



# Sorption and desorption of anionic, cationic and zwitterionic polyfluoroalkyl substances by soil organic matter and pyrogenic carbonaceous materials

Yue Zhi, Jinxia Liu\*

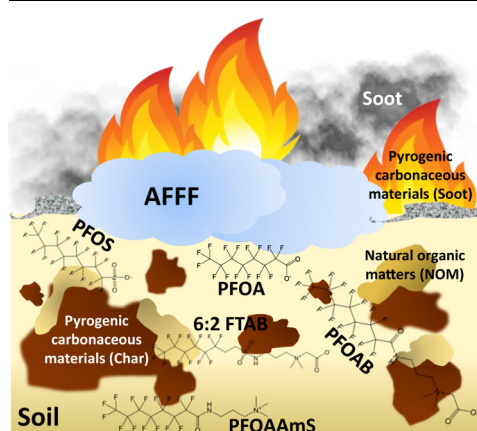
Department of Civil Engineering, McGill University, Montréal, Québec H3A 0C3, Canada



## HIGHLIGHTS

- Sorption of PFASs to PCMs is substantially stronger and more extensive than SOM.
- PCMs are potentially a significant sink of PFASs in AFFF-impacted sites.
- Cationic PFAS has the highest sorption and the lowest mobility towards PCMs and SOM.
- Fouling of PCMs would hinder the sorption, thereby facilitating PFAS mobility.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

PFOS  
PFOA  
Pyrogenic carbonaceous materials  
Soil organic matter  
Biochar  
Soot

## ABSTRACT

The fraction of pyrogenic carbonaceous materials (PCMs) left in aqueous film-forming foams (AFFFs) source zones may strongly affect the persistence of perfluoroalkyl and polyfluoroalkyl substances (PFASs). To examine the hypothesis and gain an additional perspective on the potential contributions of different organic phases present in soil, we measured sorption and desorption of five AFFF relevant PFASs, one cationic (perfluorooctaneamido ammonium iodide, PFOAAmS), two anionic (perfluorooctane sulfonate, PFOS; perfluorooctanoic carboxylate, PFOA), and two zwitterionic (perfluorooctane amido betaine, PFOAB; 6:2 fluorotelomer sulfonamido betaine, 6:2 FTAB), by three types of PCMs (biochar, soot, and oil-free soot) and soil organic matter (SOM, presented by Pahokee peat) by single-solute batch sorption experiments. It was found that sorption to PCMs is substantially stronger and nonlinear than SOM, especially for the cationic PFOAAmS. Strong sorption to PCMs discovered in this study suggests that such phenomenon can lead to high retardation of PFASs in the AFFF source zone and decreased mobility of PFASs in groundwater, especially for the precursor compounds to the legacy perfluoroalkyl acids. Fouling of PCMs by unburnt oil would hinder the surface activity of PCMs and consequently lower the sorption of PFAS, thereby facilitating PFAS mobility. Moreover, sorption hysteresis was observed in all the systems with sorption of 6:2 FTAB by biochar being the most significant. This study for the first time provided the evidence that PCMs are potentially a significant sink of PFASs in AFFF-impacted sites.

\* Corresponding author.

E-mail address: [jinxia.liu@mcgill.ca](mailto:jinxia.liu@mcgill.ca) (J. Liu).

## 1. Introduction

Aqueous film forming foams (AFFFs) that contain perfluoroalkyl and polyfluoroalkyl substances (PFASs) to lower the surface tension along the foam-air interface are commonly used for controlling Class B flammable liquid fuel fires [1]. Firefighting training activities and emergency responses using AFFFs have led to elevated levels of PFASs in soil [2–6], sediments [3,7,8], groundwater [2,4,9,10] and biota [8] in many countries and regions. Knowledge of the environmental fate of PFASs is urgently needed for risk assessment, site management, and remediation of AFFF-impacted sites.

Inadequate understanding of organofluorine chemistry and the high number of PFASs pose a great challenge for characterizing and remediating AFFF-impacted sites. Early studies mostly focused on perfluoroalkyl acids (PFAAs) including perfluoroalkyl sulfonic acids (PFSA) and carboxylic acids (PFCAs), as well as partially fluorinated fluorotelomer sulfonic acids (FTSAs). Recently, more than 100 new highly fluorinated compounds have been identified in AFFF formulations [9] and historical AFFF-impacted groundwater [11], sediments and biota [8,12]. Betaine-type PFASs have been found to dominate composition profiles in soil and sediments following a major AFFF deployment in the aftermath of 2013 Lac-Mégantic railway accident (Quebec, Canada) [8,13]. Notably, many of these newly identified PFASs are zwitterionic or cationic surfactants, which have complex molecular structures and contain functional groups such as sulfonyl, thioether, amine, quaternary ammonium, carboxylate, sulfonate, amine oxide, and betaine [9,11]. These newly identified PFASs may be prone to microbial or chemical transformations to produce persistent PFAAs upon the loss of hydrocarbon moiety [14,15], hence are called precursors to PFAAs (PrePFAAs). It is conceivable that PrePFAAs would have different environmental fate and effects from those of legacy PFAAs. For instance, the quaternary ammonium group present in betaine type PrePFAAs possesses a permanent positive charge and can probably engage electrostatic interactions with a negatively charged surface, promoting their sorption and decreasing mobility. Though a good understanding of mobility and sorption of PFAAs in soil–water or sediment–water systems has been established [16,17], no research has been reported in characterizing the mobility of PrePFAAs.

