it has been considered a very important property for both adsorption and catalytic activity of activated carbon <sup>46</sup>.



Figure 3.4 Relationship between the micropore volume located in the pores less than 8 Å and adsorption distribution coefficient  $K_d$  (expressed on a mass basis) for all the ten adsorbents. The adsorbents that deviated most from the general trend were encircled.

### 3.3.4 Effect of carbon physical properties

Results of Spearman rank correlation (Table 3.4) showed that none of the physical properties was correlated with  $K_d$  expressed on a mass basis (L g<sup>-1</sup>) with statistical significance. No correlation was found for any pore size range listed in Table 3.4, as well as even narrower pore size ranges (data not shown). The findings showed that surface chemistry overall overwhelmed physical properties in influencing adsorption PFOS and PFOA by the ten sorbents. Similar conclusion was reached in the study of adsorption of anionic and cationic dyes by activated carbon <sup>38</sup>. The molecular length and diameter of a single anionic PFOA molecule estimated by Diamond 3.0 software are approximately 8 Å and 3.55 Å, respectively, and 13 Å and 4.0 Å for PFOS. Thus, primary micropores (<8 Å) may contain high energy sorption sites for PFOS and PFOA. If microporosity effect was apparent, increasing adsorption would be expected for increasing micropore volume. Despite the absence of statistically significant correlation, Figure 3.4 showed a general trend of increasing  $K_d$  with higher micropore volume in the pores less than 8 Å. Further examination showed that ACF20, 1240C, and BPL deviated most from the general trend. In addition, the three ACFs with different pore size distributions were initially introduced for examining the possible impact of sorbent pore sizes on the uptake of PFAAs, if ACFs exhibited similar surface chemistry. However, their difference in surface chemistry (e.g., total basicity and oxygen content) seemed to have overwhelmed the difference in pore size distributions. Yet the difference in their surface chemistry still cannot fully explain the deviation of ACF20 from the other two ACFs regarding PFOA adsorption.

### 3.3.5 PFAA adsorption mechanisms

Due to a larger number of factors involved in the adsorption processes and the complexity of carbon surface chemistry, no single mechanism can adequately explain the adsorption of PFOS and PFOA by carbonaceous adsorbents. There was some evidence supporting the hydrophobic effect and electrostatic interactions, through which activated carbon are known to interact with organic compounds. For instance, substantial uptake of PFOS by the sorbents with negatively charged surface suggested the significance of the hydrophobic effect despite electrostatic repulsion. Generally higher affinity shown by the sorbents with high PZC values suggested the influence of electrostatic interactions. Different from previous research, the first major finding of the study was that carbon surface polarity or hydrophobicity, as indicated by oxygen content or surface acidity, was not critical in determining adsorption affinity for PFOS and PFOA. The second major finding of the strong influence of carbon surface basicity suggested that a more appropriate conceptual model for describing adsorption of PFOS and PFOA by carbons was through acid-base interactions. The basic sites present in both oxygen-containing groups and carbon graphene plane can undergo acid-base interactions as discussed above. The finding provides a practical guide for choosing and manufacturing the carbons for the treatment of PFAA-contaminated waters. For instance, carbons activated at a higher temperature (e.g., 800-1000 °C), manufactured in the presence of nitrogen-containing compounds or subjected to post modification by ammonia gas have much higher number of basic sites <sup>47</sup>. In addition, it has been suggested that the origin of basicity might not be as important as total basicity in determining affinity for anionic sorbates <sup>26</sup>. In order to further confirm the findings, the best approach is to modify surface chemistry of carbons made of the same raw material while minimizing changes of original physical characteristics, and then to examine changes in adsorption affinity before and after modification. Such is the focus of our future investigation.

## 3.4 Conclusions

Uptake of PFOS and PFOA by ten carbonaceous sorbents with different precursors and physical and chemical properties were systematically investigated. Sorbent macroscopic size was confirmed to be the dominant factor controlling uptake kinetics, while for granular sorbents of similar sizes, carbon surface chemistry in particular total basicity and PZC contributed to variations in uptake rates. Carbon surface chemistry was found to overwhelm physical properties in controlling the extent of adsorption. For all the sorbents, the most dominant carbon character was basicity; in contrast, total acidity and oxygen content that are closely associated with carbon surface hydrophobicity had no or insignificant impact on PFOS and PFOA adsorption. Finally, synthetic polymer-based sorbents including Ambersorb and ACFs were found to be generally more effective than activated carbon made of natural materials in removing PFOS and PFOA from aqueous solutions.

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# 3.6 Appendix A. Supplementary data

Supplementary data related to this article is provided at the end of the thesis as Appendix A.

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# **CHAPTER 4**

# Surface Modification of Activated Carbon for Enhanced Adsorption of Perfluoroalkyl Acids from Aqueous Solutions

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## Abstract

The objective of the research was to examine the effect of increasing carbon surface basicity on the uptake of perfluorooctane sulfonic (PFOS) and carboxylic acids (PFOA) by activated carbon. Granular activated carbons made from coal, coconut shell, and wood, and phenolic-polymer-based activated carbon fibers were modified through high-temperature and ammonia gas treatments to facilitate systematical evaluation of the impact of basicity of different origins. Comparison of adsorption isotherms and adsorption distribution coefficients showed that the ammonia gas treatment was more effective than the high-temperature treatment in enhancing surface basicity. The resultant higher point of zero charges and total HCl uptake correlated with improved adsorption affinity for PFOS and PFOA. The effectiveness of surface modification to enhance adsorption varied with carbon raw material. Wood-based carbons and activated carbon fibers showed enhancement by one to three orders of magnitudes while other materials could experience adsorption reduction towards either PFOS or PFOA.

Keywords: PFOS; PFOA; activated carbon; activated carbon fibers; basicity; surface modification

## 4.1 Introduction

Perfluoroalkyl acids (PFAAs) are detected in surface and ground waters at many locations around the world <sup>1</sup>. They originate from manufacturing and use of perfluoroalkyl and polyfluoroalkyl substances (PFAS) as surface active agents in industrial and consumer products over half a century<sup>2</sup>. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have particularly attracted regulatory scrutiny because of their extreme persistence, bioaccumulation potential, and evidence of toxicity in laboratory animal studies <sup>3</sup>. PFOS has been included in the *Stockholm Convention on Persistent Organic Pollutants* for restricted production and uses <sup>4</sup>. U.S. Environmental Protection Agency (EPA) has proposed provisional health advisory of 0.2  $\mu$ g L<sup>-1</sup> for PFOA in drinking water <sup>5</sup>. A stringent drinking water guideline value of 0.04  $\mu$ g L<sup>-1</sup> of PFOA has been established in New Jersey, USA <sup>6</sup>.

Various treatment technologies and processes are being explored for PFAA removal and decomposition <sup>7</sup>. Adsorption by activated carbon has been mainly applied to industrial wastewater, drinking water, and groundwater treatment in real-world applications <sup>8-10</sup>. One of the major advantages of using activated carbon is that many water treatment and remediation facilities already have granular activated carbon (GAC) filtration systems in place. Activated carbon may be essential in a treatment train for capturing PFAA from waste streams before other oxidative, or reductive processes can be applied. However, overall weak interactions between PFAAs and carbon surface considerably limit treatment efficiency. Partly as a result of the weak interactions, competitive sorption by natural organic matter (NOM) further leads to an undesirable early breakthrough of PFAAs in GAC filtration systems <sup>11</sup>. Thus, developing approaches to improve the affinity of PFAAs for activated carbon and to reduce the impact of NOM is key to efficiently and economically applying activated carbon for PFAA treatment.

Previously, Zhi and Liu<sup>12</sup> have demonstrated that high carbon surface basicity was closely linked to high affinity for PFOS and PFOA while other carbon characteristics had little impact on adsorption. Carbon surface basicity is known to play a major role in sorption properties. High basicity correlates with high uptake of acidic gases (e.g., gaseous HCl, SO<sub>2</sub>, and CO<sub>2</sub>), inorganic anions (e.g., perchlorate), and aromatic organic compounds (e.g., benzene and toluene) <sup>13,14,15</sup>. The origin of carbon surface basicity is a subject of ongoing research. As of today, three main origins

of basicity have been proposed <sup>16</sup> :  $\pi$ -electrons from carbon atoms of the basal plane and graphene edges, oxygen functional groups, and nitrogen functional groups (as well as other heteroatoms like sulfur and phosphorus). The basicity imparted by oxygen groups are due to pyrone-type structures (i.e., carbonylic and etheric oxygens in close vicinity). Other oxygen groups including carboxyl groups, lactones, phenol, and lactol groups contribute to carbon surface acidity. High-temperature treatment under an inert atmosphere can reduce the amount of surface oxygen and increase the basicity originated from  $\pi$ -electrons because of weakened electron-withdrawing effect of oxygen <sup>17</sup>. The basicity contributed by surface nitrogen groups is usually not significant because of low nitrogen content in commercial activated carbons. However, by including nitrogen-containing materials during the activation process or by reacting activated carbon with ammonia gas (amination), a range of nitrogen-containing groups can be incorporated into carbon surface to enhance basicity <sup>17</sup>.

As of today, few have investigated the influence of carbon basicity on adsorption of PFAAs. As PFAAs are present as anions at environmentally relevant pH of 5–8 because of their low  $pK_a$  values, we hypothesize that increasing basicity can benefit adsorption of organic anions such as PFAAs <sup>18</sup>. If this proves feasible, then surface modification to increase carbon basicity can be applied to improve PFAA removal efficiency. To validate such hypothesis, we modified the surface chemistry of four GAC and one type of activated carbon fibers (ACF) through high-temperature treatment in an inert atmosphere and anhydrous ammonia gas, respectively. The extent of PFOS and PFOA uptake before and after the modification was examined in batch adsorption experiments with respect to changes in carbon characteristics. In the end, adsorption site energy was analyzed to determine further the alteration of average sorption site energy and heterogeneity caused by surface modification. The information allows a better understanding of sorption mechanisms of PFAAs to carbonaceous adsorbents.

## 4.2 Materials and Methods

### 4.2.1 Chemicals

Perfluorooctanoic acid (PFOA, purity > 96%) and sodium perfluorooctane sulfonate (PFOS, purity  $\geq$  98.0%) were obtained from Sigma-Aldrich (Oakville, ON, Canada). The chemical properties are

summarized in Table B.1 in the Appendix B. Sodium chloride (A.C.S. certified) and acetonitrile (HPLC grade) used for adsorption experiments were purchased from Fisher Scientific (Ottawa, ON, Canada). Acetic acid (LC-MS grade) and ultrapure water (LC-MS grade) used for chemical analysis were also from Fisher Scientific. Isotope-labelled sodium perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]- octanesulfonate (MPFOS) and perfluoro-n-[1,2-<sup>13</sup>C<sub>2</sub>] octanoic acid (MPFOA) were provided by Wellington Laboratories (Guelph, ON, Canada) and DuPont USA (Wilmington, DE, USA), respectively. All aqueous solutions used for the experiments were prepared with deionized water with a minimal resistivity of 18 M $\Omega$  cm<sup>-1</sup>.

#### 4.2.2 As-Received and Surface-Modified Activated Carbon

Four GAC and one type of ACFs previously tested were included in the present study as "asreceived" carbons <sup>12</sup>. They included: coal-based FILTRASORB 400 (F400) from Calgon Inc. (USA), wood-based WVB 14x35 (WVB) and BioNuchar (BioNC) from MeadWestvaco Co. (USA), and coconut shell-based GAC AquaCarb 1240C (1240C) from Siemens Inc. (USA). Phenolic-based ACFs (ACF20) were from Kynol Inc., Japan. The adsorbents were first washed in deionized water, sonicated for three hours, and then dried at 103 °C for 24 h. Subsequently, all the GAC was sieved, and particles retained between sieves 0.85 and 1.00 mm were used for the experiment.

The cleaned adsorbents served as the starting materials for surface modification. The four GAC were subject to high-temperature treatment in an inert argon (Ar) atmosphere to reduce the amount of surface oxygen functional groups. Six grams of carbon materials were placed in a horizontal quartz tube within a hinged high-temperature split tube furnace (4 cm  $\times$  36 cm, ThermCraft Inc., USA). The tube was saturated with ultra-high-pure Ar gas and then heated to 1000 °C in a flow of Ar (100 mL min<sup>-1</sup>). After two hours, the samples were cooled to room temperature under the Ar atmosphere. A portion of the heat-treated carbons was further treated under an ammonia atmosphere using the same system. A quartz tube holding the adsorbents was initially saturated with Ar and then replaced by anhydrous ammonia gas (purity > 99.99%). The carbon materials were heated to 700 °C in a flow of ammonia gas. Adsorbents obtained after the high-temperature for one hour, and cooled down in the ammonia gas. "AT" after the ammonia treatment.

The modified carbons were washed with deionized water to remove generated powered materials and residual ammonia.

### 4.2.3 Adsorbent Characterization

The as-received and surface-modified adsorbents were characterized using the same methods described in the authors' previous study <sup>12</sup>, and the properties are detailed in Table 4.1. Physical characteristics were determined by nitrogen adsorption isotherms measured at 77 K with an Autosorb-1 analyzer (Quantachrome Co., USA). Point of zero charge (PZC) was measured by mass titration/pH equilibration method <sup>19</sup>. Total surface acidity (NaOH uptake) and basicity (HCl uptake) were measured by Boehm technique <sup>20</sup>. Elemental compositions of the sorbents were analyzed using a PerkinElmer 2400 series elemental analyzer by a certified commercial laboratory. Further identification and quantitative measurement of nitrogen groups on the surface of ammoniatreated adsorbents was conducted using X-ray photoelectron spectroscopy (XPS). A K-Alpha<sup>TM+</sup> X-ray Photoelectron Spectrometer system was operated in a constant-pass energy mode at 50 eV with a step size of 0.100 e V for C1s, N1s, and O1s photoelectron lines. Survey scans in the range of  $-10 \sim -1350$  eV were recorded at a pass energy of 200 eV and with a step size of 1.000 eV. Prior to analysis, adsorbents were dried at 103 °C and then kept under vacuum. All binding energies were corrected for charging of the sample by calibration to the graphitic carbon C1s peak at BE 284.8 eV 14, 21. The acquired data were analyzed using a Gaussian–Lorentzian linear least squares fitting program. The relative abundance of each nitrogen functional group (an average of three regions per sample) was calculated from the XPS survey spectra and reported in Table 4.2. The relative peak areas were corrected by the sensitivity factors based on the transmission characteristics of physical electronics of the XPS system.

		Chemical Properties										Physical Properties					
Adsorbents	Total acidity <sup>1</sup>	Total basicity <sup>1</sup>	DZC	0	Ν	С	Н	Ash <sup>2</sup>	11/NI 3	Surface Area	Pore Volume		Pore vol	ume distrib	ution (mL g <sup>-</sup>	<sup>1</sup> )	
	µeq m <sup>-2</sup>	µeq m <sup>-2</sup>	PZC	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	H/N <sup>3</sup>	$H/N^{-3}$ m <sup>2</sup> g <sup>-1</sup>	mL g <sup>-1</sup>	<8 Å	8-20 Å	20-100 Å	100-200 Å	>200 Å	
1240C	0.09	0.41	9.27	1.25	0.05	93.45	0.13	5.12	36.4	1428	0.64	0.3	0.24	0.10	0	0	
1240 HT	0.10	0.38	10.50	0	0.05	96.04	0.10	3.81	28.0	1129	0.51	0.25	0.18	0.07	0.01	0	
1240 AT	0.03	0.61	11.70	0	1.31	94.42	0.10	4.17	1.07	1098	0.45	0.22	0.19	0.04	0	0	
F400	0.27	0.44	8.29	1.00	0.11	86.75	0.10	12.0	12.7	948	0.58	0.15	0.14	0.29	0	0	
F400 HT	0	0.42	11.10	0	0.14	87.85	0.10	11.9	10.0	881	0.47	0.20	0.12	0.11	0.02	0.02	
F400 AT	0	0.67	11.40	0	0.38	88.31	0.10	11.2	3.68	937	0.50	0.19	0.14	0.12	0.03	0.02	
BioNC	0.38	0.10	4.07	3.18	0.05	85.18	1.06	10.5	297	2341	3.79	0	0.14	3.14	0.39	0.11	
BioNC HT	0.32	0.18	6.67	0.77	0.65	90.66	0.10	7.82	2.15	1347	0.72	0.16	0.16	0.36	0.05	0	
BioNC AT	0.07	0.42	10.30	0.57	2.46	91.41	0.10	5.46	0.57	1061	0.71	0.16	0.16	0.34	0.03	0.02	
WVB	0.08	0.16	4.50	3.40	0.05	66.30	3.04	27.2	851	1558	1.53	0.09	0.29	0.74	0.25	0.16	
WVB HT	0.14	0.18	8.84	1.18	0.05	90.53	0.10	8.14	28.0	974	0.68	0.17	0.14	0.27	0.07	0.04	
WVB AT	0.14	0.42	10.50	0.68	2.18	89.97	0.10	7.07	0.64	1048	0.74	0.18	0.15	0.30	0.07	0.04	
ACF20	0.17	0.21	7.28	3.50	0.05	93.20	0.10	3.15	28.0	2055	1.15	0.39	0.37	0.32	0.09	0.04	
ACF20 AT	0.06	0.66	9.84	1.25	1.81	93.78	0.10	3.06	0.77	1707	1.06	0.24	0.36	0.47	0	0	

 Table 4.1 Activated Carbon Characteristics

<sup>1</sup> Total surface acidity (NaOH uptake) and basicity (HCl uptake) were measured by titration using CO<sub>2</sub>-free water and under a nitrogen atmosphere.

<sup>2</sup> Ash content was calculated by subtracting the weight of O, N, C and H.

<sup>3</sup> H/N– mole-based ratio

### 4.2.4 Adsorption Isotherms

The isotherm experiments were conducted using 100-mL polypropylene copolymer bottles in triplicates at a sorbent to solution ratio of 10 mg:100 mL. The background electrolyte was 10 mM sodium chloride and the initial PFOS or PFOA aqueous concentrations ranged from 5 µg L<sup>-1</sup> to 5000  $\mu$ g L<sup>-1</sup>. The time to reach equilibrium was determined in the range of 7 - 14 d in preliminary kinetics experiments. The second set of triplicate bottles containing only the aqueous phase and PFOS or PFOA served as controls. The tubes were shaken on an orbital shaker (Multitron Pro, Infors HT, Switzerland) maintained at 25 °C and 150 rpm. At designated times, the bottles were centrifuged at 4,000 g for 20 min and supernatants were sampled and diluted with equal volume of acetonitrile. Identification and quantitation of PFOS and PFOA in aqueous solutions ( $C_e$ ) were performed using liquid chromatography tandem mass spectrometry (LC-MS/MS) under a negative, electrospray, and multiple- reaction-monitoring (MRM) mode. Detailed information on the LC/MS/MS parameters is listed in the Appendix B. Detection limits for PFOS and PFOA were estimated to be 0.005 and 0.010  $\mu$ g L<sup>-1</sup>, respectively, with an injection volume of 5  $\mu$ L. Quantitation was performed using 1/x weighted calibration curves with the use of internal standards of MPFOS and MPFOA. Two sets of calibration standards were prepared to cover high-concentration and low-concentration solutions, respectively, to maintain linearity within the concentration range in the study. The corresponding adsorbent concentrations  $(C_s)$  were calculated via an aqueous mass loss method as described in Appendix B.

## 4.3. Results and discussion

### 4.3.1 High-temperature treatment

The major goal of the high-temperature treatment was to remove surface oxygen groups so as to increase carbon surface basicity, yet other chemical characteristics and physical properties of the carbons could change during the modification. As shown in Table 4.1, the bituminous coal-based F400 and coconut shell-based 1240C exhibited minor modifications in surface area, pore volume, and pore size distributions. They were physically more resistant to the treatment than the wood-based WVB and BioNC. The latter two experienced extensive loss of surface area and total pore volume (Table 4.1), as well as adsorbent mass (data not shown). Despite the significant loss of

total pore volumes, the wood-based carbons gained pore volumes in the pores with a width < 8 Å. The increase could benefit the uptake of low-molecular-weight organics including PFAAs with a diameter less than the pore width (Table 4.1) from water due to microporosity effect <sup>12, 22</sup>.

The bulk oxygen content of 1240C HT and F400 HT was reduced to below the detection limit while the wood-based BioNC HT and WVB HB lost about 70% of oxygen. Under temperatures as high as 1000 °C, most of the oxygen groups were removed through gasification, but to a less extent for pyrone and pyrone-like structures <sup>23</sup>. The loss of surface oxygen groups was accompanied by a concurrent reduction in elemental hydrogen of WVB and BioNC (Table 4.1), as hydrogen is mainly contributed by oxygen functional groups, except for pyrone-like structures that are not associated with any hydrogen. Corresponding to changes in elemental composition, PZC of all materials increased and mostly above 7 (except for BioNC HT), suggesting an overall enhancement of adsorbent basic character. However, the change in total HCl uptake, which is another measure of surface basicity, varied with carbon materials. Both WVB HT and BioNC HT showed a substantial increase in total HCl uptake compared to the as-received one. Similarly, total NaOH uptake, a measure of surface acidity, did not decline for all adsorbents as shown in Table 4.1. Compared to the as-received adsorbents, the total NaOH uptake was reduced for both F400 HT and BioNC HT, practically the same for 1240C HT, and higher for WVB HT. Previously, Menéndez, et al.<sup>24</sup> showed that although high-temperature treatment under an inert atmosphere was effective in removing surface oxygen groups, it may not produce very basic surface because of susceptibility of a treated surface to re-oxidation. The researchers suggested that a hydrogen atmosphere would be ideal for creating a stable basic surface for activated carbon.

