Release of perfluoroalkyl substances from AFFF-impacted concrete in a firefighting training ground (FTG) under repeated rainfall simulations

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ABSTRACT

Historical use of per- and polyfluoroalkyl substances (PFAS) at firefighting training grounds (FTGs) has prompted questions regarding possible PFAS retention within concrete and subsequent releases to the environment. This investigation seeks to better understand the release of five PFAS from concrete cores collected from a legacy FTG. The vertical profile of cores were assessed, then surface ponding and rainfall simulations were conducted on the cores. Perfluorooctane sulfonate (PFOS) had the highest concentrations in both the core (up to 10,000 μg kg^{-1}) and in ponded water on their surface (up to 100 μg L^{-1}), followed by 6:2 fluorotelomer sulfonate (6:2 FTS) and perfluorohexane sulfonate (PFHxS). The maximum concentrations of PFAS in runoff water of five rainfall simulations were similar, suggesting recurring release of PFAS from AFFF impacted concrete, which could be sustained by upward transport of PFAS in the concrete subsurface layers through a potential "wicking" effect. The estimated mass of PFAS released during a simulated rainfall of 60 mm was approximately 1% of the total PFAS mass estimated within the top 1 cm of the concrete core. The results of the study suggest that concrete at FTGs may present an ongoing secondary source of PFAS in runoff water events.

1. Introduction

The ability to reliably extinguish Class B fires in accordance with national and international codes is an important task that requires regular training. Firefighting training requirements and activities have resulted in the use of a variety of aqueous film-forming foam (AFFF) chemistries that contain various per and polyfluoroalkyl substances (PFAS) (Place and Field, 2012). PFAS were a critical component of AFFF due to their physical and chemical characteristics that are extremely well suited for timely extinguishment of Class B fires (Moody and Field, 2000). AFFF have been used at sites such as military bases, airports, and oil refineries for emergency and training purposes (Moody and Field, 2000). The repeated use of AFFF has resulted in firefighting training grounds (FTG) with high concentrations of diverse PFAS within the built infrastructure and surrounding environment, with observations of up to hundreds of micrograms per liter PFAS in surface water runoff from the FTG (Baduel et al., 2015; Bhavsar et al., 2016; Dauchy et al., 2019).

Previously, 90% of residual PFAS associated with an AFFF-impacted concrete pad at a FTG was estimated to generate PFOS in runoff water of at least 0.2 μg L^{-1} for more than 200 years (until 2230) (Baduel et al., 2015). However, that estimation was based on the conditions of continuous release of PFAS from concrete to static ponded water, which could be different than the release of PFAS from sloped concrete during a rainfall event. Such differences could have an important consequence for any realistic assessment of long-term release of PFAS from concrete associated with historical AFFF usage at FTGs and to support the evaluation of potential mitigation measures.

Hence, in this study we aimed to investigate the dynamic release of PFAS associated with concrete cores collected from a FTG under ponding and rainfall simulations.

2. Materials and methods

2.1. Concrete cores and concrete samples

Several concrete cores (d = 120 mm) were collected from a PFAS-impacted FTG. The cores penetrated the entire thickness of the concrete pad (i.e., 10 cm) to enable an investigation of the PFAS profile along the entire depth of the pad. To vertically discretize PFAS within the core, samples of concrete were collected by drilling into the side of the cores at depths of 0.5 cm, 1 cm, 2 cm, 3 cm, 4 cm, 6 cm, 8 cm, and 10 cm. At each depth, the core was drilled at 6–7 different spots around its circumference to collect concrete dust. Those subsamples were composited to generate a representative concrete sample of each depth.

2.2. Release kinetics from consecutive ponding simulations

In this step, we repeated the previous ponding experiment of Baduel et al. (2015) to ascertain the kinetics of PFAS released from impacted concrete cores into static water. For this purpose, water was ponded on the surfaces of the cores with MilliQ water (pH 7) using a PVC ring (d= 90 mm) sealed to the top surface of the concrete core using a silicon adhesive/sealant (Selleys®). A water depth of 30 mm (190 mL) was used for each core to minimize losses due to evaporation and permeation into the concrete. Water samples (1 mL) were collected at different time points over a 24 h period (i.e., 0; 0.5; 1; 2; 4; 6; 10; 14; 18; and 24 h) and filtered into a vial and stored at − 20 °C until analysis. An experimental blank sample was obtained by soaking the dried silicon adhesive and the PVC ring in MilliQ water for 24 h and collecting a 5 mL aliquot of the soaking solution.

Ponding was repeated 3 times on each core. Between each ponding event, ponding water was completely removed, and the core surface was left to air-dry for 24 h to simulate alternating wet and dry conditions that may occur in the field.

