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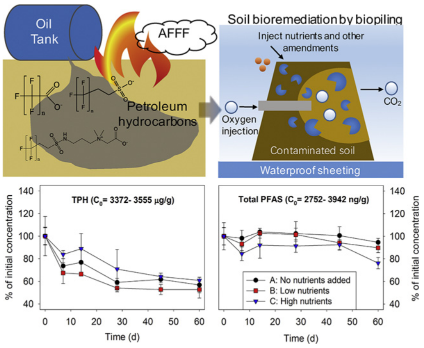
Transformation of novel polyfluoroalkyl substances (PFASs) as co-contaminants during biopile remediation of petroleum hydrocarbons

Rui Li[a,b], Gabriel Munoz[a,c], Yanan Liu[b], Sébastien Sauvé[c], Subhasis Ghoshal[a], Jinxia Liu[a,*]

[a] *Department of Civil Engineering, McGill University, Montreal, Quebec, H3A 0C3, Canada*
[b] *School of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China*
[c] *Department of Chemistry, Université de Montréal, Montréal, QC, Canada*

GRAPHICAL ABSTRACT



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ABSTRACT

Aqueous film forming foams (AFFFs) containing perfluoroalkyl and polyfluoroalkyl substances (PFASs) are commonly deployed to extinguish hydrocarbon fuel fires, resulting in petroleum hydrocarbons coexisting with PFASs in contaminated soil. Nutrient-amended and aerated biopiles used for petroleum hydrocarbon bioremediation could cause unintended transformation of polyfluorinated substances into perfluoroalkyl carboxylates (PFCAs). The study sought to examine environmental behaviors of PFASs in engineered treatment facilities by monitoring AFFF-derived PFASs under three nutrient conditions. The influence of nutrient levels on degradation kinetics and efficiency was found to vary between the two chemical classes and among individual PFASs. A high number of compounds including the zwitterionic polyfluoroalkyl betaines that have aged in the field for two years were continuously biotransforming in lab reactors, demonstrating their slow kinetics and environmental persistence. The low yield to PFCAs implies that the processes such as the formation of bound residues or irreversible sorption might play a major role in reducing detectable levels of zwitterionic PFASs. The high persistence of betaines was further confirmed by the behaviors of a freshly spiked sulfonamide betaine. The study demonstrated complex chemical dynamics in AFFF-impacted soils and the challenges for predicting the fate of PFASs in soil biopiling facilities.

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

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1. Introduction

Per- and polyfluoroalkyl substances (PFASs), due to excellent tensioactive properties, chemical and thermal stability, have been in widespread use since the 1950s as strategic chemicals in multiple applications including aqueous film forming foams (AFFFs). AFFFs are critical firefighting agents against Class B flammable liquid fires [1]. Deploying large volumes of such formulations has contributed to the distribution of PFASs in water or sediments downstream from major urban and industrial centers or AFFF-impacted sites in airports and military bases [2–8]. As legacy perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) show persistent, bioaccumulative and toxic properties, there are grave concerns regarding the risks posed by many PFASs with similar chemical structures.

Although the full composition of AFFFs is of proprietary information, the application of high-resolution mass spectrometry has recently unveiled dozens of PFAS classes and over 240 individual compounds in AFFF formulations and AFFF-impacted groundwater [3,9–12]. A considerable fraction of the newly-identified PFASs is likely to generate perfluoroalkyl acids (PFAAs) through abiotic or biotic processes, as suggested by their structures and recent experimental work [13–17]. Two cationic fluorosurfactants with a quaternary ammonia group, several zwitterionic fluorosurfactants (e.g., 6:2 fluorotelomer sulfonamide betaine, 6:2 FTAB), and an alkylamine fluorosurfactant (6:2 fluorotelomer sulfonamide amine) have been demonstrated to biotransform to PFAAs [14,15,18]. The full implications of such natural transformation processes to the site investigation and risk assessment of AFFF-impacted sites are yet to be understood.

PFASs in AFFF-impacted sites are rarely the only organic compounds. Mixed contamination with legacy pollutants (e.g., chlorinated solvents, petroleum hydrocarbons, etc.) is expected. Due to the nature of AFFF applications, PFASs can coexist with oil or fuel residues at AFFF impacted sites, as shown in our recent study of soil pollution in the aftermath of a train derailment accident in Lac-Mégantic (Quebec, Canada) [19]. During the cleanup efforts, soils with elevated levels of crude oils were subjected to bioremediation in a biopiling facility to reduce hydrocarbon levels, a widely adopted low-cost technology for soil treatment. Since PFAS levels in soils are not yet regulated or routinely monitored, whether such soil remediation approaches could unintendedly accelerate the generation of PFAAs from the concurrent biotransformation of some PFASs, however, remains an open question. The concern was raised by McGuire et al. [20], who attributed the unusual ratios of perfluorohexane sulfonate (PFHxS) to PFOS found in groundwater to past site remediation activities that aimed at legacy pollutants but probably caused unintended accelerated transformation of the precursors to PFAAs. In fact, a lack of the knowledge of the behaviors of PFASs in engineered soil bioremediation facilities, or the factors that can accelerate or decelerate the natural PFAS degradation processes is quite concerning. For petroleum hydrocarbons, the dosage of nutrient supplement, temperature, and temperature variations in cold climates are critical factors in ensuring optimal microbial activity and successful hydrocarbon removal [21–25]. The knowledge of how these factors may influence PFAS biotransformation is useful for predicting PFAS behaviors in engineered treatment systems.