Groups	Nitrile	Pyridine	Amides	Aromatic amines, aniline and/or amines	Quaternary nitrogen	Protonated amide	Total surfa	ce N content
Binding energy (eV)	397.1	398.7	399.5	400.5	402.6	403.2	<sup>1</sup> atom%	<sup>1</sup> weight%
1240C AT	-	-	-	-	-	-	2.40	2.66
F400 AT	-	-	-	-	-	-	1.06	1.20
BioNC AT	29.09	57.89	-	13.01	-	-	7.76	9.81
WVB AT	33.06	58.07	0.99	1.75	7.11	-	4.17	4.60
ACF20 AT	-	66.30	0.10	15.70	14.00	3.90	3.78	4.46

Table 4.2 XPS analysis of nitrogen functional groups on the surface of the ammonia-treated adsorbents (% of total N groups)

<sup>1</sup> the percentages were calculated based on the total amount of C, N and O on the surface that was analyzed by XPS.

#### 4.3.2 Ammonia gas treatment

The primary goal of the ammonia gas treatment was to increase carbon surface basicity by creating new nitrogen functional groups. According to the higher elemental nitrogen content for all ATtreated adsorbents compared to the as-received or HT-treated ones, incorporation of nitrogen functional groups into the carbons was successful (Table 4.2). Carbons of different origins responded to the same the same amination process differently, as reflected by varying degree of nitrogen incorporation and dissimilar changes in surface properties. The elemental nitrogen content ranged from 0.38% (weight percentage of bulk material) for F400 AT to >2.00% for the wood-based carbons WVB AT and BioNC AT. To further confirm that nitrogen was covalently bound to surface, nitrogen groups on adsorbent grain surface (3-10 nm deep) were further analyzed using XPS. The technique allowed for semi-quantitative evaluation of total nitrogen content on the surface and relative abundance of various nitrogen functionalities as listed in Table 4.2. A representative N1s photoelectron spectrum (XPS) is presented in Figure 4.1. The estimated surface nitrogen contents (Table 4.2) were higher than the bulk nitrogen contents (Table 4.1), confirming that the nitrogen incorporation occurred mostly on the carbon surface. For 1240C AT and F400 AT, the surface nitrogen content was too low to allow nitrogen speciation information to be resolved by XPS. For other ammonia-treated adsorbents, assignment of nitrogen groups was made according to previous studies <sup>14, 21</sup> and NIST X-ray Photoelectron Spectroscopy Database. The assignments were: nitrile at 397.2, pyridine 398.7 eV, amides 399.5 eV, aromatic amines, aniline and/or imines (C=NH) 400.5 eV, quaternary nitrogen 402.6 eV, and protonated amide 403.2 eV.

Mangun et al. <sup>14</sup> and Stöhr, et al. <sup>25</sup> have proposed the reactions occurring during ammonia treatment. Briefly, ammonia under a high temperature decomposes to nitrogen radicals (NH<sub>2</sub> or NH), which attack carbon atoms to lead to carbon gasification and formation of NH<sub>2</sub> or NH functional groups. The reaction temperature and adsorbent materials dictate the types of nitrogen groups that can be formed. Previous studies showed that aromatic amines and pyridines tend to dominate at reaction temperatures above 600 °C, because the energy is high enough to allow for the amination of ring structures <sup>14, 25</sup>. Thus, the significant formation of pyridine (Table 4.2) at 700 °C in the study confirmed the previous findings. BioNC AT and WVB AT showed abundant nitrile groups, whereas ACF20 AT included a substantial amount of aromatic amines and quaternary nitrogens. Also, oxygen contents for the wood-based carbons were further reduced

compared to the HT-treated ones, suggesting the further decomposition of oxygen-containing groups during the ammonia gas treatment. As elemental compositions have changed, *PZC* of AT-treated carbons shifted towards to higher pH values, except for F400, which also showed minimal incorporation of nitrogen. The total NaOH uptake decreased for three adsorbents (1240C AT, BioNC AT and ACF20 AT) while the total HCl uptake increased for all the materials. Overall, ammonia treatment effectively increased surface basicity in all adsorbents.



**Figure 4.1** Representative N1s photoelectron spectrum (XPS) of the ammonia-treated activated carbon fibers (ACF20 AT). Peak I – pyridine, peak II – aromatic amines, peak III – quaternary nitrogen, and peak IV – protonated amide.

Minor changes in carbon physical properties including surface area, pore volume, and pore size distributions occurred after the ammonia treatment (Table 4.1). Surface area and pore volume were either largely unchanged (e.g., F400 and WVB) or slightly decreased (e.g., 1240C and ACF20). In particular, the changes in ACF20 was very similar to what Mangun, Benak, Economy and Foster <sup>14</sup> reported for another Kynol ACF sample under the treatment condition (700 °C and 60 min). Mangun et al. <sup>14</sup> also reported that when ACFs were subject to ammonia treatment at a higher temperature (e.g., 800 °C), significant etching can occur in existing pores to increase surface area and pore volume, and to shift pore size distribution to small pores. However, the present study

intended to maintain the least changes in physical properties to examine how changing basicity affected adsorption affinity for PFOS and PFOA.

### 4.3.3 Adsorption isotherms

Adsorption isotherms of PFOS and PFOA by as-received and surface-modified carbons are illustrated in Figure 4.2, and isotherm constants are reported in Table 4.3. The adsorption equilibrium data were found to be best modeled with the classical Freundlich isotherm equation (listed in Appendix B) with high  $R^2$  values while Langmuir did not fit the data as well. As shown in Figure 4.2, striking improvement was observed for two wood-based GAC (i.e., BioNC HT, BioNC AT, WVB HT, and WVB AT) as well as the polymer-based activated carbon fibers (ACF20 AT) after surface modification. The ammonia gas treatment resulted in the greater extent of enhancement than the high-temperature treatment. Adsorption of PFOA by ACF20 AT was substantially improved, as shown by very low equilibrium aqueous concentrations (< 1  $\mu$ g L<sup>-1</sup>, Figure 4.2) and  $K_F$  values that were several orders of magnitude higher than those of as-received ACF20. It was notable that the  $K_F$  values for ACF20 AT were potentially subject to larger errors because of very high adsorption. As shown in Figure 4.2, adsorption enhancement also varied with equilibrium aqueous concentrations. For the adsorption of PFOS, the isotherms of the as-received and surface-modified carbons had the tendency to intersect at low levels (Figure 4.2). The observation indicated that the surface-modified carbons were more competent in removing PFOS at relatively higher initial concentrations. For the adsorption of PFOA, there were fewer tendencies for isotherms to intersect, suggesting that the adsorption improvement occurred over the whole concentration ranges under study. However, for the coconut shell-based 1240C HT, substantial adsorption enhancement only occurred to adsorption of PFOS after either modification, but not for PFOA. The bituminous coal-based F400 responded the least to the surface modifications, and there was an even reduction in PFOS uptake.





Figure 4.2 Adsorption isotherms at 25 °C of PFOS and PFOA onto as-received and surfacemodified carbons

### 4.3.4 Impact of surface basicity

Given relative minor changes in physical properties, the enhancement in adsorption of PFOS and PFOA was most likely caused by variations in chemical properties. In the authors' previous study <sup>12</sup>, it was found that total surface basicity was the only sorbent-specific parameter that was positively correlated with adsorption affinity (expressed by adsorption distribution coefficient,  $K_d$  $= C_s/C_e$ ) with statistical significance. In the present study, the significant enhancement of adsorption as shown by  $K_d$  (L mg<sup>-1</sup>, calculated at C<sub>e</sub> = 0.3 µg L<sup>-1</sup> as listed in Table B.2 in Appendix B) was found to correlate positively with total basicity (or total HCl uptake) and PZC (Figure 4.3). Consistent with the trends shown in the adsorption isotherms (Figure 4.2), the wood-based BioNC and WVB showed very significant improvement in adsorption affinity for PFOS and PFOA. Some of their  $K_d$  values (Table B.2 in Appendix B) after surface modification greatly exceeded those of F400 or 1240C series carbons by larger than one order of magnitude. The adsorption affinity of ACF20 AT for PFOS and PFOA increased by one to three orders of magnitude. In comparison, Mangun et al. previously reported an enhancement of adsorption capacity about five times for HCl gas phase adsorption by ammonia-treated ACF<sup>14</sup>. Such substantial adsorption enhancement observed in this study has been little reported. In contrast, F400 and 1240C showed either a minor improvement or a decline in performance. Overall, a similar conclusion can be reached if  $K_d$  was calculated at higher aqueous concentrations such as 10  $\mu$ g L<sup>-1</sup>, or when  $K_d$  was expressed as per surface area basis ( $L m^{-2}$ ) as listed in Table B.2.



**Figure 4.3** Correlations between adsorption distribution coefficient  $K_d$  at Ce = 0.3 µg L<sup>-1</sup> and carbon surface basicity (PZC or total basicity as measured by total HCl uptake) for all adsorbents.

The high correlation with carbon surface basicity suggests that the adsorption of PFOS and PFOA anions can be interpreted as acid-base interactions. Thus, strength, abundance, and accessibility of basic sites on the adsorbent surface should be considered for understanding increasing adsorption from as-received to HT-treated, and to AT-treated carbons. The high-temperature treatment overall reduced the basicity from oxygen functional groups and enhanced basicity from  $\pi$ -electrons while the ammonia treatment introduced additional nitrogen-containing groups to impart basic property. In terms of basic strength of surface nitrogen groups, the *pK*<sub>a</sub> values of nitrogen functional groups are not necessarily higher than those of oxygen (pyrone-type) groups or  $\pi$ -electrons. Most nitrogen
functional groups have  $pK_a$  values lower than 8, and pyridine-like groups on carbons would exhibit  $pK_a$  values in the range of  $4-6^{16}$ . In comparison,  $pK_a$  values for weak bicyclic and tricyclic pyrone groups on carbon surface were calculated based on quantum chemistry theories to be ~5-6 and ~ 7-8, respectively <sup>26</sup>. Strong basic sites with  $pK_a$  ~10-13 have been proposed for the pyrone groups whose ketone and etheric rings are separated by 2-3 carbon rings <sup>26</sup>. Therefore, the high adsorption onto the AT-treated carbons had to do with the abundance and accessibility of newly introduced nitrogen groups, rather than the basic strength of the surface nitrogen groups.

In addition, another source of basicity in activated carbon aside from the three discussed above is inorganic matter (or ash) if its content was high <sup>17</sup>. Different from other types of basicity, the basicity of inorganic matter can be transferred from the carbon surface to aqueous solutions to raise solution pH when it dissolves in aqueous solutions. Because of a small amount of sorbents (10 mg) used in batch sorption experiments, pH of aqueous solutions used during adsorption experiments did not show observable difference caused by ash content. Also, the carbons after surface modifications showed less ash content and thus increasing adsorption to PFOS and PFOA was not caused by ash content change.

#### 4.3.5 Site energy change

In addition to changes in  $K_F$ , a considerable increase in the values of heterogeneity parameter (*n*) for the surface-modified carbons was observed (Table 4.3), suggesting changes in adsorption site energy. Thus, approximate site energy distributions F(E) underlying Freundlich isotherm was introduced to relate the changes in adsorption isotherms to alteration of energetic characteristics of PFAA-adsorbent interactions <sup>27, 28</sup>. It was based on the assumption of condensation approximation and expressed by the equation 4.1 :

$$F(E) = \frac{K_F \cdot n \cdot S^n}{RT} exp\left(\frac{-nE}{RT}\right)$$
(eq. 4.1)

In the equation, *S* is the water solubility of the adsorbate, *R* the universal gas constant, and *T* absolute temperature. *E* is the net energy that equals to  $E_{total} - E_s$ , where  $E_{total}$  is the difference of adsorption energy to a given site between adsorbate and water, and  $E_s$  the adsorption energy at  $C_e = S$ .



**Figure 4.4** Adsorption site energy distributions for adsorption of PFOS and PFOA onto activated carbon and carbon fibers

Comparisons of site energy distributions for adsorption of PFOS and PFOA onto all adsorbents were illustrated in Figure 4.4. The area under each distribution curve is determined by the maximum adsorption capacity, which is  $K_F$  in this scenario. This area indicates the maximum amount of available adsorption sites for PFOS or PFOA on the surface. The position of the distribution curve against the x-axis (or energy axis, E) represents the mean energy of adsorption sites. It is regarded as an indicator of adsorbent surface affinity and the sites with higher energy is more favorable to adsorbates of interest. Moreover, the heterogeneity value n controls the width of the distribution, which reflects the diversity of the energy sites. As illustrated in Figure 4.4, modified carbons showed steeper curves than as-received carbons. In particular, the AT-carbons had the narrowest site energy distribution and were located to the right side of the as-received and HT carbons, suggesting these carbons had the most available adsorption sites with the greatest affinity. The wood-based carbons exhibited the most drastic changes in site energy while F400 and 1240C experienced some milder changes. Both surface modification methods gave rise to more homogeneously distributed energy on the adsorbent surfaces, suggesting the shift in the sites that are responsible for enhanced uptake of PFOS and PFOA.

# 4.4 Environmental implications

With respect to carbon surface chemistry, the two PFAAs appeared to exhibit the similar adsorption behaviors as shown by NOM: they are favorably taken up by basic carbons such as ammonia-treated ones <sup>29-31</sup>. However, adsorption of NOM onto activated carbon is also known to be actively controlled by physical interactions, which are denoted by the molecular size distribution of NOM and pores size distribution of activated carbon <sup>22, 31, 32</sup>. Cheng et al. <sup>29</sup> found that for ammonia-treated carbons enhanced NOM uptake was attributed to the enlarged carbon pores and an increase in accessible surface area. In a separate study on co-uptake of NOM with either trichloroethylene or MTBE, the impact of competitive sorption by NOM was only slightly affected by chemical characteristics of activated carbons <sup>31</sup>. In contrast, adsorption of PFAAs is not influenced by the pores size distribution of activated carbon. Give such differences, fine tuning of pore size distribution of activated carbon is thus required in conjunction with surface chemistry modification, to improve selective uptake of PFAAs and to reduce competitive sorption by NOM. Cheng et al. have reported that the ACFs with the majority of pores less than 1 nm exhibited negligible NOM uptakes <sup>29</sup>, because NOM in natural waters mostly comprises of molecules with a hydrodynamic diameter larger than 1 nm. Furthermore, the wood-based carbons examined in the study would probably be less affected by NOM fouling because of their larger pores. As competitive adsorption by NOM is one of the major causes of early breakthrough of PFAAs in full-scale treatment systems <sup>11</sup>, it warrants further investigations to what extent the surface modification methods discussed herein would facilitate selectivity for PFAAs in the presence of NOM. It would be very useful to examine in future studies how the carbons made with nitrogencontaining precursors perform in removing PFOS and PFOA in comparison to the carbons that were post modified as those investigated in the study.

Adsorbents	PFOS			PFOA		
	$K_F$	$K_F$	n	$K_F$	$K_F$	n
	$(\mu g/mg)(\mu g/L)^{-n}$	$(\mu g/m^2)(\mu g/L)^{-n}$		$(\mu g/mg)(\mu g/L)^{-n}$	$(\mu g/m^2)(\mu g/L)^{-n}$	
12400	1 72	1 20	0.61	1.02	1.24	1 1 2
12400	1.72	(0.95, 2.99)	(0.52, 0, (0))	1.92	1.34	1.13
1240C UT	(1.21-2.44)	(0.85-2.88)	(0.53 - 0.69)	(1.38-2.67)	(0.96-1.86)	(0.95 - 1.30)
1240C H I	1/.8	14.3	1.84	0.82	0.73	0.73
12400 45	(12.4-25.6)	(9.93-20.6)	(1.62-2.07)	(0.48 - 1.42)	(0.43 - 1.26)	(0.56-0.89)
1240C AT	17.0	15.5	1.51	1.14	1.04	0.77
	(7.35-39.3)	(6.70-35.89)	(1.02 - 1.99)	(0.76 - 1.70)	(0.69 - 1.55)	(0.65 - 0.92)
F400	1.11	1.17	0.58	3.06	3.44	1.98
	(0.73 - 1.69)	(0.77 - 1.77)	(0.68 - 0.78)	(2.50-3.73)	(2.64 - 3.94)	(1.79 - 2.17)
F400 HT	0.66	0.75	1.60	2.53	2.87	1.12
	(0.43 - 1.00)	(0.50 - 1.20)	(1.33 - 1.86)	(1.83-3.50)	(2.07 - 3.97)	(0.96 - 1.29)
F400 AT	2.16	2.31	1.51	3.39	3.62	0.87
	(1.68-2.78)	(1.80-2.96)	(1.34 - 1.68)	(2.13-5.40)	(2.28-5.77)	(0.68 - 1.07)
BIONC	0.97	0.41	0.59	0.18	0.08	0.71
	(0.85 - 1.10)	(0.36 - 0.46)	(0.57 - 0.61)	(0.15 - 0.21)	(0.07 - 0.09)	(0.68 - 0.74)
BIONC HT	1.71	1.27	0.77	0.65	0.48	0.68
	(1.12 - 2.60)	(0.83 - 1.92)	(0.63 - 0.92)	(0.52 - 0.81)	(0.38 - 0.60)	(0.63 - 0.74)
BIONC AT	23.5	22.1	1.53	6.58	6.3	0.98
	(18.6-29.5)	(17.5 - 27.78)	(1.08 - 1.97)	(3.86 - 11.21)	(3.64 - 10.57)	(0.73 - 1.22)
WVB	1.27	0.82	0.54	0.14	0.09	0.75
	(1.04 - 1.54)	(0.67 - 0.99)	(0.51 - 0.57)	(0.12 - 0.17)	(0.07 - 0.11)	(0.71 - 0.79)
WVB HT	2.70	2.77	0.81	1.16	1.19	0.69
	(1.80-4.40)	(1.84 - 4.50)	(0.65 - 0.96)	(0.91 - 1.48)	(0.93 - 1.52)	(0.62 - 0.76)
WVB AT	85.2	81.3	2.33	6.68	6.37	1.06
	$(30 \ 3-239)$	(28.9-228)	(174-293)	$(4\ 29-10\ 41)$	$(4\ 09-9\ 92)$	(0.86 - 1.27)
ACE20	3 54	1 72	0.81	0.51	0.25	3.86
110120	$(1 \ 61 - 3 \ 43)$	(0.78-1.66)	(0.71 - 1.030)	$(0 \ 33 - 0 \ 79)$	(0.16-0.39)	(3 12 - 4 62)
ACE20 AT	85.6	50 1	1 92	$2.28 \times 10^4$	$1.33 \times 10^4$	4 24
110120111	(45, 1, 303)	(26.34 - 1.77)	(1.84-2.35)	$(2.60 \times 10^3 - 1.02 \times 10^5)$	$(1.57 \times 10^3 - 1.12 \times 10^5)$	(3, 25, 5, 24)
	(43.1-303)	(20.34 - 177)	(1.04-2.33)	$(2.09 \times 10^{\circ} - 1.92 \times 10^{\circ})$	$(1.37 \times 10^{3} - 1.12 \times 10^{3})$	(3.23 - 3.24)

**Table 4.3** Freundlich isotherm constants ( $K_F$  and n) at 25 °C for PFOS and PFOA

# 4.5 Acknowledgement

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# 4.6 Appendix B. Supplementary data

Supplementary data related to this article is provided at the end of the thesis as Appendix B.

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# **CHAPTER 5**

Sorption of Anionic and Zwitterionic Perfluoroalkyl and Polyfluoroalkyl Surfactants to Soil Organic Matter

## Abstract

Previous work has focused on the mobility of perfluoroalkyl carboxylic (PFCAs) and sulfonic acids (PFSAs) in soil and sediment, yet little information is available concerning the mobility of newly identified amphoteric polyfluoroalkyl surfactants, such as betaines. PFAS-based betaines, which are major polyfluoroalkyl surfactants found in some contaminated sites, differ from anionic PFAS in chemical properties as well as mobility and sorption interactions with solid environmental matrices. In this study, interactions between 15 PFASs (6 PFCAs, 3 PFSAs, 3 fluorotelomer sulfonates (FTSAs), and 3 fluoroalkyl betaines) and soil organic matter (SOM, Pahokee peat) were examined using a novel dynamic HPLC-based column method. Corresponding distribution coefficients (log  $K_d$ ) and organic carbon-water partitioning coefficients (log  $K_{oc}$ ) were reported. Results show that the log Koc of FTSAs with perfluoroalkyl chain-length of 4, 6, and 8 are similar to that of corresponding PFSAs with values of 1.42, 1.51, and 2.56 respectively. FTSAs also respond to changes in solution chemistry similarly as PFSAs. At solution pH of 5.9, the predominance of the neutral molecule over zwitterion gives rise to the relatively higher sorption of the betaines than PFCAs of equivalent chain-length. Calcium ion (concentration ranges from 0.5 - 50 mM) has a positive impact on the sorption of anionic PFASs to SOM, but a negative impact on the sorption of the betaines. Moreover, the increase in pH reduces sorption of all to SOM. Sorption of the betaine compounds follows the trend of log  $K_{oc}^{cation} > \log K_{oc}^{neutral} > \log$  $K_{oc}^{anion}$ ; sorption edges for three betaines are: 1.82 - 3.34 for perfluorooctaneamide betaine (PFOAB), 2.35 - 4.01 for perfluoroctane sulfonamide betaine (PFOSB), and 1.96 - 3.37 for 6:2 fluorotelomer sulfonamide betaine (6:2 FTAB). This is the first study to investigate the transport potential of FTSAs and polyfluoroalkyl betaines.