The sorption of anionic PFAAs is dominated by hydrophobic interactions primarily with organic matter in soil or sediment, though short-chain PFAAs also strongly engage in electrostatic interactions [16–18]. The organic matter present in soil is not homogenous and contains naturally occurring and amorphous organic matter (or humic substances), as well as carbonaceous materials, many of which are pyrogenic. Pyrogenic carbonaceous materials (PCMs) refer to incompletely combusted and carbonized biomass and fossil fuel materials in a solid state. PCMs are part of the combustion continuum commonly termed as black carbon and by average accounts for 4% of total organic carbon (TOC) in soil (interquartile range 2–13%, calculated from 90 soil samples), but can reach up to 30–45% of TOC in fire-impacted soils [19]. PCMs are typically highly porous and thus highly surface-active, which makes them stronger sorbents of organic compounds than humic substances, particularly at low concentrations [20]. Sorption of hydrophobic organic compounds by black carbons can exceed sorption by humic substances by a factor of 10–100 [21]. In some cases, sorption in soils and sediments can be dominated by the PCM fraction [22,23]. Substantial experimental evidence from the early studies suggests the potential importance of PCMs in the retention of PFASs in AFFF-impacted sites, where combustion residues might be prevalent. It is also necessary to investigate sorption of PFASs by humic substances and PCMs, separately, to account for the different site characteristics.

PCMs are also responsible for sorption hysteresis or irreversible sorption of many organic compounds in contact with soil and sediment [20,24]. 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. 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 such as biochar 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 the PFAS-contaminated soil [25]. 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 [26]. However, no enhanced retention of PFAAs by soil was observed, probably due to competitive sorption of co-contaminants and fouling by humic substances. Certainly, further research is required to elucidate how PCMs interact with PFAS, 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 carbon.

The goal of the present study is to evaluate the role of PCMs in PFAS sorption in comparison to soil organic matter (SOM). The working hypothesis is that strong sorption to PCMs could control the persistence of PFASs in AFFF source zones under certain conditions. In this study, representative PFASs from several classes of PFAS, as well as both electrochemical fluorination and fluorotelomerization chemistry, were used to compare sorption by SOM to that of three model PCMs. The PFASs under investigation included two anionic (perfluorooctane sulfonate, PFOS; perfluorooctanoic carboxylate, PFOA), one cationic (perfluorooctaneamido ammonium iodide, PFOA<sub>AmS</sub>) and two zwitterionic PFASs (perfluorooctane amido betaine, PFOAB; 6:2 fluorotelomer amido betaine, 6:2 FTAB). The later three PFASs may undergo environmental degradation to yield PFCAs or PFSA and therefore are PrePFAAs. SOM was presented by Pahokee peat, and PCMs by biochar, oil-free soot, and soot with fuel residues. Sorption and short-term sorption reversibility of PFAS-PCMs and PFAS-SOM interactions were examined using single-solute batch experiments to avoid potential competitive sorption. The study findings provide a new perspective on the potential importance of PCMs as sorbents for PFASs in AFFF-impacted sites.

## 2. Materials and methods

### 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 Perfluorooctaneamido ammonium iodide (PFOA<sub>AmS</sub>,  $F(CF_2)_7CONH(CH_2)_3N^+(CH_3)_3I$ , 98%) were custom-synthesized at Beijing Surfactant Institute (Beijing, China) [12]. 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB,  $F(CF_2)_6CH_2CH_2SO_2NH(CH_2)_3N^+(CH_3)_2CH_2COOH$ ) 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- $^{13}C_4$ ] octanoic acid (MPFOA), perfluoro-1-[1,2,3,4- $^{13}C_4$ ] octanesulfonate (MPFOS), and 1H,1H,2H,2H-perfluoro-1-[1,2- $^{13}C_2$ ]-octane sulfonate (M6:2 FTSA). HPLC-grade solvents including acetonitrile (ACN), methanol (MeOH), LC/MS-grade water and acetic acid (HAc) were purchased from Fisher Scientific (Ottawa, ON).

Acronyms, molecular structures, acid dissociation constants ( $pK_a$ ) and isoelectric points (IEPs) of the investigated PFASs are listed in Table 1. IEP of PFOAB and 6:2 FTAB was determined by measuring zeta potential of a series of aqueous solutions ( $1\text{ g L}^{-1}$ ) as a function of solution pH, as detailed in the Supporting Information (SI). Speciation of PFOA<sub>AmS</sub>, PFOAB and 6:2 FTAB and their macroscopic  $pK_a$  values were determined using SPARC (ARCHem, GA, USA), a physicochemical calculator.

Download English Version:

<https://daneshyari.com/en/article/6579237>

Download Persian Version:

<https://daneshyari.com/article/6579237>

[Daneshyari.com](https://daneshyari.com)