Given the knowledge gaps, the study sought to examine the behaviors of PFAS using lab-simulated soil biopiles under the conditions typical for enhancing bioremediation of petroleum hydrocarbons. The test soil with elevated levels of both contaminants was collected from a biopiling facility constructed as part of the cleanup efforts following the Lac-Mégantic railway accident [19]. The transformation of PFASs that have aged in the field soil, as well as that of a representative AFFF-derived component (6:2 FTAB), was closely examined. The effect of the nutrient level was investigated as a key environmental factor, and the particular focus was placed on the influence on removal kinetics and efficiency of total and individual PFASs. To our best knowledge, this is the first study to examine the behaviors of a large suite of PFASs in AFFF-impacted soils as co-contaminants of legacy compounds. The study provides critical data on the effect that hydrocarbon contamination remediation efforts could have on AFFF-derived PFASs.

2. Materials and methods

2.1. Standards and reagents

42 target PFASs for which authentic standards were available are listed in the Supporting Information (SI) (Table SI-1). Unique to this study was PFOSAm, PFOSAmS, PFOAAmS, PFOSNO, PFOANO, PFOSB, and PFOAB to allow quantitative or semiquantitative analysis of zwitterionic and cationic PFAS [19]. 6:2 FTAB and 6:2 FTNO as representative fluorotelomer compounds were obtained from Shanghai Kingpont Industrial Company, Ltd. (Shanghai, China). Chemical standards used for quantitation of total petroleum hydrocarbon included diesel fuel and motor oil from Restek Corporation (Bellefonte, PA, US). Details of the chemicals and their sources are provided in the SI.

2.2. Soil microcosm setup

The soil impacted by both petroleum hydrocarbons and AFFFs in 2013 during an oil spill and subsequent fire-fighting activities is described in previous studies [19]. Soils from the accident site were excavated and transferred to a biopile bioremediation facility during 2014–2015, and the soil used for the study was sampled in 2015 as a composite sample in a newly constructed section of the biopiling facility. A non-impacted background soil (within top 20 cm layer) was sampled approximately 5 km away from the accident site to demonstrate PFAS background in the region. The soils were sieved via a 2-mm sieve immediately after collection and stored at 4 °C until use. Soil characteristics are listed in Tables SI-3 and SI-4, and the background PFAS levels of the non-impacted soil in Table SI-5.

The biopiles were simulated at the lab-scale in 1000-mL glass bottles with two openings: one to capture volatile compounds and the other for headspace sampling. 200 g (oven dry weight) of the soil was added to each bottle and adjusted to a gravimetric moisture content of 14%, and were pre-incubated for 7 days. In **Experiment I**, the transformation of the residual PFASs present in the field soil was examined under three treatments conditions: high nutrient amendment (C_{TPH}:N:P = 100:10:2), low nutrient amendment (C_{TPH}:N:P = 100:5:1), and no nutrient amendment (C_{TPH}:N:P = 100:2:0.2). Weathered Bakken formation crude oil collected from the accident site was spiked to the biopiles to increase the concentration of total TPH to 3372–3555 μg/g. In **Experiment II**, the transformation of a representative precursor, 6:2 FTAB, was spiked into the biopile soil at about 10 μg/g to examine its fate in the presence of TPH background. Each treatment condition had three replicates. More details on the experimental setup can be found in the SI.

2.3. Sampling and sample preparation

The test vessels were incubated at ~20 °C in the dark for 60 days and periodically sampled. During sampling, filtered air was purged through the soil vessel to flush the volatile compounds onto a C_{18} cartridge. The methanol eluent (5 mL) of the cartridge was stored at −20 °C before chemical analysis for both total petroleum hydrocarbons (TPH, C10-C50) and PFASs. Then the vessel cap was removed to allow soil sampling. For the simulated biopiles, the collected soil was homogenized and divided into two portions, one for PFAS extraction and the other for TPH extraction as detailed in the SI.

2.4. Instrumental analysis

Quantitative analysis of PFASs followed the previously developed method [19] using a Shimadzu UHPLC system coupled to an AB Sciex