# Graphical Abstract



### 5.1 Introduction

Aqueous Film-Forming Foams (AFFFs) that are used to extinguish hydrocarbon fuel fires have been recognized as significant sources of the contamination of soil and groundwater by perfluoroalkyl and polyfluoroalkyl substances (PFAS) <sup>1</sup>. Apart from persistent perfluoroalkyl acids (PFAAs) that have been intensively studied, dozens of new classes highly fluorinated anionic, zwitterionic and cationic surfactants have been identified in AFFF formulations and AFFF-impacted water, sediment, and biota <sup>2-7</sup>. Recently, Munoz et al. (2016) have found that betaine-type PFAS dominated composition profiles (~ 94 % of total PFAS) in sediments following a major AFFF deployment during the Lac-Mégantic railway accident (Quebec, Canada) <sup>4</sup>. Different from the "legacy" PFAAs which are largely anionic sulfonate or carboxylate, the newly-identified PFASs may be anionic, cationic or zwitterionic, and include functional groups such as sulfonyl, thioether, amine, ammonium, carboxylate, sulfonate, amine oxide, and betaine. Referred to as "precursors" to PFAAs (or PrePFAAs), the newly identified PFASs have become a major focus of interest in AFFF site investigations and remediation.

Transport behaviours of PrePFAA are expected to be distinct from that of PFAA; it needs to be separately considered for anionic, cationic and amphoteric surfactants owing to different modes of interactions with natural geosorbents (e.g., soil, sediment, and aquifer materials). According to past studies, if PFASs are released to soil via AFFF deployment, organic carbon content strongly dictate the magnitude of sorption to soil and sediment.<sup>8, 9</sup>. Changes in solid-water distribution coefficient ( $K_d$ ) with solution pH and concentrations of divalent inorganic ions suggest that electrostatic interactions (or anion exchange) and steric effect also play an important role, especially for short-chain PFAAs <sup>8-15</sup>. To date, there is only one study has examined the sorption behavior of Perfluoroalkyl phosphonates (PFPAs) and perfluoroalkyl phosphinates (PFPiAs) in soils, and found sorption of PFPiAs ( $log K_d 1.6-2.1$ ) was overall higher than PFCAs and PFSAs, while PFPAs which molecular size is smaller than PFPiAs sorb relatively weaker and would likely to partition in aqueous phase due to a greater extent of desorption <sup>16</sup>. However, there is still no study has been conducted on cationic or zwitterionic PrePFAAs. Strong sorption is expected for a cationic PrePFAA because of attractive electrostatic interactions with predominantly negatively charged surfaces of natural geosorbents. Besides, sorption of a zwitterionic PrePFAA is fairly

variable because it can function as a non-ionic, anionic or cationic surfactant, depending on the pH of the surrounding medium relative to the isoelectric point of the amphoteric surfactant. Despite the complex interactions that the charged PFAS can engage with geosorbents, we hypothesize that similar to many organic contaminants, the eventual fate of the precursors in soils and groundwater may be profoundly influenced by sorption to soil organic matter (SOM), which in turn determines mobility, persistence, and bioavailability <sup>9, 11, 17</sup>.

Sorption of PFAAs, including perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFSAs) to soil, sediment, soil minerals and oxides has been studied using batch systems, saturated columns, and field systems <sup>8, 9, 16-22</sup>. Recently, a dynamic flow-through HPLC-based method has been developed to investigate the sorption of a series of anionic and nonionic organic contaminants to SOM packed in an HPLC column <sup>23, 24</sup>. The approach is advantageous than the traditional batch or saturated column methods that it specifically focuses on SOM-chemical interactions because the absence of soil minerals and metal oxides eliminates confounding effects. Short equilibration time (e.g., minutes to several hours) reduces potential microbial or chemical degradation of target compounds, sorbent aging, and time-dependent covalent binding to SOM <sup>23-25</sup>. Temperature, solution pH, and background electrolytes can be easily controlled. However, the method has been shown to only work for the organic compounds that can be detected by conventional HPLC detectors such as UV and fluorescence detectors, but not for PFASs that at environmentally relevant concentrations can only be analyzed by LC-MS/MS.

In this study, we demonstrated that the HPLC-based method could be applied to PFAAs and PrePFAAs to generate  $K_{oc}$  (organic carbon normalized  $K_d$ ) values that are urgently needed or site characterization and risk assessments of AFFF-impacted sites. We coupled a fraction collector to HPLC to allow the eluent to be fractionally collected and then separately analyzed by LC-MS/MS with proper quality control. Then PFAS elution profiles from an SOM-packed HPLC column were constructed to allow determination of retention volume, retention time, and subsequently, values of  $K_d$  and  $K_{oc}$ . We started with method validation by comparing  $K_{oc}$  values of PFAAs with those generated by batch sorption experiments. Then the method was applied to fluorotelomer sulfonates (FTSAs) and three polyfluoroalkyl betaines. FTSAs are often present as the most dominant PFASs in AFFF-impacted groundwater and soil samples while their  $K_{oc}$  values have been sparsely reported <sup>5, 7, 26-29</sup>. Sorption of polyfluoroalkyl betaines has never been investigated. The validated

method can be readily used for investigating other PFAS with ionizable groups should authentic standards be made available.

### 5.2 Materials and methods

#### 5.2.1 Chemicals

PFASs under investigation (see Figure 5.1 for chemical structures) include six PFCAs (perfluoroalkyl chain length, n = 3 - 8), three PFSAs (n = 4, 6, and 8), three FTSAs (n = 4, 6, and 8), three polyfluoroalkyl betaines, which are 6:2 fluorotelomer sulfonamide betaine (6:2 FTAB), perfluorooctaneamide betaine (PFOAB) and perfluoroctane sulfonamide betaine (PFOSB). Details on the chemicals and other reagents are provided in the Appendix C. Standards of PFASs were prepared in the methanol-water mixture (1:1, v/v) at concentrations around  $1 - 2 \text{ g L}^{-1}$ , and stored at - 20 °C in the dark. Prior to injection onto the SOM-packed HPLC column, these solutions were further diluted in HPLC water, resulting in injection solutions with a methanol content below 0.2%.



Figure 5.1 Chemical structures of the PFASs under investigation

The isoelectric point (IEP) of the three polyfluoroalkyl betaines was determined by the measuring zeta potential of their aqueous solutions (1 g  $L^{-1}$ ) as a function of solution pH. Solution pH was adjusted as needed with HCl (1 N) or NaOH (1 N) to the desired pH range of 2-12. Zeta potential of triplicate solutions was recorded with a Zeta Potential/Particle Size Analyzer (ZetaPlus/Bl-

PALS, Brookhaven Instrument Corp., NY, USA). Full speciation of betaines as a function of pH and the corresponding macroscopic  $pK_a$ 's were determined using a chemical calculator SPARC (ARCHem, GA, USA).

Pahokee peat from the International Humic Substances Society (IHSS, Golden, CO) was chosen as the model SOM. Sorption by the peat has previously been studied for 32 organic acids <sup>23</sup>. The peat was first homogenized, micronized, and freeze-dried using similar methods as recommended by Tülp et al. (2009), it has organic carbon  $f_{oc}$  of 46.9% <sup>23, 30</sup>. The mean particle size of the micronized peat was measured to be 6.88 µm by laser scattering particle size distribution analyzer (Horiba Instruments, Inc. Irvine, USA). The small particle size was necessary to shorten diffusion path to allow local equilibrium to be rapidly reached.

#### 5.2.2 Sorption Experiment

The experimental sorption setup recommended by Bronner and Goss (2010), and Tülp et al. (2009) was implemented on an Agilent 1100 HPLC system <sup>25</sup>,<sup>23</sup>. A Shimadzu fraction collector was connected to the end of a HPLC column to allow eluents to be fractionally collected and separately analyzed for PFASs on a LC-MS/MS system. Details of the LC-MS/MS analytical methods are provided in the Appendix C.4. The distribution coefficients were derived from the measured retention times on a stainless steel HPLC column (3.9 mm ID × 23 mm L, Waters, Canada), which was filled with a mixture of micronized peat and an inert support material (silicone carbide, SiC, diameter  $3 \pm 0.5 \mu$ m, ESK-SiC, Frechen, Germany). The column contained 0.150 g peat-SiC mixture with 28.5 % (w/w) peat. HPLC-grade water with 5 mM CaCl<sub>2</sub> served as mobile phase. The column was flushed for 24 h at a flow rate of 50  $\mu$ L min<sup>-1</sup> to allow full stabilization of packing material, experiment was conducted in duplicates. The mobile phase was collected for TOC analysis; the mass loss was found negligible with respect to the total mass of the initial packing material. The injection volume was 20  $\mu$ L for PFCAs, PFSAs, and n:2 FTSAs, and 50  $\mu$ L for the betaines per loop.

Sorption at a constant temperature of 25 °C was investigated at an environmentally relevant pH range and at three  $Ca^{2+}$  concentrations. The mobile phase for testing pH dependence was 5 mM CaCl<sub>2</sub> solution. The column was equilibrated for about 48 h after each pH adjustment and when the effluent pH stabilized. The value of pH was recorded when the pH of the mobile phase entering

and leaving the column was identical; it was assumed that this pH value represents the pH in the column. The minute amount of PFASs injected onto the column did not affect the solution pH. In separate experiments, CaCl<sub>2</sub> solutions (pH = 5.3) with concentrations of 0.5, 5, and 50 mM were used for testing Ca<sup>2+</sup>-dependence. The flow rate was 50  $\mu$ L min<sup>-1</sup>, which was chosen based on a preliminary study using flow rates between 10 and 500  $\mu$ L min<sup>-1</sup>. It was found that the retention volumes remained largely the same with flow rates  $\leq$  50  $\mu$ l min<sup>-1</sup>, suggesting that local equilibrium partitioning conditions were reached <sup>23, 25</sup>. Prior to each experiment, NaNO<sub>3</sub> (10 mM) as a tracer was injected into the system to determine the system hold-up volume. In accordance with the local equilibrium assumption, the first statistical moment denoting the average retention time in the column was recorded <sup>31</sup>.

#### 5.2.3 Determination of Sorption Coefficient

 $K_{oc}$  (L Kg<sup>-1</sup>) values were obtained by dividing the net retention volume ( $V_{net,PFAS}$ ) with the mass of organic carbon in the SOM ( $m_{oc}$ ) as previously reported <sup>23</sup>:

$$K_{oc} = \frac{V_{net, PFAS}}{m_{oc}} = \frac{\left(t_{net, PFAS}^{peat} - t_{net, PFAS}^{SiC}\right) \times flow rate}{m_{peat} \times f_{oc}}$$
(eq. 5.1)

In the above equation,  $V_{net,PFAS}$  was determined from the flow rate of the mobile phase (mL min<sup>-1</sup>) multiplied by the net retention time ( $t_{net,PFAS}^{peat} - t_{net,PFAS}^{SiC}$ , min) of the respective peaks obtained from the first statistical moment <sup>31</sup>. Sorption to the chromatographic system (capillaries, frits, and column wall) and SiC packing material was negligible for PFAS in comparison with sorption to SOM in the column. The uncertainty on  $K_{oc}$  values considerably increases when  $V_{net,PFAS}$  becomes very small compared to those for the non-retaining tracer ( $V_{peat,tracer}$ ). Consistent with a previous study, to minimize error, all data for which  $V_{net,PFAS}$  was below 30 % of  $V_{peat,tracer}$  were discarded <sup>24</sup>. The method has been applied to investigate the sorption of a series of natural toxins and acidic organic chemicals to SOM with a lower limit of log  $K_{oc} = 0.7$  and a higher range of log  $K_{oc} = 4.25 \text{ L kg}^{-1}$  <sup>23, 24</sup>.

# 5.3 Results and discussion

#### 5.3.1 Sorption of PFCAs and PFSAs

To facilitate the comparison of distribution coefficients determined in this and other studies <sup>8, 17</sup>, all the  $K_d$  values (L kg<sup>-1</sup>) were normalized to organic carbon content ( $f_{oc}$ ) to obtain  $K_{oc}$  (L kg<sup>-1</sup>). For PFCAs and PFSAs, the log  $K_{oc}$  values determined using the dynamic column method in the present study (see Table C.8) ranged from 1.27 to 2.28 (perfluoroalkyl chain length n = 3 - 8) and from 1.38 to 2.55 (n = 4, 6, and 8), respectively. As illustrated in Figure C.5, the values from the present study fall into the medium to high ranges of log  $K_{oc}$  values computed from previous studies, where sorption of PFASs to various types of whole soil and sediment were examined <sup>8, 17</sup>. For sorption of organic chemicals from water to soil that is dominated by sorption to SOM, the natural variability of log  $K_{oc}$  values has been found to be less than 0.3 log units no matter the type of soil and polarity of the organic chemical <sup>25</sup>. The larger variability than 0.3 log units found in previous studies (as illustrated in Figure C.5) suggests that partitioning into organic matter due to the hydrophobic effect alone cannot fully explain the sorption of anionic PFCAs and PFSAs to soil. Rather, interactions such as ion exchange and steric effects, and the role of other soil components such as minerals and oxides cannot be neglected.



**Figure 5.2** Dependence of organic carbon normalized distribution coefficient (*Log K<sub>oc</sub>*, L kg<sup>-1</sup>) on solution pH and perfluoroalkyl chain length for PFCAs, PFSAs and FTSAs. Each data point represents an average value of two or three measurements

Sorption of PFCAs and PFSAs did not exhibit the same chain-length trend over the entire series as observed for longer chained species, as illustrated in Figure 5.2. C3, C4 and C5 PFCAs had almost identical log  $K_{oc}$  values (0.93) or showed a slight increase with increasing carbon chain length, and log  $K_{oc}$  values increased when perfluoroalkyl chain length was greater than 6.  $\Delta \log K_{oc}/\Delta nCF_2$  of ~0.45 - 0.55 was reported previously by Higgins and Luthy 2006, however this trend is only applicable to PFCAs with perfluoroalkyl chain length C7-C10 <sup>9</sup>. Similar increasement  $\Delta \log K_{oc}/\Delta nCF_2$  of 0.45-0.51 was observed in Guelfo and Higgins (2013) for C5-C10 PFCAs, whereas shorter chained (C3 and C4) PFCAs were outliners from the trend <sup>8</sup>.

As the point of zero charge of SOM is between 1.5 - 2.0, SOM is negatively charged in an environmentally relevant pH range (6 - 9) <sup>32</sup>. Thus, sorption of PFAS to SOM is also the consequence of electrostatic interactions. Short-chain compounds interact with SOM in a similar way as their longer chain homologues via hydrophobic effects and electrostatic interactions where the enhanced sorption is due to the steric effect <sup>8</sup>.

Sorption of FTSA exhibits the similar chain-length dependence as PFSAs. The slightly higher log  $K_{oc}$  values for FTSAs than those for PFSAs with identical perfluoroalkyl chain-length can be attributed to the extra ethyl group in FTSA molecules. No other laboratory derived partitioning coefficients are available for FTSA, which are among the most frequently detected classes of PFASs in AFFF-impacted groundwater. The field-derived log  $K_{oc}$  of 6:2 FTSA to bottom sediments (sampled from an urban water body with  $f_{oc} = 2.04\%$ ) and estuary sediments were 2.2 and 4.4 respectively <sup>33</sup>, higher than the laboratory-observed log  $K_{oc}$  values of 1.57 ± 0.19. Field-derived  $K_{oc}$  values have often been found to be higher than those determined in laboratory batch experiments, possibly attributed to nonlinear isotherms, sorption hysteresis, or sediment or soil aging <sup>26, 34</sup>.



**Figure 5.3** Dependences of (a) zeta-potential and (b) organic carbon normalized distribution coefficient (*log K<sub>oc</sub>*, L kg<sup>-1</sup>) on solution pH for three polyfluoroalkyl betaines (1 g L<sup>-1</sup>).

#### 5.3.2 Sorption of fluoroalkyl betaines

For the polyfluoroalkyl betaines, log  $K_{oc}$  values at pH of 5.90 are 1.95, 2.40, and 2.11 (L kg<sup>-1</sup>) for PFOAB, PFOSB and 6:2 FTAB, respectively. Sorption of 6:2 FTAB and PFOAB is stronger than their PFAA counterparts (PFH<sub>p</sub>A and PFOA, respectively) with equivalent perfluoroalkyl chainlength by 0.57 ~ 0.60 log units. Sorption of PFOSB is weaker than PFOS by 0.15 log units but higher than PFNA. As the betaines are amphoteric compounds, their speciation dictates interactions with SOM aside from the hydrophobic effect. As illustrated in Figure 5.3, the IEPs of 1 g L<sup>-1</sup> aqueous solutions of PFOAB, PFOSB, and 6:2 FTAB correspond to 4.5, 3.5, and 4.0 - 8.0 according to zeta-potential measurements. IEPs calculated by averaging the  $pK_a$  values predicted by SPARC (see the Appendix C) were 5.0, 4.5, and 7.0. Slightly higher than, or in the same range as, the zeta-potential measurement. It is noteworthy that the wide range of measured IEP for 6:2 FTAB is due to the great distance between two of its  $pK_a$  values and therefore a wide pH range at which 6:2 FTAB stays neutral (Figure C.3).

At pH of 5.9, the percentage of neutral species predicted by SPARC was 99.0 %, 90.4 % and 100 % for PFOAB, PFOSB, and 6:2 FTAB, respectively. Amphoteric compounds show minimum solubility in their isoelectric areas due to "tail-biting" between their ionic groups <sup>27</sup>, and minimum electrostatic repulsion between the negatively charged sorbent and a neutral sorbate. Therefore, the relatively higher retention of betaines than PFAAs with the same chain length by the SOM was expected. Their non-fluorinated moiety results in a favorable impact to sorption and retention, which is attributed to the incensement of hydrophobicity and the presence of a permanent positive charge. Since amphoteric compounds contain both cationic and anionic groups, the cationic groups (under conditions where they dominate) can act to decrease repulsion between anionic negatively charged groups, promoting closer packing of the head groups along the interfaces <sup>27</sup>. Most notably, this is the first study to our knowledge to report experimental distribution coefficients of FTSA and polyfluoroalkyl betaines, which are among the most abundant PFASs in real environmental samples <sup>5</sup>.

#### 5.3.3 Impact of solution pH

As demonstrated previously, sorption of anionic PFAS to sediment, soil and mineral surfaces normally decreases with increasing solution pH (3.8 - 8.0), mainly as a result of changes in sorbents rather than speciation of the ionic PFASs <sup>9, 13, 14</sup>. Figure 5.2 demonstrates that raising pH from 3.8 to 8.0 only slightly reduces sorption of all PFASs to the SOM. Each increase of unit pH reduces the sorption by approximately 0.11 - 0.13 log units for PFCAs, PFSAs and FTSAs. The influence of pH observed in the study, though small, is statistically significant and useful for mechanistic interpretation of sorption.



Figure 5.4 Illustration of interactions of PFOSB with SOM at different solution pH: (a) low solution pH all the ionisable groups of PFOSB are protonated, (b) medium solution pH when the carboxyl group of PFOSB is deprotonated, and (c) high solution pH when the carboxyl and sulfonamide groups are deprotonated

In Bronner and Goss <sup>25</sup> where the same dynamic column method was applied, it was found that the protonation/deprotonation of carboxylic groups in peat has a negligible influence on sorption of 60 nonionic organic chemicals regardless of the polarity of the compounds over the pH range of 4.5 - 7.2. Early studies on SOM also suggested that hydrophobic binding sites, i.e., nonpolar portions of humic substance polymer, are not affected by solution pH, and the hydrophobic partition mechanism can be independent of pH <sup>35</sup>. In view of these findings, the small effect of solution pH observed in this study can be attributed to changes in charge state of SOM and

electrostatic interactions between anionic PFASs and the sorbent, rather than changes in the strength of hydrophobic interactions.

By adjusting pH to allow cationic, neutral molecule or anionic forms to predominant, sorption of the amphoteric betaines as a function of solution pH was assessed and given in Figure 5.3b. We fitted the observed log  $K_{oc}$  to a speciation model:

$$K_{oc} = K_{oc}^{cation} \alpha^{cation} + K_{oc}^{neutral} \alpha^{neutral} + K_{oc}^{anion} \alpha^{anion}$$
(eq. 5.2)

Where  $\alpha$  is the mass fractions of the cation, neutral or anion species in the solution and,  $K_{oc}^{cation}$ ,  $K_{oc}^{neutral}$ ,  $K_{oc}^{anion}$  are corresponding  $K_{oc}$ , more details were given in Appendix C.6. Two attempts have been made to predict the pH-dependent sorption. In *simulation 1*,  $K_{oc}^{cation}$ ,  $K_{oc}^{neutral}$ ,  $K_{oc}^{anion}$ , and macroscopic acid dissociation constants ( $K_{a2}$  and  $K_{a1}$ ) were all regarded as unknown variables and were determined by fitting the equations with observed data. In *simulation 2*,  $K_{a2}$  and  $K_{a1}$  estimated by SPARC were substituted into the model as known parameters, whereas  $K_{oc}^{cation}$ ,  $K_{oc}^{neutral}$ , and  $K_{oc}^{anion}$  were computed as the most optimal values by data fitting. Both simulation results were given in Figure 5.5, Table C.8, and Table C.9.

As shown in Figure 5.5, the dashed curves are fitting results of betaine under varying pH through two simulation approaches. By comparing the relative errors (Table C.9), the simulation 1 has provided a better fitting result than the simulation 2. In Figure 5.5, the upper and lower boundaries of the fitting curves reveal the maximum and the minimum sorption of betaine-type PFASs. The sorption edges ( $Log K_{oc}$ ,  $L kg^{-1}$ ) are determined as: 1.90 - 3.81 for PFOAB, 2.03 – 2.65 for PFOSB, and 2.00 – 3.04 for 6:2 FTAB. It is noted that electrostatic repulsion seems to be profound for 6:2 FTAB at pH 11, as it is barely sorbed on SOM. Because the sorption of 6:2 FTAB at pH 11 (57.1 % in neutral form and 42.9 % in anionic form) is too low, the data point at pH 11 could not fit with the speciation model and unable to give the log  $K_{oc}$  value of anionic form 6:2 FTAB.

Sorption of betaine species follows the trend of log  $K_{oc}^{cation} > \log K_{oc}^{neutral} > \log K_{oc}^{anion}$ . Log  $K_{oc}$  values of cationic form PFOAB is 1.91 log units higher than that of the anionic form, and log  $K_{oc}$  values of cationic form PFOSB is 0.61 log units higher than its anionic form. As illustrated in Figure 5.4, at low solution pH carboxyl and sulfonamide groups of betaine (PFOSB) are protonated, sorption of the betaine (herein the compound exists as a cation, Figure 5.4a) is enhanced relative

to the neutral form (Figure 5.4b) due to electrostatic attraction with the negatively charged sites on peat, likewise, sorption of the anion (Figure 5.4c) is suppressed by electrostatic repulsion. Furthermore, due to the deprotonation of carboxyl and phenoxyl groups on the surface of the peat, peat contains an abundance of charged sites that enable peat to undergo ion exchange of cations with native cations and therefore increase sorption.



**Figure 5.5** Adsorption edges (log  $K_{oc}$ , L kg<sup>-1</sup>) of betaine-type PFASs to SOM. Solution composition is 5 mM CaCl<sub>2</sub>. The solid curves are speciation of betaine under varying pH. Dashed curves are fitting results. Hollow circles represent observed log  $K_{oc}$  from experiments.

#### 5.3.4 Impact of Ca<sup>2+</sup>

As displayed in Figure 5.6, calcium ion has a positive impact on the sorption of anionic PFASs to SOM. As illustrated in Figure C.6, the log  $K_{oc}$ -log[Ca<sup>2+</sup>] relation exhibits a linear trend for PFCAs, PFSAs and FTSAs.  $\Delta \log K_{oc}/\Delta \log[Ca^{2+}]$  for these PFASs varies from 0.18 to 0.27, which is very close to the change per log unit [Ca<sup>2+</sup>] reported for linear alkylbenzene sulfonate (0.22), but smaller for PFAAs sorption by sediments (0.36) <sup>9</sup>. Divalent cations such as Ca<sup>2+</sup> can neutralize negative surface charges of negatively charged SOM as manifested by the increase of zeta potential <sup>36, 37</sup>. Moreover, they can bridge negatively charged groups (carboxyl, phenolic or hydroxyl groups) and PFASs anions. This divalent cation-bridging effect has been substantive in many investigations of different adsorptive materials, e.g. sediments <sup>9, 11, 15, 37</sup> and black carbon <sup>38</sup>.

The increasing calcium ion has an opposite effect on sorption of FTAB, as illustrated in Figure 5.6.  $\Delta \log K_{oc}/\Delta \log [Ca^{2+}]$  for PFOSB was about - 0.16, and about - 0.30 for PFOAB and 6:2 FTAB. A similar trend was noticed in Li et al.<sup>39</sup>, where sorption of betaine-type hydrocarbon surfactants on the quartz sand surfaces was reduced with the addition of CaCl<sub>2</sub>. They concluded that the decline of sorption was related to the alteration of the adsorption pattern of the betaine surfactant on the surface of quartz by Ca<sup>2</sup>. Our interpretation was that the charge neutralizing or ion-bridging effects of Ca<sup>2+</sup> still apply, but cationic and anionic groups on betaines respond differently to changing  $[Ca^{2+}]$ . Without Ca<sup>2+</sup> or at low  $[Ca^{2+}]$ , the quaternary nitrogen group orientates towards the surface to interact with peat surface while the anionic part of the betaine surfactant positions away from the surface. The pattern is disrupted when the solid surface is covered with an increasing number of Ca<sup>2+</sup>, and the peat surface is becoming less negatively charged or even positively charged. Then, the anionic part of a betaine surfactant is moving closer towards the solid surface, while the quaternary ammonium group is being pushed away. The increasing repulsion seems to outweigh other effects, leading to less sorption at higher  $[Ca^{2+}]$ .



**Figure 5.6** Dependence of organic carbon normalized distribution coefficient ( $K_{oc}$  in L kg<sup>-1</sup>) on Ca<sup>2+</sup> concentration for 15 model PFASs. Note that figure (d) has logarithmic CaCl<sub>2</sub> concentration as the x-axis while other figures have perfluoroalkyl chain length.

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# 5.5 Appendix C. Supplementary data

Supplementary data related to this article are provided at the end of the thesis as Appendix C.

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# CHAPTER 6

Comparative Investigation of Sorption of Perfluoroalkyl and Polyfluoroalkyl Substances to Soil Organic Matter (SOM) and Pyrogenic Carbonaceous Materials (PCMs)

## Abstract

The fraction of carbonaceous combustion residues (termed as pyrogenic carbonaceous materials or PCMs) left in Aqueous Film-Forming Foams (AFFFs) source zones may strongly affect the environmental fate of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs). To examine the hypothesis, the present study assessed the sorption and desorption behaviors and sorption hysteresis of five PFASs, one cationic, two anionic, and two zwitterionic, in the presence of three types of PCMs (biochar, soot, and soot with fuel residues) and soil organic matter (Pahokee peat). Sorbents were characterized, and sorption-desorption isotherms were constructed using singlesolute batch sorption experiments. Electron microscopy imaging results showed that peat, biochar and soot samples all show a dual-domain structure with both amorphous and glassy sectors. Sorption results show that sorption of PFASs to biochar is the strongest compared with other sorbents and that to peat is the weakest, indicating that total sorption is dominated by sorption to PCMs. In addition, sorption to PCMs is more nonlinear than sorption to peat. Therefore sorption to PCMs overwhelms sorption in SOM particularly at a lower aqueous concentration (<1  $\mu$ g L<sup>-1</sup>) in the absence of attenuation effect. The surface activity of raw soot was attenuated by the oil deposit on soot surface, resulting in a decreased sorption of PFASs. Apparent sorption-desorption hysteresis exhibited by biochar was sorbate-specific and the most significant among all the sorbents, soot showed relatively high sorption hysteresis. The magnitude of hysteresis showed dependence on the stiffness of the sorbent matrix. This study for the first time showed that PCMs are potentially an important sink of PFASs in AFFF-impacted sites.

# Graphical Abstract



### 6.1 Introduction

Aqueous film forming foams (AFFFs) formulations, which contain perfluoroalkyl and polyfluoroalkyl substances (PFASs) to lower the surface tension along the AFFF-air interface, are used to extinguish hydrocarbon-based fuel fires <sup>1</sup>. The U.S. military accounts for 75 % of all the AFFF formulations used in the United States, municipal entities, and oil refineries make up the other main users <sup>2</sup>. Elevated PFAS concentrations in AFFF-affected areas have been observed in soil <sup>3-7</sup>, sediments <sup>4, 8, 9</sup>, groundwater <sup>3, 7, 10, 11</sup> and biota <sup>9</sup>.

Challenges of characterizing and remediating AFFF-impacted sites originate from an inadequate understanding of organofluorine chemistry and the high number of compounds involved. A major focus of early studies was on perfluoroalkyl acids (PFAAs, including perfluoroalkyl sulfonic acids, PFSAs and carboxylic acids, PFCAs) and partially fluorinated fluorotelomer sulfonic acids (FTSAs). Recently, more than 100 new anionic, zwitterionic and cationic fluorosurfactants have been identified in AFFF formulations <sup>10</sup> and in AFFF-impacted groundwater <sup>2</sup>, sediments and biota<sup>9</sup>. Recently, Munoz et al. (2016) have found that betaine-type PFAS dominated composition profiles (~ 94 % of total PFAS) in sediments following a major AFFF deployment during the Lac-Mégantic railway accident (Quebec, Canada) <sup>9</sup>. These newly identified PFASs have complex molecular structures containing functional groups such as sulfonyl, thioether, amine, ammonium, carboxylate, sulfonate, amine oxide, and betaine<sup>2, 10</sup>. They could undergo microbial or chemical transformations to produce persistent PFAAs, and therefore called precursors to PFAAs (PrePFAAs) <sup>12</sup>. PrePFAAs have become a major point of interest in the AFFF-impacted site investigation and remediation.

The environmental fate (i.e., mobility, persistence, and bioavailability) of anionic PFAA is strongly impacted by interactions with soil or sediment organic matter <sup>13-15</sup>. However, the organic matter present in soil is not homogenous and may contain both naturally occurring organic matter (or humic substances) and pyrogenic carbonaceous materials (PCMs). PCMs are part of the combustion continuum commonly termed as black carbon (BC), which refers to incompletely combusted and carbonized biomass and fossil fuel materials in a solid state. PCMs by average accounts for 4 % of total organic carbon (TOC) in soil (quartile range 2 - 13 %, calculated from 90 soil samples), but can reach up to 30 - 45 % of TOC in fire-impacted soils <sup>16</sup>.

Studies have shown that sorption of hydrophobic organic compounds in soils and sediments is often dominated by the PCM fractions <sup>17, 18</sup>, exceeding sorption by humic substances by a factor of 10 - 100 <sup>19</sup>. PCMs are also responsible for sorption hysteresis or irreversible sorption of many organic compounds in contact with soil and sediment <sup>20, 21</sup>. When a sorptive release is markedly slower than the uptake, a major fraction of the contaminant can appear to be irreversibly sorbed. Entrained contaminant molecules are considered to be inaccessible to microorganisms. As of today, little is known about the sorption of PFAS by PCMs. Given the state of knowledge on PFAS sorption, it is reasonable to assume that PCMs in the AFFF source zone may play a critical role in retaining PFAS in soil and sediment. PFAS molecules may be prone to hysteresis because their long tails could hinder diffusion in small pores and even lead to entrapment. PFASs tied up in PCM particles may slowly leach out over exceedingly long periods of time.

In a different perspective, PCMs could be the low-cost materials to replace expensive activated carbon as a soil amendment to prevent PFAS migration off site. Kupryianchyk et al. (2016) recently assessed the effect of biochar amendment to PFAS-contaminated soil <sup>22</sup>. Sorption of three PFAAs to biochar was found significant without the presence of contaminated soil, and the values of Freundlich coefficients  $K_F$  were lower than those derived from activated carbon in the study, but comparable to the values reported by another study <sup>23</sup>. However, no enhanced sorption of PFAAs was observed in the presence of soil, probably due to competitive sorption of co-contaminants and biochar fouling by humic substances. Hale et al. (2017) explored activated carbon amendment as a remediation approach to reduce PFOS mobility from a PFASs-contaminated sandy soil. It was found that PFOS leaching was reduced by 99% for activated carbon <sup>6</sup>. Chen et al. (2009) reported that sorption of PFOS onto oil-derived BC was highly influenced by solution chemistry such as [Ca<sup>2+</sup>] and pH <sup>24</sup>. Certainly, research is required to elucidate how PCMs interact with PFAS, in order to evaluate whether PCMs could behave as a reservoir of PFASs in AFFF-impacted sites or be used as low-cost remediation agents to replace activated carbons.

The goal of the present study is to evaluate the role of PCM in PFAS sorption in comparison to soil organic matter (SOM). The working hypothesis is that strong sorption to PCMs, rather than to humic substance, could control the persistence of PFASs in AFFF source zones. The PFAS species (Table 6.1) under investigation included two anionic, one cationic and two amphoteric PFASs; the

later three PFASs are the PrePFAAs, sorption of which by PCMs has been reported for the first time. Mechanisms and reversibility of PFAS-PCMs and PFAS-SOM interactions were examined using single-solute batch experiments. Sorption-desorption isotherms were constructed and fitted with empirical Freundlich models, and solid-water distribution coefficients were computed at different aqueous concentrations for comparing sorption capacity of PCMs and SOM. The sorption reversibility was quantified using a hysteresis index.

# 6.2 Experimental Section

#### 6.2.1 Standards and Reagents

Perfluorooctanoic acid (PFOA, 96 %) and sodium perfluorooctane sulfonate (PFOS, >98 %) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Perfluorooctane amido betaine (PFOAB,  $C_7F_{15}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$ , 95 %), and Perfluoroctaneamido ammonium iodide (PFOAAmS, F(CF<sub>2</sub>)<sub>7</sub>CONH(CH<sub>2</sub>)<sub>3</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>I, 98 %) were custom-synthesized at Beijing Surfactant Institute (Beijing, China). 6:2 fluorotelomer betaine (6:2)FTAB, F(CF<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>COOH) was obtained from Shanghai Kingpont Industrial Company, Ltd (Shanghai, China). The isotope-labeled internal standards obtained from Wellington Laboratories (Guelph, ON) were perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>] octanoic acid (MPFOA,  $F(CF_2)_4({}^{13}CF_2)_3{}^{13}COOH),$ perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanesulfonate (MPFOS,  $F(CF_2)_4({}^{13}CF_2)_4SO_3^{-})$ , 1H,1H,2H,2H-perfluoro-1-[1,2- ${}^{13}C_2$ ]-octane sulfonate, and M6:2 FTSA (F(CF<sub>2</sub>)<sub>6</sub><sup>13</sup>CH<sub>2</sub><sup>13</sup>CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>). HPLC-grade solvents including acetonitrile (ACN), methanol (MeOH), LC/MS-grade water and acetic acid (HAc) were purchased from Fisher Scientific (Ottawa, ON).

PFAS Species	Acronyms	Molecular structure	$pK_a{}^a$	IEP <sup>b</sup>
Perfluorooctane Sulfonate	PFOS	F F F F F F F F F F F F F F F F F F F	-3.3 <sup>25-27</sup>	
Perfluorooctanoic acid	PFOA		1.1 <b>-</b> 2.8 <sup>25-27</sup>	
Perfluorooctane amido betaine	PFOAB	$F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} H \xrightarrow{O^{-}} O^{-}$	$pKa_1 = 2.25$ $pKa_2 = 7.79$	4.5
6:2 fluorotelomer betaine	6:2 FTAB	$F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} F \xrightarrow{F} O \xrightarrow{O^{+}} O \xrightarrow{V^{+}} O^{-}$	$pKa_1 = 2.26$ $pKa_2 = 11.10$	4.0 - 8.0
Perfluoroctaneamido ammonium iodide	PFOAAmS		7.71	

#### Table 6.1 Target analyte classes, acronyms, and structures

<sup>a.</sup> The corresponding macroscopic *pKa*'s were determined by a physicochemical calculator SPARC (ARCHem, GA, USA).

<sup>b.</sup> Isoelectric point (IEP) of PFOAB and 6:2 FTAB was determined by measuring zeta potential of a series of FTAB aqueous solutions (1 g L<sup>-1</sup>) as a function of solution pH, more details are provided in Chapter 5.

Acronyms, molecular structures, acid dissociation constants and iso-eclectic points (IEPs) of the investigated PFASs are listed in Table 6.1. The isoelectric point (IEP) of PFOAB and 6:2 FTAB was determined by measuring zeta potential of a series of FTAB aqueous solutions (1 g L<sup>-1</sup>) as a function of solution pH, as introduced in our previous study (see Figure 5.3). Speciation of PFOAAmS, PFOAB and 6:2 FTAB as a function of pH and the corresponding macroscopic *pKa*'s were determined using SPARC (ARCHem, GA, USA).

#### 6.2.2 Sorbents

Biochar and chimney soot representing two types of PCMs were selected. Biochar (Charcoal Green® Pure Biochar MIXED) was purchased from Charcoal House LLC (Crawford NE., USA) and it was made from mixed hardwoods via slow pyrolysis. The biochar is clean commercial product thus it underwent a simple pre-treatment process before sorption studies. The biochar was washed with deionized water and dried at 103 °C. Then it was sieved through a 250-µm sieve and the fractions less than 250-µm was collected for sorption experiments.

The chimney soot was collected by local chimney sweeping companies, and it contained many impurities such as unburned sawdust, animal carcasses, inorganic ash and etc.. Therefore it was subjected to a more complex cleaning protocols. Soot samples were first passed through a 250-µm sieve, and the fractions less than 250-µm was collected for pre-treatments. After washed with DI water under constant agitation for one day, the soot slurry was centrifuged, and the supernatant was discarded. This cleaning procedure was repeated seven times. Afterward, the soot was washed in 1 M of HCl for three times, and the acid-washed soot was further washed with DI water until the pH of supernatants became neutral. The treated soot was then dried at 80 °C for 4 days. Finally, the soot was ground in a mortar and sieved through a 250-µm sieve again.

A portion of the pre-treated soot was extracted by 50:50 (vol:vol) hexane: acetone to eliminate oil residues. Solvent extraction was performed in an automatic Soxtherm extraction apparatus (Gerhardt Soxtherm, UK) and the amount of extracted oil was quantified using the Quebec method (MA400HYD11) for total petroleum hydrocarbon (TPH) analysis. TPH was determined using gas chromatograph (GC) equipped with a flame ionization detector. Details of oil extraction procedure are provided in the Appendix D. The soot after five cycles of extractions was deemed oil free, as the TPH concentration in the solvent extract was below the limit of quantification.

Pahokee peat (2BS103P) from the International Humic Substances Society (IHSS, Golden, CO) was selected as the model SOM. It is well-humidified with low ash and high organic content, and no undecomposed plant matter is visible under a microscope.

#### 6.2.3 Sorbent Characterization

The sorbents were characterized in terms of surface area, pore volume and distribution, and elemental composition. Nitrogen adsorption isotherms measured at 77 K with an Autosorb-1 analyzer (Quantachrome Co., USA) were used to determine the pore structures of the biochar and soot. Specific surface area was computed by using a Multi-BET equation. Pore volume and distribution were generated by applying density-functional theory and Monte Carlo simulation <sup>28, 29</sup>. The point of zero charge (PZC) of sorbent, the pH at which the total net surface charge is zero, was measured by mass titration equilibration method <sup>30</sup>.

Elemental compositions of the sorbents were analyzed at certified commercial laboratories. The
contents of carbon, hydrogen, nitrogen, and sulfur were analyzed by dynamic flash combustion method (Fisons EA-1108 CHNS-O Element Analyzer, Thermo Scientific), oxygen content was measured by infrared (IR) absorption (TCH600 N/O/H Determinator, LECO Co. MI, USA) and ash content was calculated by the mass difference of charred sample before and after 30 min ashing at 600 °C.

Sorbents were imaged by Transmission Electron Microscopy (TEM, Tecnai G2 F20, OR, USA) under high-resolution model using a carbon coated copper micro-grid as substrate. Morphologies of the sorbents were also revealed by Scanning Electron Microscopy (TEAM EDS Analysis System and iXRF XBeam XRF) with Octane Super Silicon Drift Detector. Before the SEM analysis, sorbents were dried until constant weight and coated with 4 nm platinum nanoparticles (Edwards Auto306, Sussex, UK).

### 6.2.4 Sorption and Desorption Experiments

Sorption and desorption kinetics and equilibrium isotherms were determined using single-solute batch experiments. Sorption kinetics was determined using a similar approach as described in the previous study <sup>31</sup>. Briefly, the kinetics experiments were conducted in triplicate 15-mL PP centrifuge tubes which contained a predetermined amount of PFAS and a sorbent in 5 mM CaCl<sub>2</sub> solution, as well as 200 mg L<sup>-1</sup> NaN<sub>3</sub> as a biocide. The solution to sorbent ratio (150 - 300) was chosen as such to ensure the final aqueous concentration within 20 - 80 % of the initial concentration, which was 500  $\mu$ g L<sup>-1</sup>. The second set of triplicate tubes containing the same aqueous phase without sorbent and PFASs was prepared and analyzed as a control. The tubes were shaken on an orbital shaker (Multitron Pro, Infors HT) at 20 °C and 250 RPM. At each sampling time, the tubes were centrifuged (3000 g and 20 min) and an aliquot of supernatant was sampled and diluted with methanol at 1:2 - 1:20 ratio and analyzed with LC-MS/MS. The corresponding solid phase concentration was calculated using an aqueous loss method.

Desorption kinetics was determined after the uptake kinetics experiments using the same set of tubes. The supernatant of each tube was removed as much as possible and replaced with 15 ml of PFAS-free solution. The tubes were resealed and shaken and sampled over the course of 14 days using the same procedure as described above.

Once the sorption-desorption kinetics were determined, sorption isotherms were determined using the same setup with the initial concentrations ranging from 2 to 3500  $\mu$ g L<sup>-1</sup>. Time of sampling was the equilibration times determined in the kinetic studies plus five days to account for the possible influence of varying concentrations on kinetics. Desorption isotherms were measured using the same tubes for sorption after decanting the supernatants and replace with a PFAS-free solution. pH of the system was measured at the beginning and the end of the experiments.

### 6.2.5 Mass Balance Test

At the end of desorption isotherm experiments, the sorbents in the tubes with the initial concentration of 1000  $\mu$ g L<sup>-1</sup> were subjected to solvent extraction. The tubes were centrifuged at 3000 g for 20 min and the supernatants were discarded. Peat and biochar were extracted in 13.5 mL of acetonitrile (ACN) plus 1.5 mL of 250 mM NaOH with 30 min of sonication and 2-h vigorous shaking. Extraction was repeated three times, and in the second and third extractions, 2.7 mL of ACN with 0.30 mL of 250 mM NaOH was used. PFASs concentrations of each extract were analyzed by LC-MS/MS. The presence of potential microbial degradation products was also checked for each solvent extract.

### 6.2.6 Quantitative LC-MS/MS Analyses

Quantitative analysis was performed using a Shimadzu UHPLC system coupled to an AB Sciex 5500 Qtrap mass spectrometer (LC-MS/ MS), working in multiple reaction monitoring (MRM) mode. Separation of PFASs was performed with a Kinetex C18 column (2.6  $\mu$ m, 50 × 3.0 mm, Phenomenex, Torrance, CA, USA), and ionization was achieved with both positive (for ammonium salts) and negative (for the amine) electrospray ionization. In both cases, a Kinetex EVO C18 column (5  $\mu$ m, 50 × 3.1 mm, Phenomenex) installed upstream of the UHPLC autosampler was used as a delay column to separate the PFASs leaching from polytetrafluoroethylene parts of the instrument, particularly the degasser. The details on chromatographic methods, mobile phases, monitored transitions, and calibration methods can be obtained from the Appendix D.

### 6.2.7 Sorption Isotherms

PFASs sorption isotherms were fitted with the Freundlich equation:

$$C_s = K_F C_w^n \tag{eq. 6.1}$$

Where  $C_s$  and  $C_w$  are the concentrations in the respective solid phase and liquid phase,  $K_F$  is the Freundlich sorption coefficient, and n reflects the isotherm linearity. Interpolated values of  $K_d$  were calculated at a concentration of  $C_w = 0.5$ , 2, 10, and 100 µg L<sup>-1</sup> to facilitate comparison of sorption between PFASs as well as the sorbents.

	Surface area	Pore volume	PZC	Elemental compositions, wt %							
	$m^2 g^{-1}$	cm <sup>3</sup> g <sup>-1</sup>		Ν	С	Η	0	S	molar H/C	molar O/C	Ash
Peat	0.90 32	NA	1.5 - 2.0	3.4	46.9	3.9	30.3	0.6	1.00	0.48	14.9
Biochar	442	0.36	8.6	0.3	86.3	1.1	1.3	0.0	0.16	0.01	11.0
Soot	N/A <sup>a</sup>	NA	2.8	3.4	62.8	4.1	4.4	0.0	0.78	0.05	25.3
Oil-free soot	0.55	0.08	2.6	3.6	62.2	4.5	4.2	0.0	0.87	0.05	25.5

 Table 6.2 Sorbent characteristics

<sup>a</sup> Not applicable, as the BET analysis could not be performed to the soot that contains oil residue.

# 6.3 Results and Discussion

### 6.3.1 Sorbent characterization

The results of the sorbents characterization are summarized in Table 6.2. According to the BET analysis, the biochar has the largest specific surface area of 442 m<sup>2</sup> g<sup>-1</sup> while the soot (oil-free) and the peat have 0.55 and 0.90 m<sup>2</sup> g<sup>-1</sup>, respectively. The pore volume of biochar is 0.36 cm<sup>3</sup> g<sup>-1</sup>, higher than the soot (0.08 cm<sup>3</sup> g<sup>-1</sup>) but lower than typical commercial activated carbons due to lack of activation (0.58 - 3.79 cm<sup>3</sup> g<sup>-1</sup>) <sup>31</sup>. Pore size distributions of the biochar and soot are given in Figure D.2. The biochar has 86.1 % of the pore volume located in micropores (< 20 Å, IUPAC definitions) whereas 94.7 % of the pore volumes of the soot is in the pores with the width ranging 1300 - 1700 Å.



**Figure 6.1** Morphology of Pahokee peat, biochar, soot and oil-free soot imaged by scanning electron microscopy (SEM)

Morphology of each sorbent is illustrated in the SEM and TEM images (Figure 6.1 and Figure D.3). The peat material is characterized as a random-network macromolecular organic solid with the irregular and chaotic arrangement (Figure 6.1a and Figure D.3a). In contrast, biochar has a well-developed microporous structure with a large number of hollow and through-holes (Figure 6.1b). The soot has a cheese-like structure that shallow pits and holes are located on the surface plugged with amorphous residues while the oil-free soot exhibits relatively clean surface with less amorphous residues (Figure 6.1c and d). It was conceived in past studies that both SOM (e.g., peat) and PCMs (e.g., biochar and soot) are composed of both "amorphous" and "glassy" domains, and this is confirmed with Figure D.3. More details on how to distinguish glassy/amorphous domians are provide in Appendix D.4. Peat mainly exhibits rubbery character, but crystal part was also observed (Figure D.3b). Biochar and soot show typical crystal patterns (Figure D.3c and e) and

carbon atom columns can be seen adjacent to the amorphous domain. In the nanometer scale, biochar and soot are similar in structure in accordance with a previous study <sup>33</sup>.

PZC indicates the overall charge status of the sorbents at a given solution pH. As listed in Table 6.2, Biochar has the highest PZC of 8.6, suggesting a basic character and positive to the neutral surface when present in the environmentally relevant pH range (pH 6 - 9). PZC of the peat and the oil-free soot are 1.5 - 2.0 and 2.6, respectively, indicating an acidic character. As for the elemental compositions, the biochar has the highest carbon content (86.3 %) while peat has the lowest (46.9 %). Elemental composition of the soot is very similar with the oil-free soot. Ash content of all sorbents ranges from 11.0 to 25.5 %; ash content of soot remains high even after intensive acid washing. Sorption strength of PFASs highly depends on the degrees of carbonization of the sorbent and aromaticity, which can be described by the molar H/C ratio <sup>34</sup>. Biochar has the lowest molar H/C ratio (0.16), showing the highest degree of carbonization and aromaticity, whereas the peat (1.00) has the lowest. The molar O/C ratio approximates surface hydrophilicity <sup>34</sup>. The O/C molar ratios of soot (0.05), oil-free soot (0.05), and biochar (0.01) are low, suggesting their surfaces are hydrophobic. By contrast, the molar O/C ratio of the peat is 0.48, indicating a more hydrophilic surface.



Figure 6.2 Sorption isotherms (at 20 °C) of PFASs to peat and biochar. Hollow circles represent data of desorption branch while solid black circles represent data of sorption branch

### 6.3.2 Sorption to Biochar

The Freundlich isotherm provided a good fit to the experimental data as demonstrated by the high correlation coefficients  $(r^2)$ , and fitted parameters are summarized in Table 6.3. Interpolated values of  $K_d$  (Table 6.3 and Figure 6.3) were calculated at a concentration of  $C_w = 0.5, 2, 10$ , and 100 µg L<sup>-1</sup>.As indicated by Table 6.3, PFAS sorption affinity or the extent of sorption (based on the magnitude of  $K_d$ ) for all the test compounds follows the order: biochar > oil-free soot > soot  $\approx$  peat. Sorption isotherms for the biochar are given in Figure 6.2. Biochar features high surface area (442  $m^2 g^{-1}$ ) and abundant microporosity (Figure D.2), which makes it a stronger sorbent than peat (0.9  $m^2 g^{-1}$ ) and soot (0.08  $m^2 g^{-1}$ ). Besides, sorption of PFASs, as indicated by log  $K_d$  values of PFOS  $(3.19 - 3.81 \text{ L kg}^{-1})$ , is lower than activated carbons <sup>31</sup>, and higher than the values reported for two other types of biochar in a recent study  $(1.78 - 3.11)^{22}$ . Likewise, the log K<sub>d</sub> values of PFOA sorption to biochar (2.65 - 3.07) are also higher than the previous study (~1.56)<sup>22</sup>. High sorption of biochar is not only attributed to its highly microporous structure but also favorable surface chemistry, being highly hydrophobic (low oxygen content) and positively charged (high PZC) <sup>31</sup>. However, values of  $K_d$  were normalized by the corresponding surface area, values of  $K_d$  (L m<sup>-2</sup>) are listed in Table D.4. It is found that sorption of biochar is the lowest among all the sorbent. This indicates that strong sorption by biochar is due to its large hydrophobic surface area and abundant micropores that contain higher sorption energy than macropores. Chemical properties may also played an important role in sorption, and it is noteworthy that for microporous carbonaceous adsorbents surface chemistry properties (e.g., surface basicity) are often highly dependent on the BET surface areas.

Thermodynamic driving forces for PFASs sorption from aqueous solution depends on the difference in free energy of the interactions with water compared to those with a sorbent. Principally, hydrophobic effect, electrostatic interactions/ion exchange, hydrogen bonding, and steric effect function simultaneously and result in distinct sorption behaviours. Comparing newly-identified PrePFAAs with the legacy PFAAs, stronger sorption of PrePFAAs to biochar than PFAAs was observed. PFOAAmS and 6:2 FTAB possess the highest log  $K_d$  values (3.86 – 4.43 and 3.39 – 4.66, relatively), followed by PFOAB (3.24 – 4.09) while sorption of PFOS and PFOA are the weakest. PFAAs ( $pK_a \le 2.80$ ) stay as anions at a solution pH of 8.1, which was measured after 14-day mixing for the system of 15 ml liquid phase with 0.05 g biochar. Thus sorption of

PFAAs is driven by the combination of hydrophobic effect and electrostatic attraction force. In contrast, PrePFAAs may exist in water as a cation, a neutral molecule, or an anion depending on ambient pH.

	Sorption isotherm parameters			Calculated concentrations dependent Log $K_d$ (L kg <sup>-1</sup> )					
	$K_F$		2	$C_w =$	$C_w =$	$C_w =$	$C_w =$		
	(µg g <sup>-1</sup> )(µg L <sup>-1</sup> ) <sup>-n</sup>	n	Γ-	0.5 μg L <sup>-1</sup>	2 μg L <sup>-1</sup>	10 μg L <sup>-1</sup>	100 μg L <sup>-1</sup>		
Peat									
PFOS	0.28	0.82	0.99	2.51	2.40	2.26	2.08		
PFOA	0.07	1.05	0.98	1.85	1.85	1.90	1.95		
PFOAB	0.05	1.10	0.98	1.70	1.70	1.78	1.90		
6:2 FTAB	0.04	1.29	0.94	1.48	1.70	1.90	2.18		
PFOAAmS	0.45	0.97	0.98	2.66	2.64	2.62	2.59		
Biochar									
PFOS	5.37	0.73	0.99	3.81	3.65	3.46	3.19		
PFOA	1.03	0.82	0.98	3.07	2.96	2.83	2.65		
PFOAB	9.52	0.63	0.97	4.09	3.87	3.61	3.24		
6:2 FTAB	31.20	0.45	0.89	4.66	4.33	3.94	3.39		
PFOAAmS	22.80	0.75	0.95	4.43	4.28	4.11	3.86		
Soot									
PFOS	0.19	0.80	0.98	2.34	2.23	2.08	1.90		
PFOA	0.04	0.91	0.94	1.60	1.60	1.48	1.48		
PFOAB	0.20	0.82	0.98	2.36	2.26	2.11	1.95		
6:2 FTAB	0.23	0.69	0.96	2.46	2.28	2.04	1.78		
PFOAAmS	0.45	0.76	0.96	2.72	2.58	2.41	2.18		
Oil-free soot									
PFOS	0.44	0.75	0.96	2.72	2.57	2.40	2.15		
PFOA	0.46	0.80	0.97	2.72	2.60	2.46	2.26		
PFOAB	0.44	0.80	0.98	2.71	2.58	2.45	2.26		
6:2 FTAB	0.62	0.78	0.97	2.86	2.72	2.57	2.36		
PFOAAmS	1.03	0.73	0.94	3.09	2.93	2.74	2.48		

**Table 6.3** Sorption isotherm parameters, calculated concentrations dependent  $K_d$  (at  $C_w = 0.5, 2, 10, \text{ and } 100 \ \mu\text{g L}^{-1}$ )



**Figure 6.3** Pair-wise comparison of solid-water distribution coefficients ( $K_d$ , L·g<sup>-1</sup>) of different sorbents, where the values of  $K_d$  are calculated at C<sub>w</sub> = 0.5, 2, 10 and 100 µg·L<sup>-1</sup>.

Chemical speciation of the three PrePFAAs was predicated by SPARC, and the results are provided in Figure C.2 and Figure C.4 in Appendix C (for the two betaines PFOAB and 6:2 FTAB) and the Figure D.6 of Chapter 6 (for PFOAAmS). At pH 8.1, PFOAB stays 33.25 % as a neutral molecule and 66.75 % as anion whereas 6:2 FTAB stays 99.90 % as its neutral molecule. The neutral species of the betaines have a minimum solubility at their isoelectric point, which is due to

the "tail-biting" effect between their ionic groups <sup>35</sup>, and therefore tend to show high sorption. For the anionic species, such as the one for PFOAB, the sorption may be reinforced by the electrostatic attraction to the positively charged biochar. PFOAAmS contains an amide group [-C(O)NH-] and a quaternary amine group  $[-NR_4^+]$  carrying a permanent positive charge. As the macro *pKa* of PFOAAmS is estimated to be 7.71 (by SPARC), 70.8 % of the PFOAAmS exists as a neutral species and 29.2 % of cationic species. Electrostatic repulsion between the quaternary amine group and the positively charged biochar surface may reduce the PFOAAmS sorption. The amide group can act as a hydrogen bond acceptor due to the presence of a C=O dipole and, to a lesser extent an N–C dipole, strengthening the sorption of PFOAAmS to biochar.

Sorbent	Sorbate	$\frac{\log K_d}{(\mathrm{L \ kg^{-1}})}$	f <sub>oc</sub> of sorbents (%)	$\log K_{oc}$ (L kg <sub>oc</sub> <sup>-1</sup> )	Reference
Soil with black carbon amendment	PFOS	1.78 - 3.11			22
Freshwater sediments 1	PFOS	3.94 - 4.26	0.75	2.9 - 3.2	36
Freshwater sediments 2	PFOS	1.11	0.56 - 9.66	2.7	13
Freshwater sediments 3	PFOS	0.27 - 1.37	0.16 – 1.49	3.0 - 3.2	37
Freshwater sediments 4	PFOS		0.03 - 1.6	3.4 - 3.7	38
Freshwater sediments 5	PFOS	2.40	4.80	3.7	39
Loam	PFOS	2.62 - 15.6	0.80 - 1.70	2.8	14
Soil with black carbon amendment	PFOA	~ 1.56			22
Freshwater sediments 2	PFOA		0.56 - 9.66	2.1	13
Freshwater sediments 4	PFOA		0.03 - 1.60	2.3 - 2.5	38
Loam	PFOA	0.63 - 3.50	0.80 - 1.70	1.9	14

 Table 6.4 Comparison with literature data

Sorption of PFASs to the biochar was highly nonlinear, which is consistent with past studies with other organics <sup>20</sup>. In Table 6.3, the values of n in the Freundlich equation range from 0.45 to 0.82, indicating high nonlinearity. Due to the severe nonlinearity, the distribution coefficient ( $K_d$ ) decreases with increasing C<sub>w</sub> and may range over several orders of magnitude for a given sorbate. For example, the  $K_d$  value for 6:2 FTAB (n = 0.45) varies by 2 orders of magnitude from C<sub>w</sub> = 0.1 µg L<sup>-1</sup> (limit of detection) to 1000 µg L<sup>-1</sup>. The nonlinearity is caused by a combination of surface site heterogeneity and pore size heterogeneity, and the nonlinearity may have many implications, such as ascertaining the possible sink of PFASs in soil with a significant percentage of PCMs, as discussed later.

### 6.3.3 Sorption to Soot

Sorption isotherms for the soot samples can be found in Figure D.5 in the Appendix D. Though both biochar and soot are BCs, sorption of PFASs to the soot and oil-free soot is weaker and more linear than the biochar. Sorption of PFOS to the oil-free soot ( $\log K_d = 2.15 - 2.72 \text{ L kg}^{-1}$ ) is one order magnitude lower than sorption to biochar (3.19 - 3.81), with a log  $K_d$  value calculated at C<sub>w</sub> = 0.5 µg L<sup>-1</sup> similar to that derived from freshwater sediments (2.40, Table 6.4) <sup>39</sup>. The lower sorption capacity of soot than biochar can be interpreted by lower surface area, lacking micropores, and acidic surface character. As shown in TEM images (Figure D.3c and e), despite that both the biochar and the soot have similar structures in the nanoscale, the soot does not possess the highly developed micropore structures. Pore volume of the biochar ( $0.36 \text{ cm}^3 \text{ g}^{-1}$ ) is 803 times higher than the soot ( $0.08 \text{ cm}^3 \text{ g}^{-1}$ ), whereas the surface of the biochar ( $442 \text{ m}^2 \text{ g}^{-1}$ ) is 803 times higher than the soot ( $0.55 \text{ m}^2 \text{ g}^{-1}$ ), which results in the low sorption capacity mass-basis and high sorption in surface-area basis. As mentioned above, the biochar losses the pre-eminence after surface area normalization, which reveals that the affinity of the soot per unit surface are to PFASs is greater than that of biochar.

Furthermore, the PZC of the oil-free soot and soot are 2.57 and 2.80, respectively, thus the surface of the soot is negatively charged at ambient pH (pH<sub>solution</sub> = 5.1 for oil-free soot and 5.0 for soot, measured 14 days after mixing 0.1 g sorbent with 15 ml of liquid phase). Concurrently, neutral species is dominant for PFOAB and 6:2 FTAB, PFOAAmS stays as cation while PFOS and PFOA are anions in the solution. For sorption to the oil-free soot, PFOAAmS possesses the highest value of log  $K_d$  (3.09 L kg<sup>-1</sup> at C<sub>w</sub> = 0.5 µg L<sup>-1</sup>), followed by 6:2 FTAB; PFOA, PFOS and PFOAB that have similar values of log  $K_d$  (2.71 – 2.86 L kg<sup>-1</sup>). Sorption of the cationic PFOAAmS may be facilitated by electrostatic attractions. It is worth noting that the soot sample contains relatively high ash content, which probably may play an equally important role as sorbent porous texture and surface chemistry in PFAS sorption.

The oil-free soot shows a higher affinity (2 - 10 folds) to PFASs compared to the soot with high oil content. In a past study conducted by Guelfo and Higgins <sup>14</sup>, the presence of non-aqueous phase

liquid (NAPL) had varying impacts on the sorption of PFAAs with different chain-length. The NAPL has facilitated the sorption of PFAAs to the soil with low organic carbon content ( $f_{oc}$ ) and hindered that to high foc soil. Critical separate phase concentration (CSPC) was proposed to evaluate the impact of oil 40, 41. Previous work with PAHs and PCBs indicated an increase in sorption when oil is present above the CSPC, typically 1000-3000 mg Kg<sup>-1</sup>, where oil serves as an additional sorbent. Although this paradigm is true for soil, it does not appear applicable for the soot. In the present study, the sorption of PFASs invariably diminishes even when the oil concentration goes as high as 16.7 g Kg<sup>-1</sup> of soot. The surface activity of the raw soot is attenuated by the presence of unburned liquid fuel or fuel byproducts, whose GC chromatograph had a similar profile as a motor oil reference material, indicating a high percentage of heavy hydrocarbon components (Figure D.1). High adsorptive sites are abundant on the soot surface; oil is a less competitive sorbent for PFASs. Rather, the presence of oil has lowered the sorption by blocking the access to microspores of soot <sup>40, 41</sup>. This may have a practical implication to real AFFFimpacted sites. After frequent fire activities, substances besides fuel (or NAPL) and its byproducts (e.g., incompletely carbonized biomass polymer fragments) or natural humic substances in the environment can coat PCM surfaces. Such would hinder the surface activity of PCMs and consequently lower the sorption of PFAS to PCM thereby facilitating PFAS mobility.

### 6.3.4 Comparison of sorption to BCs and peat

Sorption to peat is weaker and more linear than the above PCMs. The  $K_d$  values of PFOA, PFOAB, and 6:2 FTAB are similar (Log  $K_d \cong 1.82 \text{ L kg}^{-1}$ ) whereas PFOAAmS (2.62) and PFOS (2.31) are higher. As mentioned above, the structure of peat is conceptualized as a hydrated, "loosely-knit" gel phase, which acts as a dissolution medium for hydrophobic molecules expelled from the polar aqueous phase. According to the historic paradigm for sorption to SOM, the partitioning process generally follows linear isotherms under diluted conditions. Therefore, the magnitude of sorption to the peat largely depends on the hydrophobicity of sorbates. PFOS with the longest perfluoroalkyl chain showed stronger sorption than 6:2 FTAB with the shortest chain. Besides, the peat contains an abundance of charged sites such as deprotonated carboxyl and phenoxyl groups, allowing interactions with PFASs via ion exchange or electrostatic interactions. The pH of the system is measured as 5.3, at which betaine-type PrePFAAs are neutrally charged and therefore the sorption is primarily van der Waals force driven. Besides, sorption of PFOAAmS is enhanced due to the favorable electrostatic interactions between the negatively charged peat and the permanent positively charged quaternary ammonium group.

To further compare the sorption of the five PFASs by the four sorbents, Figure 6.3 provides a pairwise comparison of the interpolated  $K_d$  values at four concentrations, between the sorbents for sorption of all the five PFASs. Further statistical analysis based on Pearson correlation method was also performed to reveal correlations of magnitudes of  $K_d$  values, and more details can be found in Appendix D. Generally, roughly linear correlations were found between  $K_d$  of soot and oil-free soot (Figure 6.3d), suggesting oil residues did not fundamentally alter the nature of sorption to soot. Likewise, sorption behaviours of two different types of PCMs (Figure 6.3b), i.e., the biochar and oil-free soot, are correlated and similar, despite showing differences in  $K_d$  values up to two orders of magnitude. Adversely, no correlation was found between the peat to either biochar or the oil-free soot (Figure 6.3a and 6.3b).

	Γ	n	Hysteresis indices $I_i$				
	$K_F$ (µg g <sup>-1</sup> )(µg L <sup>-1</sup> ) <sup>-n</sup>	n	$\mathbb{R}^2$	$\begin{array}{c} \operatorname{Log} K_d \\ (\operatorname{L} \operatorname{Kg}^{-1})^a \end{array}$	$C_w = 1 \ \mu g \ L^{-1}$	$C_{\rm w} = 10 \ \mu g \ L^{-1}$	C <sub>w</sub> = 100 μg L <sup>-1</sup>
Poat							
PFOS	0.30	0.81	0.96	2.53	0.05	0.04	0.03
PFOA	0.16	1.04	0.94	2.20	1.33	1.24	1.16
PFOAB	0.10	1.13	0.96	1.95	0.80	0.92	1.04
6:2 FTAB	0.07	1.17	0.94	1.78	0.94	0.48	0.12
PFOAAmS	0.43	0.99	0.99	2.63	0.00	0.00	0.02
Biochar							
PFOS	4.99	0.86	0.98	3.74	0.00	0.25	0.69
PFOA	1.03	0.84	0.99	3.06	0.00	0.07	0.14
PFOAB	16.00	0.70	0.94	4.29	0.68	1.00	1.38
6:2 FTAB	178.00	0.37	0.80	5.44	4.72	3.85	3.12
PFOAAmS	23.60	0.81	0.96	4.43	0.03	0.17	0.33
Soot							
PFOS	0.60	0.69	0.95	2.87	2.18	1.46	0.91
PFOA	0.58	0.90	0.87	2.79	14.34	14.00	13.67
PFOAB	0.30	0.88	0.91	2.52	0.54	0.78	1.07
6:2 FTAB	0.25	0.75	0.90	2.48	0.08	0.25	0.45
PFOAAmS	0.82	0.71	0.90	3.00	0.84	0.66	0.49

**Table 6.5** Desorption isotherm parameters, and hysteresis indices calculated at different aqueous concentrations

Oil-free soot							
PFOS	0.82	0.80	0.94	2.97	0.86	1.09	1.33
PFOA	0.84	0.88	0.98	2.96	0.83	1.22	1.70
PFOAB	0.95	0.74	0.97	3.06	1.15	0.86	0.61
6:2 FTAB	1.42	0.72	0.91	3.24	1.29	1.03	0.79
PFOAAmS	1.16	0.76	0.96	3.14	0.13	0.20	0.27

<sup>a</sup>  $K_d$  is calculated at  $C_w = 0.5 \ \mu g \ L^{-1}$ 

### 6.3.5 Adsorption-desorption Hysteresis

A 14-day equilibration period was used to construct the sorption-desorption branches of the isotherm as illustrated in Figure 6.2. The desorption branches come off each sorption equilibrium point, and the desorption points correspond to total replacement of the liquid phase with sorbate-free simulant water. Desorption equilibrium data were also fitted by the Freundlich sorption model as a convenient means to assess isotherm linearity. Interpolated values of  $K_d$  for the desorption branch were calculated at a concentration of  $C_w = 0.5 \ \mu g \ L^{-1}$ . Results of model fitting and values of desorption  $K_d$  are provided in Table 6.5.

Sorption-desorption hysteresis for each PFAS sorbate varies from sorbent to sorbent. The phenomenon of sorption hysteresis is widely encountered in the literature <sup>20</sup>. This phenomenon sometimes can be attributed to experimental artifacts, such as degradation, the insufficient time allowed for mass transfer to reach a static condition, and perturbation of a competitive sorption. As mentioned earlier, hysteresis caused by degradation can be eliminated in the present study as no degradation products were found. The preliminary study also showed that the time was sufficient for the experimental system to approach *apparent sorption and desorption equilibria:* subsequent solution phase concentration changes were too small to be quantified over a reasonable period or further elapsed time.

The variation in irreversibility over the accessible isotherm is quantified using the thermodynamic index of irreversibility:

$$I_{i} = \frac{q_{e}^{d} - q_{e}^{s}}{q_{e}^{s}} | \tau, c_{e}$$
 (eq. 6.1)

Where  $q_e^s$  and  $q_e^d$  are are solid-phase solute concentrations for the single-cycle sorption and desorption experiments, respectively at  $C_i$  and temperature of T. Index of irreversibility,  $I_i$ , at constant temperature (20°C) and at three different concentration levels ( $C_i = 1$ , 10, and 100 µg L<sup>-1</sup>) that were calculated for each PFAS using the Freundlich model are listed in Table 6.5.

Apparent sorption-desorption hysteresis exhibited by biochar is most significant while peat is the least significant among all the sorbents. Major underlying causes of true hysteresis have been proposed to be pore deformation, which occurs to sorbents undergo physical swelling. For peat, except PFOAAmS showing minor hysteresis, the other four compounds exhibit hysteresis that increases with increasing C<sub>w</sub>. On the contrary, hysteresis is decreasing with decreasing concentration for biochar, except 6:2 FTAB for which sorption is too strong. Past studies have proven that the magnitude of hysteresis depends on the matrix stiffness. Hysteresis effect of rubbery-glassy solid declines with increasing loading of sorbates <sup>42</sup>. In this context, from the hysteresis index and sorbents characterization results, the increasing stiffness of sorbents investigated follows this order: peat (more rubbery), soot, and biochar (between glassy and fixed-pore). From the perspective of compounds, hysteresis varies with different compounds. For example, the hysteresis effect is similar for PFOAB with all sorbents while the effect is insignificant for PFOAAmS.

# 6.4 Environmental Implication

Soil and sediment organic matter may contain a mixture of SOM and PCMs. PCMs content may be exceedingly high (30 - 45 % of TOC) in AFFF source zones impacted by frequent fire activities. Past studies always use dual-domain isotherm to estimate the apportionment of sorption between SOM and PCMs<sup>16</sup>. As shown in the present study, sorption of PFASs to PCMs is nonlinear and exceeds absorption to SOM by a factor of ~2 - 5000 at an aqueous concentration of 0.1  $\mu$ g L<sup>-1</sup>. To better assess the role of PCMs or SOM, we assume a soil in which PCMs make up 30 % of TOC. The apportionment of sorption between peat and biochar was calculated based on the parameters of the Freundlich model listed in Table 6.3 and 6.5. As indicated in Figure 6.4, nonlinear sorption to PCMs would completely dominate total sorption (> 90 %) at low aqueous concentrations (< 0.1 µg L<sup>-1</sup>). However, peat plays an increasingly important role when the aqueous concentration of PFASs exceeds 1 µg L<sup>-1</sup> or higher. Figure 6.4 was created under the assumption that no attenuation effect occurred. In fact, in a real contaminated site, native organic compounds and/or SOM molecules compete for and block PCM sorption sites. This attenuation effect of PCMs (e.g., black carbon and coal) fouling by humic substances have been seen in many previous studies <sup>43, 44</sup>. If the attenuation effect was taken into account, the intersection of peat/biochar in Figure 6.4 would move towards the left, suggesting sorption to SOM is relatively more important even at lower aqueous concentration. Future study is needed to determine the apportioning of PFASs sorption to PCMs and SOM in the same system. Furthermore, strong sorption to PCMs found in this study suggests that such can lead to high retardation of PFASs in the AFFF source zone and decreased mobility of PFASs in groundwater. If sorption to soil is dominated by sorption to PCMs, a positive correlation between the spatial distributions of PCMs and PFASs concentration can be expected. Sorption to PCMs can also reduce the bioavailability of PrePFAAs to microorganisms and thus inhibit their biotransformation into perfluoroalkyl sulfonic acids (PFSAs) and carboxylic acids (PFCAs).



**Figure 6.4** Sorption of PFASs to peat and biochar in a hypothetical soil where PCM makes up 30 % of organic carbon, with the assumption of no attenuation effect of peat on biochar.

Sorption hysteresis or irreversible sorption has important implication for environmental transport, natural attenuation, bioavailability, and bioremediation and physicochemical remediation strategies. For years, pollutant transport and bioavailability models rest on the assumption of sorption reversibility ( $K_d$  derived from sorption equals to that derived from desorption). Sorption coefficients applied in such models are normally derived from adsorption isotherm, yet the prediction could be wrong due to the sorption hysteresis. Apparently, at the same aqueous concentration, values of Log  $K_d$  provided in Table 6.3 is distinct from that listed in Table 6.5, where hysteresis is noticed for both PCMs and SOM. Therefore, the issue of great importance in regard to contaminant interactions with PCMs is sorption irreversibility, manifested in hysteresis, or the non-singularity of the sorption and desorption branches of the isotherm <sup>21, 45, 46, 47</sup> Log  $K_d$  values provided in Table 6.5 can be applied in future studies for prediction of PFASs transport and bioavailability in the AFFF-impacted sites.

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# 6.6 Appendix D. Supplementary data

Supplementary data related to this article is provided at the end of the thesis as Appendix D.

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# **CHAPTER 7**

Summary, Conclusions, and Future Work

### 7.1 Summary and Conclusions

This thesis aimed to elucidate the interactions between PFASs and anthropogenic carbonaceous sorbents such as activated carbons and other carbonaceous adsorbents and naturally occurring carbonaceous materials such as SOM and PCMs. The investigations of interactions between PFASs and anthropogenic carbonaceous sorbents have provided the key information for adsorbent manufacturing and selection for water treatment. Moreover, understanding the sorption of major families of PFASs to SOM and PCMs is essential to predicting the environmental fate of PFASs in soil and groundwater, particularly for the AFFF-impacted sites. The major findings of the two parts are summarized below.

In Chapter 3, a series of carbonaceous sorbents with a wide range of precursor material, pore structure, and surface chemistry were systematically evaluated as potential adsorbents to treat PFOS and PFOA. Results show that adsorbent surface chemistry plays a more important role in controlling the extent of uptake rather than physical properties. The adsorption affinity was positively correlated with carbon surface basicity, reflected by total HCl uptake, suggesting that high acid neutralization or anion exchange capacity was critical for substantial uptake of PFOS and PFOA. Carbon surface acidity, which had been shown to affect organics uptake in early studies, had no impact on the extent of adsorption of PFOS or PFOA. Among all the adsorbents, synthetic polymer-based Ambersorb and phenolic-polymer-based activated carbon fibers were more effective than other activated carbons in removing PFOS and PFOA from aqueous solutions.

In Chapter 4, the findings from Chapter 3 were further explored by applying surface modification techniques, namely high-temperature and ammonia gas treatments, to enhance the sorption capacity of major commercial sorbents. Comparison of adsorption isotherms and adsorption distribution coefficients showed that surface modification can result in remarkable improvement of the sorption capacity towards PFOS and PFOA for wood-based carbons and activated carbon fibers. The ammonia gas treatment was more effective than the high-temperature treatment in enhancing surface basicity. The resultant higher point of zero charge and total HCl uptake correlated with improved adsorption affinity for PFOS and PFOA. The effectiveness of surface

modification to enhance adsorption varied with carbon raw material with wood-based carbons and activated carbon fibers showing enhancement by one to three orders of magnitudes. Coal-based and coconut shell carbons experienced little improvement or even a reduction in adsorption towards either PFOS or PFOA.

In Chapter 5, sorption of a total 15 PFAS compounds including both PFAAs and PrePFAAs to model SOM (Pahokee peat) was studied using a novel dynamic HPLC-based column method at varying aqueous chemical conditions (i.e., pH of the solution, and background divalent ion). Results show that the distribution coefficients (log  $K_{oc}$ ) of FTSAs with perfluoroalkyl chain-length of 4, 6, and 8 are similar to that of corresponding PFSAs with values of 1.42, 1.51, and 2.56 respectively. FTSAs also respond to changes in solution chemistry similarly as PFSAs. At solution pH of 5.9, the predominance of the neutral molecule over zwitterion gives rise to the relatively higher sorption of the polyfluoroalkyl betaines than the PFCAs of equivalent perfluoroalkyl chainlength. Calcium ion (concentration ranges from 0.5 - 50 mM) has a positive impact on the sorption of anionic PFASs to SOM, but a negative impact on the sorption of the betaines. Moreover, the increase in pH reduces sorption of all to SOM. Sorption of the betaine compounds follows the trend of log  $K_{oc}^{cation} > \log K_{oc}^{neutral} > \log K_{oc}^{anion}$ ; sorption edges for three betaines are determined to be: 1.82 - 3.34 for PFOAB, 2.35 - 4.01 for PFOSB, and 1.96 - 3.37 for 6:2 FTAB. This is the first study to investigate the transport potential of FTSAs and polyfluoroalkyl betaines.

In Chapter 6, sorption of a cationic PFAS (perfluoroctaneamido ammonium iodide, PFOAAmS), PFOA, PFOS and two FTABs (6:2 fluorotelomer betaine, 6:2 FTAB and perfluorooctane amido betaine, PFOAB) by PCMs was investigated and compared with SOM using single-solute batch sorption experiments. Sorption hysteresis was quantitatively assessed. Pahokee peat served as model SOM, and wood-derived biochar and chimney soot served as model PCMs. Results show that sorption of PFASs to biochar is the strongest compared with other sorbents and that to peat is the weakest, indicating that total sorption is dominated by sorption to PCMs. In addition, sorption to PCMs is more nonlinear than sorption to peat, therefore sorption to PCMs overwhelms sorption in SOM particularly at a lower aqueous concentration (<1  $\mu$ g L<sup>-1</sup>) in the absence of an attenuation effect. Apparent sorption-desorption hysteresis exhibited by biochar is sorbate-specific and the

most significant among all the sorbents; soot shows relatively high sorption hysteresis as well. The magnitude of hysteresis showed a dependence on the stiffness of the sorbent matrix. This study for the first time provided the evidence that PCMs are potentially an important sink of PFASs in AFFF-impacted sites. In the perspective of PFASs, cationic PFOAAmS had the highest sorption while PFOA sorbed relatively weaker than other PFASs. The discrepancy between  $log K_d$  values tends to diminish with increasing aqueous concentration.

# 7.2 Future Work

Studies have shown that a given polluted water sample usually contains more than one PFAS compound and they may compete for the sorption sites available in carbonaceous adsorbents that are used for water treatment or remediation purposes. Natural colloids such as humic and fulvic acids or polymeric substances of microbial origins may also compete for the same sorption sites since their molecules are rich in weakly acidic carboxylate and phenolate groups. In addition, those colloids are largely composed of relatively larger molecules than PFASs that can foul the carbon surface by plugging some pores that would be otherwise accessible to PFASs. However, this study was conducted in single-solute batch systems and free of competing species, and the competitive sorption was not considered. Therefore, it would be pertinent for real-world treatment scenarios to investigate competitive sorption among various PFAS species, as well as competition from non-PFAS constituents that could be present at higher concentrations than PFASs. It is necessary to examine both carbon physical properties and surface chemistry for their correlation with minimal carbon fouling potential by natural colloids as well as removal efficiency of PFASs from water. The knowledge can be applied to designing an economical treatment train where low-cost pretreatment methods can be applied to prolong the lifetime of high-cost activated carbon filters.

This research has provided critical preliminary data that many PrePFAAs such as zwitterionic betaines and cationic quaternary ammonium compounds can engage strong interactions with PCMs. The  $pK_a$  values of many of the PrePFAAs lie within the normal environmental pH range, and their molecular charge is sensitive to pH, a fact that complicates sorption behaviors. For instance, the sulfonamide group (-SO<sub>2</sub>NHR) has a  $pK_a$  between ~6 and ~9 depending on whether

R is H, alkyl, or –CH<sub>2</sub>CO<sub>2</sub>H. However, this study was conducted only at a fixed pH condition for each PCM and has not considered pH- and ionic strength-dependent sorption behaviors. Furthermore, the PCM surface also has variable (pH- and ionic strength-dependent) net charge. The positive charges present on some PFAS molecules can interact electrostatically with negatively charged sites on PCMs via cation exchange, and vice versa for negatively charged groups interacting with positively-charged sites via anion exchange. Therefore, it is essential to investigate the sorption behaviors of PrePFAAs under varying pH and ionic strength conditions to generate the knowledge that can be extrapolated to predicting the transport potential of PreFAAs in field conditions.

Furthermore, the hydrophobic effect and electrostatic interactions have been considered the main sorption mechanisms by which simple PFOS and PFOA interact with carbonaceous sorbents. The simplistic view is inadequate in explaining the strong sorption by PCMs of PFAAs as well as some PrePFAAs, which are hydrophilic. For instance, based on the simplistic view, weak acid functional groups (e.g.,  $R-CO_2^-$ ) in organic compounds cannot form strong interactions with PCM surfaces with weak acid functional groups (e.g.,  $-O_2C-$ ) due to the same negative charge. However, recent studies have demonstrated the existence of a class of exceptionally strong hydrogen bonds, which occur between those weak acid functional groups (i.e.,  $R-CO_2\cdots H\cdots O_2C-$ )<sup>-</sup>. Therefore, it is necessary to develop a deep mechanistic understanding of the interactions between PFAS compounds of various structures and PCMs of different physico-chemical characteristics in the future work. The findings from such a study might be used towards designing carbon materials can be tailored for removing PFAS.

Additionally, PCMs present in the soil are also influenced by the presence of natural colloidal materials in a similar fashion to the way activated carbon is affected. The colloids may affect not only sorption, but also desorption of PFASs by trapping a certain fraction of the PFAS molecules already in the pores of PCMs, or greatly slow down their rate of escape from these pores. Future research should focus on addressing the likely major role of those natural colloids in PCM-PFAS interactions.

# Appendix A

Supplementary Information For Chapter 3

# A.1 Materials and Methods

### A.1.1 Additional chemicals and reagents

Sodium chloride (A.C.S. certified) and acetonitrile (HPLC grade) used for adsorption experiments were purchased from Fisher Scientific (Ottawa, ON, Canada). Acetic acid (LC-MS grade), acetonitrile (HPLC grade), and ultrapure water (LC-MS grade) used during chemical analysis were also from Fisher Scientific. All aqueous solutions used for the experiments were prepared with water with a minimal resistivity of  $18 \text{ M}\Omega \text{ cm}^{-1}$ .

### A.1.2 Comparison of containers of different materials

Recoveries of PFOS from aqueous solutions were examined in 100-mL plastic bottles made of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene copolymer (PPCO), and polypropylene (PP) Nalgene containers. The test was conducted in triplicates and under acidic, neutral and basic conditions. The final test solutions of 100  $\mu$ g L<sup>-1</sup> of PFOS was prepared by adding 0.1 ml of PFOS stock solutions (1000 mg L<sup>-1</sup>) into 100 mL of 10 mM NaCl. Solution pH was then adjusted to 3, 7 and 10 using 0.1 M HCl or 0.1 M NaOH. The bottles were placed horizontally on an orbital shaker and shaken at the speed of 150 RPM and 25 °C for 48 h. Afterwards, 0.25 ml of the solution was transferred into in an HPLC vial which was pre-filled with 0.25 mL acetonitrile. Samples were stored at -18° C until LC-MS/MS analysis. Recoveries of PFOS in containers of different materials were shown in Appendix D. There was no statistically significant difference among different materials at the same pH. Recovery appeared to be more affected by solution pH. Considering that the adsorption experiments were to be conducted at neutral pH, PP and PPCO which had the highest recoveries was selected for this study.

Solution pH was found to exert a larger impact than the type of materials on mass recovery. Lowdensity polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polypropylene copolymer (PPCO) showed satisfactory and statistically identical recoveries at pH 7 or 10. One can conclude that all the materials evaluated can be used for adsorption experiments conducted under non-acidic conditions.



Figure A.1 Recovery of PFOS in containers of different materials

### A.1.3 Evaluation of filtration media

Recoveries of PFOS through filtration media was evaluated in duplicates by using Whatman<sup>®</sup> syringeless filters which are consisted of PP housing, cap, and a membrane made of 1) PP, 2) Nylon (NYL), or 3) polyvinylidene fluoride polymer (PVDF). Each filter has a capacity of about 1 mL. All membrane tested have a pore size of 0.20  $\mu$ m. The initial concentrations of PFOS before filtration were 100  $\mu$ g L<sup>-1</sup>, and concentrations after filtration were measured by LC-MS/MS. Average recoveries of PP, NYL, and PVDF were calculated as compared with controls and the recoveries were 0.11%, 0.10% and 5.19%, respectively. Substantial sorption to filters might have to do with large membrane surface area. Previously, Deng, et al. <sup>1</sup> used syringe filters for solid-liquid separation, and discarded the first 24 mL filtrate in order to minimize the impact of sorption to filters.

### A.1.4 Sorption experiments

The kinetics experiments were conducted in triplicate 50-mL PP centrifuge tubes with an initial PFOS or PFOA concentration of 500  $\mu$ g L<sup>-1</sup>. Sorbent to solution ratio was 10.0 mg: 50 mL, and 0.01 M NaCl was present as a background electrolyte. The tubes were placed an orbital shaker (Multitron Pro, Infors HT) maintained at 25 °C and 150 rpm, and sampled over 5-20 d. The second set of triplicate tubes containing only the aqueous phase and PFOS or PFOA was prepared and analyzed as controls. Adsorption isotherms were measured using PPCO bottles using sorbent to solution ratio of 10.0 mg:100 mL, and with initial aqueous PFOS or PFOA concentrations ranging from 5 to 5000  $\mu$ g L<sup>-1</sup>. Sampling took place according to the equilibration times determined in the kinetic studies, plus a few days to account for the possible influence of varying concentrations on kinetics. At each sampling time, test solutions were centrifuged at 5000 *g* for 15 min, and then 0.25 mL of supernatant was sampled and diluted with 0.25 mL acetonitrile. Acetonitrile diluted samples were further centrifuged at 10,000 *g* for 10 min to remove very fine suspended materials. The aqueous concentration was measured using LC-MS/MS and corresponding adsorbent concentration was calculated using an aqueous loss method as explained below.

The concentration of PFOS or PFOA adsorbed on adsorbents was calculated using the mass balance:

$$C_S = \frac{(C_0 - C_t) \cdot V}{M_C} \tag{eq. A.1}$$

Where  $C_s$  is the concentration of PFOS or PFOA on the solid phase (mg g<sup>-1</sup>),  $C_t$  and  $C_0$  are the aqueous concentrations at time *t* and time zero, respectively (µg L<sup>-1</sup>), *V* is the volume of the solution (L), and  $M_c$  is the mass of the adsorbent added (mg).

### A.1.5 LC-MS/MS analysis

The LC-MS/MS system comprised of a Nexera UHPLC (Shimadzu Co., Japan) and a QTRAP5500 hybrid mass spectrometer (AB Sciex, USA). All the external PTFE tubing in the UHPLC was replaced with PP tubing. Furthermore, a 100 mm  $\times$  2.1 mm Luna Max-RP column (Phenomenex

Inc., USA) was placed between the LC pumps and the autosampler to differentiate between background PFOS and PFOA present in the UHPLC system and blank contamination. The insertion of the column was essential to greatly lower the detection limits to allow for direct sample analysis without prior sample concentration. The LC-MS/MS system was operated under a negative, electrospray, and multiple reaction monitoring (MRM) mode. For each compound, two MRM transitions (PFOS: 499/79, 499/99; PFOA: 413/169, 413/369) were used for quantification and confirmation, receptively, under triple quadrupole mode. Chromatography separation using a 100 mm × 2.1mm Zorbax C8 column (Agilent Technologies Inc. Canada) was performed at a flow rate of 0.4 mL min<sup>-1</sup> with 0.15 % acetic acid (A) and acetonitrile with 0.15% acetic acid (B) as mobile phases. The LC gradient program was: B held for the first 0.5 min, ramped to 20% over 2.5 min, held at 90% for 4 min, reverted to 20% at 5.0 min. Calibration standards were prepared in 50:50 (v/v) acetonitrile/water to match with the solvent composition of water samples. Two sets of calibration standards were prepared to cover high- and low-concentration solutions respectively, in order to maintain linearity in the range of 0.005–100 ng mL<sup>-1</sup> for all sample concentrations observed. Quantitation was performed using 1/x weighted calibration curves with MPFOS and MPFOA as internal standards, which were added right before LC-MS/MS analysis.

### A.1.6 Kinetics and isotherm models

The adsorption uptake data were modeled with a pseudo-second-order kinetic model shown in eq. A.2  $^{2}$ :

$$\frac{t}{c} = \frac{1}{kC_s^2} + \frac{t}{c_s} = \frac{1}{v_0} + \frac{t}{c_s}$$
(eq. A.2)

where, *C* and *C*<sub>s</sub> are the PFOS or PFOA adsorbent concentration ( $\mu$ g mg<sup>-1</sup>) at time *t* and equilibrium, respectively,  $v_0$  is the initial adsorption rate ( $\mu$ g mg<sup>-1</sup> h<sup>-1</sup>), and *k* the rate constant (mg  $\mu$ g<sup>-1</sup> h<sup>-1</sup>).

The equilibrium adsorption data were found to be best modeled with Freundlich isotherm equation, which is shown in eq. A.3:

$$C_s = K_F C_e^n \tag{eq. A.3}$$

where,  $C_S$  is the equilibrium PFOS or PFOA adsorbent concentration,  $C_e$  the equilibrium aqueous concentration,  $K_F$  the Freundlich parameter for a heterogeneous adsorbent, and the exponential term, n, represents adsorbent site heterogeneity.

# A.2 Results and Discussion



**Figure A.2** Relationship between the initial adsorption rate ( $v_o$ ) and sorbent surface chemistry including point of zero charge (PZC), total acidity, total basicity, and bulk oxygen content for five granular adsorbents (F400, 1240C, WVB, BioNC, and Ambersorb).



**Figure A.3** Relationship between the ratio of acidity to basicity and point of zero charge (PZC) for the ten carbonaceous adsorbents


Figure A.4 Adsorption isotherms (at 25 °C) of PFOA onto the ten carbonaceous adsorbents



**Figure A.5** Relationship between the adsorption distribution coefficient ( $K_d$ , L m<sup>-2</sup>) and total acidity.

Adsorbents	K <sub>d</sub> for	r PFOS	K <sub>d</sub> for	PFOA
-	L m <sup>-2</sup>	L g <sup>-1</sup>	L m <sup>-2</sup>	L g <sup>-1</sup>
F400	2.90	2750.00	1.08	1030.00
BPL	0.06	90.00	0.07	91.70
1240C	1.14	1630.00	1.15	1640.00
WVB	1.42	2210.00	0.12	189.00
BioNC	0.68	1590.00	0.11	255.00
AquaNC	2.20	4100.00	0.58	1080.00
Ambersorb	12.40	11100.00	4.03	3640.00
ACF15	5.32	6640.00	5.90	7360.00
ACF20	2.47	5080.00	0.01	16.30
ACF25	3.69	6630.00	4.07	7320.00

**Table A.1** Adsorption distribution coefficients ( $K_d$ ) calculated at  $C_e = 0.3 \ \mu g \ L^{-1}$ .

## A.3 References

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## Appendix B

Supplementary Information For Chapter 4

#### B.1 LC-MS/MS analysis

The LC-MS/MS system comprised of a Nexera UHPLC (Shimadzu Co., Japan) and a QTRAP5500 hybrid mass spectrometer (AB Sciex, USA). The LC-MS/MS system was operated under a negative, electrospray, and multiple-reaction-monitoring (MRM) mode. For each compound, two MRM transitions (PFOS: 499/79, 499/99; PFOA: 413/169, 413/369) were used for quantification and confirmation, receptively, under triple quadrupole mode. Chromatography separation using a 100 mm × 2.1mm Zorbax C8 column (Agilent Technologies Inc. Canada) was performed at a flow rate of 0.4 mL/min with 0.15 % acetic acid (A) and acetonitrile with 0.15% acetic acid (B) as mobile phases. The LC gradient program was: 20% B held for the first 0.5 min, ramped to 90% over 2.5 min, held at 90% for 1.5 min, reverted to 20% at 5.0 min. One 100 mm × 2.1 mm Luna Max-RP column (Phenomenex Inc., USA) was placed between the LC pumps and the autosampler to differentiate between background PFOS and PFOA present in the UHPLC system and blank contamination. The insertion of the column was essential to lower greatly the detection limits to allow for direct sample analysis without prior sample concentration. Calibration standards were prepared in 50:50 (v/v) acetonitrile/water to match with the solvent composition of water samples. Two sets of calibration standards were prepared to cover high-concentration and low-concentration solutions respectively, to maintain linearity for all sample concentrations observed. Quantitation was performed using 1/x weighted calibration curves with MPFOS and MPFOA as internal standards.

# B.2 Freundlich isotherm equation and calculation of PFOS/PFOA sorbent concentrations using an aqueous loss method

Freundlich isotherm equation is described by  $C_s = K_F C_e^n$ , where  $C_s$  is the equilibrium PFOS or PFOA adsorbent concentration,  $C_e$  the equilibrium aqueous concentration,  $K_F$  the Freundlich parameter for a heterogeneous adsorbent, and the exponential term, *n*, represents adsorbent heterogeneity.

Concentrations of PFOS or PFOA adsorbed on activated carbon and carbon fibers were calculated using the mass balance:

$$C_S = \frac{(C_0 - C_t) \cdot V}{M_C} \tag{eq. B.1}$$

Where  $C_s$  is the concentration of PFOS or PFOA on the solid phase (µg mg<sup>-1</sup>),  $C_t$  and  $C_0$  are the aqueous concentrations at time *t* and time zero, respectively (µg L<sup>-1</sup>), *V* is the volume of the solution (L), and  $M_c$  is the mass of the adsorbent added (mg).

Table B.1 Properties of PFOS and PFOA

	Molecular formula	Anion size <sup>a</sup> (length x diameter, nm)	M.W. (g mol <sup>-1</sup> )	Solubility <sup>b</sup>	$pK_a$	CMC <sup>e</sup> (mM)
PFOS	$C_8F_{17}SO_3H$	1.0 x 0.5	500.1	$0.52-0.68 \text{ g L}^{-1}$ (potassium salt)	-3.3 °	8.5 (sodium salt)
PFOA	$C_7F_{15}CO_2H$	0.8 x 0.5	414.1	9.52 g L <sup>-1</sup>	-0.1 $\sim 0.7$ $^d$	9~30

<sup>a</sup> Molecular size was estimated by Diamond v3.0 based on MOLfile.

<sup>b</sup> from Kauck and Diesslin<sup>1</sup> and Kissa<sup>2</sup>.

<sup>c</sup> from Kissa <sup>2</sup>.

<sup>d</sup> from Goss <sup>3</sup>.

<sup>e</sup>CMC: critical micelle concentration, from Guo, et al. <sup>4</sup> and Kissa <sup>2</sup>

Sorbents		PFOS			PFOA			
	$C_e = 0.$	3 μg/L	$C_e = 1$	0 μg/L	$C_e = 0.$	3 μg/L	$C_e = 1$	0 μg/L
	$K_d$ (L/mg)	$K_d \left( L/m^2 \right)$	$K_d$ (L/mg)	$K_d \left( L/m^2 \right)$	$K_d$ (L/mg)	$K_d (L/m^2)$	$K_d$ (L/mg)	$K_d (L/m^2)$
1240c	2.53	1.77	0.83	0.58	1.65	1.16	2.56	1.79
1240 HT	6.26	5.55	98.00	86.80	1.15	1.01	0.44	0.39
1240 AT	9.31	8.48	53.80	48.90	1.49	1.36	0.68	0.62
F400	1.77	1.87	0.46	0.48	1.02	1.08	29.80	31.50
F400 HT	0.36	0.41	2.14	2.42	2.18	2.47	3.37	3.82
F400 AT	1.18	1.25	6.92	7.39	3.95	4.22	2.53	2.70
BioNC	1.58	0.67	0.38	0.16	0.25	0.11	0.09	0.04
<b>BioNC HT</b>	2.24	1.67	1.01	0.75	0.95	0.71	0.31	0.23
<b>BioNC AT</b>	12.50	11.70	78.70	74.20	6.18	5.82	7.76	7.31
WVB	2.21	1.42	0.44	0.28	0.19	0.12	0.08	0.05
WVB HT	3.40	3.49	1.73	1.77	1.69	1.73	0.57	0.59
WVB AT	17.10	16.30	1840.00	1750.00	6.18	5.89	7.76	7.40
ACF20	5.11	2.49	1.76	0.86	0.02	0.01	376.00	183.00
ACF20 AT	41.90	24.50	335.00	196.00	458.00	268.00	$4.00 \times 10^{7}$	2.34 x10 <sup>7</sup>

**Table B.2** Adsorption distribution coefficients  $(K_d)$  calculated for PFOS and PFOA at two equilibrium aqueous concentrations

#### **B.3 References**

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## Appendix C

Supplementary Information For Chapter 5

## C.1 Nomenclature of compounds with authentic standards

Acronym	Name	Formula
	Parfluoroallad said	F(CF <sub>2</sub> ) <sub>n</sub> COOH
ГГАА	remuoroarkyracia	F(CF <sub>2</sub> ) <sub>n</sub> SO <sub>3</sub> -
PFCA	Perfluoroalkyl carboxylic acid	F(CF <sub>2</sub> ) <sub>n</sub> COOH
PFBA	Perfluorobutanoic acid	F(CF <sub>2</sub> ) <sub>3</sub> COOH
PFPeA	Perfluoropentanoic acid	F(CF <sub>2</sub> ) <sub>4</sub> COOH
PFHxA	Perfluorohexanoic acid	F(CF <sub>2</sub> ) <sub>5</sub> COOH
PFHpA	Perfluoroheptanoic acid	F(CF <sub>2</sub> ) <sub>6</sub> COOH
PFOA	Perfluorooctanoic acid	F(CF <sub>2</sub> )7COOH
PFNA	Perfluorononanoic acid	F(CF <sub>2</sub> ) <sub>8</sub> COOH
PFSA	Perfluoroalkyl sulfonic acid	$F(CF_2)_nSO_3^-$
PFBS	Perfluorobutane sulfonate	F(CF <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> -
PFHxS	Perfluorohexane sulfonate	F(CF <sub>2</sub> ) <sub>6</sub> SO <sub>3</sub> -
PFOS	Perfluorooctane sulfonate	$F(CF_2)_8SO_3^-$
n:2 FTSA	n:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>n</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
4:2 FTSA	4:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>
6:2 FTSA	6:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> -
8:2 FTSA	8:2 Fluorotelomer sulfonate	F(CF <sub>2</sub> ) <sub>8</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> -
PFOSB	Perfluoroctanesulfonamide betaine	$F(CF_2)_8SO_2NH(CH_2)_3N^+(CH_3)_2CH_2COOH$
PFOAB	Perfluorooctaneamide betaine	$F(CF_2)_7CONH(CH_2)_3N^+(CH_3)_2CH_2COOH$
6:2FTAB	6:2 Fluorotelomer sulfonamide betaine	$F(CF_2)_6CH_2CH_2SO_2NH(CH_2)_3N^+(CH_3)_2CH_2COOH$

 Table C.1 Nomenclature of the compounds under investigation

Table C.2 Nomenclature of the isotope-labelled internal standards

Acronym	Name	Formula
MPFBA	Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>4</sub> ]butanoic acid	F( <sup>13</sup> CF <sub>2</sub> ) <sub>3</sub> <sup>13</sup> COOH
MPFHxA	Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid	$F(CF_2)_4{}^{13}CF_2{}^{13}COOH$
MPFOA	Perfluoro-n-[1,2,3,4-13C4]octanoic acid	$F(CF_2)_4({}^{13}CF_2)_3{}^{13}COOH$
MPFNA	Perfluoro-n-[1,2,3,4,5- <sup>13</sup> C <sub>5</sub> ]nonanoic acid	$F(CF_2)_4({}^{13}CF_2)_4{}^{13}COOH$
MPFHxS	Perfluoro-1-hexane[ <sup>18</sup> O <sub>2</sub> ]sulfonate	$F(CF_2)_6SO^{16}O_2^-$
MPFOS	Perfluoro-1-[1,2,3,4-13C4]octanesulfonate	$F(CF_2)_4(^{13}CF_2)_4SO_3^{-1}$

M6:2 FTSA	1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]-octane sulfonate	$F(CF_2)_6^{13}CH_2^{13}CH_2SO_3^{-1}$
M8:2 FTSA	1H,1H,2H,2H-perfluoro-1-[1,2- <sup>13</sup> C <sub>2</sub> ]-decane sulfonate	F(CF <sub>2</sub> ) <sub>8</sub> <sup>13</sup> CH <sub>2</sub> <sup>13</sup> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup>

#### C.2 Details on chemicals and reagents

Perfluoroalkyl acids (a mixture containing PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFUdA, PFDoA, PFTrDA, PFTeDA, PFBS, PFHxS, PFOS, PFDS, >98% purity) and 8:2 FTSA (>98% purity) were obtained from Wellington Laboratories (Guelph, ON, Canada). 4:2 FTSA and 6:2 FTSA were obtained from Synquest Laboratories (Alachua, FL, USA). PFOSB and PFOAB were custom-synthesized at Beijing Surfactant Institute (Beijing, China). 6:2 FTAB was obtained from Shanghai Kingpont Industrial Company, Ltd (Shanghai, China).

Isotope-labelled internal standards (MPFBA, MPFHxA, MPFOA, MPFNA, MPFHxS, MPFOS, M6:2 FTSA, M8:2 FTSA) were all obtained from Wellington Laboratories (Guelph, ON, Canada).

HPLC-grade solvents including acetonitrile (ACN), methanol (MeOH), LC/MS-grade water and acetic acid (HAc) and Optima-grade ammonium hydroxide (NH<sub>4</sub>OH) were purchased from Fisher Scientific (Ottawa, ON, Canada).

#### C.3 Characteristics of model soil organic matter (SOM)

Pahokee Peat was obtained from the International Humic Substance Society (IHSS) and the elemental analyses were originally performed by Huffman Laboratories (Wheat Ridge, CO, USA. Characterization of the peat is provided by IHSS<sup>1</sup>.

Table C. 3 Pahokee Peat Characteristics

Sample	Cat. No.	H <sub>2</sub> O	Ash	С	Н	0	Ν	S
Pahokee Peat II	2BS103P	6.2	12.7	46.9	3.9	30.3	3.4	0.6

The peat was homogenized and micronized as suggest by Bronner and Goss <sup>2</sup>. Particle size distribution (Figure C.1) was measured by laser scattering particle size distribution analyzer (Horiba Instruments, INC. Irvine, USA). The mean particles size of treated peat is 6.88  $\mu$ m.



Figure C.1 Particle size distribution of micronized Pahokee peat

### C.4 Analytical methods

Table C.4 Quantitative	analytical	method	1
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Instrument	Shimadzu Nexera UHPLC coupled to an AB Sciex 5500 QTrap mass spectrometer				
Ionization	Negative electros	pray			
Acquisition mode	Multiple reaction	monitoring (MRM)			
Analytical column	Ascentis Express	Ascentis Express F5, 2.7 µm, 100 x 2.1 mm			
Delay column	Kinetex EVO C18, 5 µm, 50 x 3.1 mm				
Column Temperature	40°C				
Mobile Phases	A: 0.15% acetic a	cid in LC-MS water			
	B: 0.15% acetic acid in acetonitrile				
Gradient Profile	<u>Time (min)</u>	Percentage B	Flow Rate (mL/min)		
	1.5	5	0.4		
	10	95	0.4		

	12	95	0.4	
	12.1	5	0.4	
	13	Stop		
Injection Volume	5 μL			
Calibration	Linear calibration	curve, 1/x weighted		
Quantified compounds	Analyte	RT (min)	Analyte	RT (min)
	PFBA	4.72	4:2 FTSA	5.86
	PFPeA	5.62	6:2 FTSA	6.97
	PFHxA	6.25	8:2 FTSA	8.01
	PFHpA	6.81	PFBS	5.38
	PFOA	7.35	PFHxS	6.2
	PFNA	7.86	PFOS	6.89

#### **Table C.5** Quantitative analytical method 2

Instrument	Shimadzu Nexera UHPLC coupled to an AB Sciex 5500 QTrap mass spectrometer			
Ionization	Positive and negative electrospray			
Acquisition mode	Multiple reaction mo	nitoring (MRM)		
Analytical column	Agilent Zorbax SB-C	8, 3.5 μm, 2.1 x 100 mm		
Delay column	Kinetex EVO C18, 5	μm, 50 x 3.1 mm		
Column Temperature	40°C			
Mobile Phases	A: 0.15% acetic acid in LCMS water			
	B: 0.15% acetic acid in acetonitrile			
Gradient Profile	Time (min)	Percentage B	Flow Rate (mL/min)	
	1	20	0.5	
	4	80	0.5	
	6	80	0.5	
	6.1	20	0.5	
	7	Stop		
Injection Volume	5 μL			
Calibration	Linear calibration curve, 1/x weighted			
Quantified compounds	Analyte		RT (min)	

PFOSB	4.23
PFOAB	3.8
6:2FTAB	3.76

Compound	Ionization	Quantifying	Qualifying	Internal standard	IS transition
Compound	mode	transition	transition	Internal Standard	
PFBA	-MRM	213 > 169		MPFBA	217 > 172
PFPeA	-MRM	263 > 219		MPFHxA	315 > 270
PFHxA	-MRM	313 > 269	313 > 119	MPFHxA	315 > 270
PFHpA	-MRM	363 > 319	363 > 169	MPFOA	417 > 372
PFOA	-MRM	413 > 369	413 > 169	MPFOA	417 > 372
PFNA	-MRM	463 > 419	463 > 219	MPFNA	468 > 423
PFBS	-MRM	299 > 80	299 > 99	MPFHxS	403 > 103
PFHxS	-MRM	399 > 80	399 > 99	MPFHxS	403 > 103
PFOS	-MRM	549 > 80	549 > 99	MPFOS	503 > 80
4:2 FTSA	-MRM	327 > 80	327 > 307	M6:2 FTSA	429 > 81
6:2 FTSA	-MRM	427 > 80	427 > 407	M6:2 FTSA	429 > 81
8:2 FTSA	-MRM	527 > 80	527 > 507	M8:2 FTSA	529 > 81
PFOSB	-MRM	641 > 538	641 > 483	MPFOS	503 > 80
PFOAB	-MRM	555 > 452	555 > 378	MPFOA	417 > 372
6:2 FTAB	+MRM	569 > 446	571 > 120	M6:2 FTSA	429 > 81

 Table C.6 Monitored transitions for Analytical Methods 1 and 2

#### Table C.7 Instrumental detection limits (iLOD)

Compound	iLOD (ng/mL)	Compound	iLOD (ng/mL)
PFBA	0.1	4:2 FTSA	0.01
PFPeA	0.05	6:2 FTSA	0.05
PFHxA	0.02	8:2 FTSA	0.01
PFHpA	0.01	PFOSB	0.1
PFOA	0.01	PFOAB	0.1
PFNA	0.01	6:2 FTAB	0.2
PFBS	0.02		
PFHxS	0.02		
PFOS	0.01		

The instrumental detection (iLOD) was defined as the smallest concentration that would yield a detectable chromatographic peak with a signal to noise ratio  $S/N > 3^{-3}$ . Instrumental detection limits ranged from 0.005–0.2 ng mL<sup>-1</sup>. The limit of quantitation was defined as the concentration that would yield a chromatographic peak with a signal to noise ratio S/N > 10 or the lowest concentration of the calibration solution, whichever value is larger <sup>3</sup>.

#### C.5 Prediction of speciation of betaine-type PrePFAAs using SPARC

For PFOAB, the macroscopic acid dissociation constants was determined as: macro  $pK_{a1} = 2.26$ , and macro  $pK_{a2} = 7.79$ . The values and the speciation in pH of 0 - 14 were predicted by a physicochemical calculator SPARC (ARCHem, GA, USA).



Figure C.2 The influence of pH (0 - 14) on speciation of PFOAB

For PFOSB, corresponding macroscopic  $pK_a$  was determined as: macro  $pK_{al} = 2.25$ , and macro  $pK_{a2} = 6.78$ .



Figure C.3 The influence of pH (0 - 14) on speciation of PFOSB

For 6:2 FTAB, corresponding macroscopic  $pK_a$  was determined as: macro  $pK_{al}$ = 2.26, and macro  $pK_{a2}$ = 11.12.



#### **SPARC Speciation Plot**

Figure C.4 The influence of pH (0 - 14) on speciation of 6:2 FTAB

#### C.6 Estimation of sorption edges of betaine-type PFASs

Adsorption is maximum in the pH region where cationic species predominates and decreases on with increasing pH. log  $K_{oc}^{cation} > \log K_{oc}^{neutral} > \log K_{oc}^{anion}$ . We fit the observed  $K_{oc}$  to a speciation model:

$$K_{oc} = K_{oc}^{cation} \alpha^{cation} + K_{oc}^{neutral} \alpha^{neutral} + K_{oc}^{anion} \alpha^{anion}$$
(eq. C.1)

$$\alpha^{cation} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a2}K_{a1}}$$
(eq. C.2)

$$\alpha^{neutral} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a2}K_{a1}}$$
(eq. C.3)

$$\alpha^{anion} = \frac{K_{a2}K_{a1}}{[H^+]^2 + K_{a1}[H^+] + K_{a2}K_{a1}}$$
(eq. C.4)

where  $\alpha$  is the mass fractions of the cation, neutral or anion species in the solution.  $K_{oc}^{cation}$ ,  $K_{oc}^{neutral}$ , and  $K_{oc}^{anion}$  (L kg<sup>-1</sup>) are the respective  $K_{oc}$  as fitting parameters, it is assumed that they are pH-independent. Fitting parameters were estimated by substituting the observed  $K_{oc}$  at different pH values into equations C.1-C.4. Two attempts have been made to captures the trends of pH-dependent sorption. In *simulation 1*,  $K_{oc}^{cation}$ ,  $K_{oc}^{neutral}$ ,  $K_{oc}^{anion}$ ,  $K_{a2}$  and  $K_{a1}$  were all regarded as unknown variables. In *simulation 2*,  $K_{a2}$  and  $K_{a1}$  estimated by SPARC were substituted into the model as known parameters,  $K_{oc}^{cation}$ ,  $K_{oc}^{neutral}$ , and  $K_{oc}^{anion}$  were computed as the most optimal values by data fitting. Both simulation results were compared, relative error is listed in the following table.

	$Log K_{oc}$ of cation		Log <i>K</i> <sub>oc</sub> of neutral molecule		$Log K_{oc}$ of anion	
	Simulation 1	Simulation 2	Simulation 1	Simulation 2	Simulation 1	Simulation 2
PFOAB	3.81	3.35	1.95	1.97	1.90	1.82
PFOSB	2.65	4.01	2.46	2.41	2.03	2.35
6:2 FTAB	3.04	3.37	2.00	1.96		

		Simulated log Koc	$\log K_{oc}$ Simulated $\log K_{oc}$		
pН	Observed log Koc	Simulation 1	Error	Simulation 2	Error
PFOAB					
4.00	2.18	2.18	0%	2.12	3%
5.90	1.95	1.95	0%	1.97	-1%
8.25	1.92	1.92	0%	1.86	3%
9.00	1.92	1.91	1%	1.83	5%
11.00	1.66	1.90	-15%	1.82	-10%
PFOSB					
4.00	2.64	2.64	0%	2.64	0%
5.90	2.40	2.50	-4%	2.40	0%
8.25	2.44	2.45	0%	2.35	4%
9.00	2.45	2.40	2%	2.35	4%
11.00	2.06	2.06	0%	2.35	-14%
6:2 FTAB					
4.00	2.28	2.28	0%	2.12	7%
5.90	2.11	2.01	5%	1.96	7%
8.25	2.00	2.00	0%	1.96	2%
9.00	1.92	2.00	-4%	1.96	-2%

Table C.9 Observed, simulated log  $K_{\rm oc}$  and relative errors

#### C.7 Comparison of the experimental observation with literature data

PFASs	$\log K_{\rm e}  \mathrm{L \ kg^{-1}}$	$\log K^{a} \log^{-1}$
	$Log K_d$ , L Kg	$\log K_{oc}$ , L Kg
PFOAB	$1.51 \pm 0.18$	$1.84 \pm 0.18$
PFOSB	$1.99 \pm 0.08$	$2.31 \pm 0.08$
6:2 FTAB	$1.57 \pm 0.19$	$1.90 \pm 0.19$
PFBS	$1.05 \pm 0.02$	$1.38 \pm 0.02$
PFHxS	$1.14 \pm 0.04$	$1.47\pm0.04$
PFOS	$2.22 \pm 0.15$	$2.55 \pm 0.15$
PFBA	$0.94 \pm 0.02$	$1.27 \pm 0.02$
PFPeA	$0.92 \pm 0.01$	$1.24 \pm 0.01$
PFHxA	$0.93 \pm 0.004$	$1.26 \pm 0.004$
PFHpA	$1.02 \pm 0.004$	$1.35 \pm 0.004$
PFOA	$1.22 \pm 0.06$	$1.54 \pm 0.06$
PFNA	$1.95 \pm 0.11$	$2.28 \pm 0.11$

Table C.10 Observed distribution coefficients of 15 PFASs (at 5 mM CaCl<sub>2</sub> and pH 5.2)

4:2 FTSA	$1.09 \pm 0.04$	$1.42 \pm 0.04$
6:2 FTSA	$1.19 \pm 0.04$	$1.51 \pm 0.04$
8:2 FTSA	$2.24 \pm 0.21$	$2.56 \pm 0.21$

<sup>a</sup> The organic carbon content  $f_{oc}$  is 0.469.



**Figure C.5** Comparison of the experimental observation of partitioning coefficients between water and Pahokee peat (log  $K_{oc}$ , L kg<sup>-1</sup> in 5 mM CaCl<sub>2</sub>, pH 5.3) with the literature data which were determined from whole soils, whole sediments or predominantly inorganic with low organic content (<sup>a</sup> cited from Guelfo et al.<sup>4</sup>; <sup>b</sup> cited from Johnson et al. <sup>5</sup>)

#### C.8 Impact of Ca<sup>2+.</sup>

The impact of calcium is illustrated in Figure C.6,  $\log K_{oc}$ - $\log[Ca^{2+}]$  relation exhibits a linear trend for PFCAs, PFSAs and FTSAs.



**Figure C.6** Dependence of organic carbon normalized distribution coefficient (Log  $K_{oc}$  L kg<sup>-1</sup>) on Ca<sup>2+</sup> concentration (mM) for 12 model PFASs.

#### C.9 References

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## **Appendix D**

Supplementary Information For Chapter 6

#### D.1 LC-MS/MS analytical method

Details on the LC-MS/MS analytical method are described in Tables D.1

Instrument	Shimadzu Nexera UHPLC coupled to an AB Sciex 5500 QTrap mass spectrometer					
Ionization	Positive and negative	electrospray				
Acquisition mode	Multiple reaction mon	itoring (scheduled MRM)				
Analytical column	Agilent Zorbax SB-C8	3, 3.5 μm, 2.1 x 100 mm				
Delay column	Kinetex EVO C18, 5 µ	um, 50 x 3.1 mm				
Column Temperature	40°C					
Malila Dhasas	A: 0.15% acetic acid i	n LC-MS water				
Mobile Phases	B: 0.15% acetic acid in acetonitrile					
	Time (min)	Percentage B	Flow Rate (mL/min)			
	1.0	5	0.5			
	7.0	95	0.5			
Gradient Profile	9.0	95	0.5			
	9.1	5	0.5			
	11.5	Stop				
Injection Volume	5 μL					
Calibration	Linear calibration curve, 1/x weighted					

Table D.1 Quantitative LC-MS/MS analytical method

Table D.2 Monitored quantitation transitions for quantitative analytical methods

Analyte	Transition Monitored	Internal standard	IS transition monitored
PFOA	413>369	MPFOA	417>372
PFOS	499>80	MPFOS	503>80
PFOAB	555>378	MPFOA	417>372
6:2 FTAB	569>120	M6:2FTSA	429>81
PFOAAmS	513>454		

#### D.2 Analysis of the oil residue extracted from the soot

The oil residue of the acid-washed soot was extracted in an automatic Soxtherm extraction apparatus (Gerhardt Soxtherm, UK) and the extracted oil was quantified using the Quebec method

(MA400HYD11) for total petroleum hydrocarbon (TPH, C10-C50) analysis. Briefly, a soot sample (3 g) was placed in a cellulose extraction thimble. In the automatic Soxtherm extraction apparatus (Gerhardt Soxtherm, UK), 150 mL of the extraction solvent comprised of 50:50 (vol:vol) hexane: acetone was added to a set of extraction beakers containing boiling stones. The extraction proceeded with an optimized extraction program, for which the recovery for an oil reference standard (weathered diesel, purchased from Restek Corporation, USA) was 98.5  $\pm$ 1.5%. The solvent extracts were concentrated by nitrogen blow-down to 10 mL and then cleaned up with 0.8 g of silica gel. The supernatant was pipetted out for analysis. TPH was analyzed by a gas chromatograph equipped with flame ionization detector. The TPH concentration was determined based on the integration of C10-C50 peaks after subtraction of a blank solvent run.

Instrument	Agilent 7820A GC-FID			
Column	Model	Agilent 125-1011, DB1 capillary column		
	Carrier gas	Helium, 5mL/min		
Oven	Rate(°C /min)	Temperature (°C) 40	Hold (min) 0.25	
	30	300	0	
	10	340	7	
ALS	Injection volume		1 μL	
	Solvent wash(PreInj)		3	
	Solvent wash(PostInj)		3	
	Sample wash		1	
	Sample pump		4	
	Viscosity delay		1 sec	
Inlet	COC inlet, oven track			
Detector	Heater		360°C	
	H <sub>2</sub> flow		45mL/min	
	Air flow		450mL/min	
	Makeup flow		45mL/min	

Table D.3 Quantitativ	e analytical metho	d for total petroleum	hydrocarbons	(TPH,	C10-C50)
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**Figure D.1** GC chromatographs of a diesel standard, a motor oil standard and the oil residue extracted from the acid-washed soot.

#### D.3 Pore size distribution of biochar and oil-free soot



Figure D.2 Pore size distribution of the biochar and oil-free soot samples

#### D.4 Results of transmission electron microscopy (TEM)

All the adsorbents were imaged by Transmission electron microscopy (TEM) (Tecnai G2 F20, OR, USA) under a high-resolution mode using a carbon coated copper micro-grid as substrate. All three adsorbents have both glassy and amorphous domains. The glassy domain has distinct characters compared with the amorphous domain: 1) Glassy domains feature clear pattern of carbon atom columns (e.g., left side on Figure D-c; 2) As shown in Figure b, with lower magnification, the black particle has a clear interface with surrounding the flocculent amorphous area. Besides, the degree of contrast of the black particles significant changed with rotation of the sample, while no change was observed in the amorphous area; 3) There are bright visible diffraction spots in the micro-diffraction imaging at the glassy domain, which is evident of the crystallographic characteristics; 4) The glassy domains (e.g., the black particle in Figure D-b) showed lattice contrast under the proper diffraction conditions. It is noted that the sorbents are not homogenous, therefore we scanned the material first and picked out the spots that can best illustrate the physical state of the matrix. More technique would be needed to quantify the actual percentage of glassy vs. amorphous domains.





Figure D.3 Morpholog \_\_\_\_\_ char soot and oil soot imaged by TEM.

#### D.5 Mass balance test

After desorption, tubes with an initial concentration of  $1000 \ \mu g \ L^{-1}$  were checked for mass balance for five PFASs individually. The supernatant of each tube was discarded after 20 min of centrifugation at 3000 g. Peat and biochar were subjected to 15 ml of acetonitrile (ACN) and NaOH (25 mM) extraction, with 30 min of sonication and 2 hrs of vigorous stirring. Extraction was repeated three times: in the second and third times, only 3 ml of ACN with 25 mM NaOH was added to each tube. Recovery of PFASs with peat and biochar is illustrated in Figure D.5.



Figure D.4 Mass balance test of PFASs from biochar and peat

After the sorption-desorption study, the recovery of all five PFASs from peat and biochar has been evaluated via extraction by ACN with 25 mM of NaOH. The recovery fractions of PFASs are between 0.76-1.34 for peat and 0.70-1.13 for biochar as illustrated in Figure D.5. For PrePFAAs, daughter compounds (e.g., PFOS, PFOA or other short-chain PFAA) were checked in solvent extracts, but none was found, indicating that biotic and abiotic transformations were negligible. Good recovery is the precondition to precisely quantify concentrations of PFAS and PrePFAAs in the various matrices. Among PFASs investigated, PFOS and PFOAB have the best recovery (among 0.92-1.10) while 6:2 FTAB has the lowest recovery (0.76 to peat, and 0.73 to biochar). Mass recovery of peat is higher than that of biochar except for PFOS. The variation of recovery could be attributed to the experimental error, such as losing of sorbents during liquid phase replacement at the beginning of desorption. The error was accumulating during the process of spiking-sampling for sorption section- sampling for desorption section. On the other side, the discrepancy of recovery could be speculated based on sorbent properties.

Sorption of PFASs to biochar is described as adsorption, whereas partitioning or dissolution better describes its sorption to peat<sup>1</sup>. Extraction of PFASs from peat is hypothesized as a re-partitioning process between rubbery organic matters and organic solvent while extraction of PFASs from biochar is more difficult. PFASs that have traveled to the deep micropores in the biochar by diffusion have a hard time finding their way back. This viewpoint may be supported by hysteresis index (Table 6.5). Apparent sorption-desorption hysteresis exhibited by biochar is most significant ( $I_i = 0.4.72$ ) among all the sorbents, more so than peat ( $I_i = 0.1.33$ ). Furthermore, the recovery test was performed after the whole sorption-desorption loop. Sorbents have been left soaking and exposed to the PFAS solution for 14 days. The materials could be conditioned by PFAS molecules during the sorption-desorption process, and the exposure may lead to irreversible deformation of the sorbent matrix. Pores may be closed afterward and PFAS thus entrapped are unavailable for extraction<sup>2</sup>.

#### D.6 Sorption and desorption of PFASs to soot and oil-free soot



Figure D.5 Sorption-desorption isotherms (at 20 °C) of PFAS to soot. Hollow circles represent data of desorption branch while black solid circles represent data of sorption branch

## D.7 Calculated concentrations dependent $K_d$ (L m<sup>-2</sup>)

	$C_w =$	$C_w =$	$C_w =$	$C_w =$
	0.5 μg L <sup>-1</sup>	2 μg L <sup>-1</sup>	10 μg L <sup>-1</sup>	100 µg L <sup>-1</sup>
Peat				
PFOS	0.360	0.279	0.202	0.134
PFOA	0.079	0.079	0.088	0.099
PFOAB	0.056	0.056	0.067	0.088
6:2 FTAB	0.034	0.056	0.088	0.168
PFOAAmS	0.508	0.485	0.463	0.432
Biochar				
PFOS	0.015	0.010	0.007	0.004
PFOA	0.003	0.002	0.002	0.001
PFOAB	0.028	0.017	0.009	0.004
6:2 FTAB	0.103	0.048	0.020	0.006
PFOAAmS	0.061	0.043	0.029	0.016
Oil-free soot				
PFOS	0.954	0.676	0.457	0.257
PFOA	0.954	0.724	0.524	0.331
PFOAB	0.932	0.691	0.512	0.331
6:2 FTAB	1.317	0.954	0.676	0.417
PFOAAmS	2.237	1.548	0.999	0.549

**Table D.4** Calculated concentrations dependent  $K_d$  (L m<sup>-2</sup>), the values were normalized by corresponding surface area of each sorbent.

### D.8 Speciation of PrePFAA

Speciation of PFOAAmS, PFOAB and 6:2 FTAB as a function of pH and the corresponding macroscopic *pKa*'s were determined using SPARC (ARCHem, GA, USA). Speciation of PFOAB and 6:2 FTAB has been reported in our previous study (see Appendix III), and here we only provide speciation of PFOAAmS.

For PFOAAmS, the macroscopic acid dissociation constants was determined as: macro  $pK_a = 7.71$ . The values and the speciation in pH of 0 - 14 were predicted as following.



**Figure D.6** The influence of pH (0 - 14) on speciation of PFOAAmS

# D.9 Pair-wise comparison of solid-water partitioning coefficients ( $K_d$ , L g<sup>-1</sup>) of different sorbents

Pearson's r is a measure of the linear dependence, the closer the Pearson's r is to  $\pm 1$ , the stronger correlation there is. A Linear dependence was noticed between PCM sorbents. Correlations were found between K<sub>d</sub> of soot and oil-free soot with Pearson's r ranging from 0.893 - 0.812 at C<sub>w</sub> = 0.5 - 10 µg·L<sup>-1</sup> and 0.654 at C<sub>w</sub> = 100 µg·L<sup>-1</sup> (with 95 % confidence level), suggesting oil residues did not fundamentally alter the nature of sorption to soot. Likewise, r for biochar and oil-free soot is 0.743 - 0.919 at C<sub>w</sub> = 2 - 100 µg·L<sup>-1</sup>, indicating sorption behaviors of two different types of PCMs are correlated and similar. Adversely, no correlation was concluded with peat to any <u>PCMs</u>. In fact, for some PFOA, PFOAB and 6:2 FTAB, *K<sub>d</sub>* values show roughly negative correlations, which is due to high sorption nonlinearity of the <u>PCMs</u>.

## D.10 References

1. Xing, B.; Senesi, N.; Huang, P. M., *Biophysico-chemical processes of anthropogenic organic compounds in environmental systems*. John Wiley & Sons: 2011; Vol. 4.

2. Braida, W. J.; Pignatello, J. J.; Lu, Y.; Ravikovitch, P. I.; Neimark, A. V.; Xing, B., Sorption hysteresis of benzene in charcoal particles. *Environmental Science & Technology* **2003**, *37*, (2), 409-417.