2.3. Release kinetics from consecutive rainfall simulations

After the ponding experiments, rainfall simulations were conducted on the same cores using a similar setup. Due to the small size of the concrete core surface within the PVC ring (63.5 cm^2), no rainfall simulator was used. Instead, 13 mL (or 2 mm depth) of MilliQ water (pH 7) was poured into the PVC ring and then pipetted out completely within 2 min. This was repeated 30 times to simulate a rainfall of 60 mm with the intensity of 60 mm h^{-1}.

A total of five rainfall simulations were performed on two concrete cores. The first two rainfall simulations were separated by a 24 h interval of ambient conditions to simulate alternating wet and dry conditions that may occur in the field. After 130 days, the additional three rainfall simulations were conducted, again allowing for a 24 h interval of ambient conditions between each simulation. During the 130-day interval, the cores were wrapped and stored at room temperature to avoid any extreme drying of the concrete core surface.

All experiments were carried indoor at room temperature of approximately 24 °C.

2.4. Chemical analysis

Concrete samples were spiked with isotope labeled internal standards and extracted with a mixture of ammonia methanol (2%) and acetone. The extract was then loaded on a solid phase extraction (SPE) cartridge for clean-up. The elutant from the SPE cartridge was blown to dryness under nitrogen and reconstituted in 0.4 mL methanol:water (1:1 v/v) for analysis. Water samples were aliquoted (0.5 mL) and spiked with isotope labeled internal standards before analysis by direct injection. More information on sample treatment can be found in the Supporting Information.

Extracts and samples were analyzed via liquid chromatography with tandem mass spectrometry (LC-MS/MS) for four perfluoroalkyl acids (PFOS, PFOA, PFHxS, PFHxA) and one fluorotelomer sulfonate precursor (6:2 FTS) to evaluate a representative group of PFAS commonly found in a variety of AFFF formulations. Detailed information on instrumental analysis can be found in the Supporting Information.

In every batch of samples analyzed (batch size from 30 to 100 samples), procedural blank samples (every 20 samples), duplicate samples (every 10 samples), and samples spiked with the native standards (every 20 samples) were included as the quality assurance and control (QA/QC) of the analysis. No target PFAS were detected in the blank samples and all the QA/QC criteria were within the acceptable ranges according to the US DoD/DoE Quality System Manual (DoD/DoE, 2018).

3. Results and discussion

3.1. Vertical profile of PFAS in the concrete cores

Vertical profiles of PFOS, PFOA, and 6:2 FTS over the entire thickness of the pad are shown in three different concrete cores (Fig. 1). Vertical profiles of PFHxS and PFHxA are shown in the Supporting Information (SI). The vertical profiles of PFAS within the different concrete cores are similar despite the anticipated heterogeneous nature of the concrete matrix. The highest concentrations were found approximately 1 or 2 cm below the surface layer of the cores. This is a reasonable finding as the concrete cores were collected from an aging concrete pad at a FTG where PFAS-containing AFFF use was discontinued and surface associated PFAS were subjected to rainfalls and water from continued training exercises. Below 2 cm, concentrations of PFAS decrease rapidly but remain at detectable levels until the bottom of the cores. The observed profile of a shallow maximum and subsequent asymptote is similar to that of observations made by Baduel et al. (2015) except for the case of PFOS, which showed the maximum concentration on the surface of the concrete in Baduel et al. (2015). The difference in PFOS profile between the two studies could be due to the heterogeneity of PFOS distribution on the concrete surface caused by the legacy AFFF use in the different two sites.

PFHxS and PFHxA may have the greatest vertical transport among the target PFAS analyzed herein, based on the ratio of the lowest concentrations to the highest concentrations among different layers. This finding is aligned with the soil-water partitioning properties of PFHxS and PFHxA compared to the remaining target PFAS analyzed (Nguyen et al., 2020).

There is an unexplained but significant increase of PFOS and PFOA concentrations (Fig. 1) and to a lesser extent of PFHxS concentration (Fig. S1) beginning at approximately 8 cm from the top of the cores, which is not observed for 6:2 FTS (Fig. 1) or PFHxA (Fig. S1). While the magnitude of the increase is variable, the general pattern is repeated. It is noted that a similar increase in PFOS was also observed by Baduel et al. (2015). This increase of selected PFAS concentrations at the bottom of the cores could be due to lateral seepage of AFFF-impacted runoff from the FTG or from another undetermined mechanism.

3.2. Release kinetics from ponding simulations

We reproduced the profile of PFAS release into ponded water from concrete surfaces as presented previously by Baduel et al. (2015). In Fig. 2, we present the data of PFOS as an example because similar profiles were observed for the remaining target PFAS analyzed (Fig. S2).

The observed PFOS release from three separate cores suggests a relatively rapid release followed by an asymptotic response for the remaining duration of the experiment. A noted difference to previous data in the literature, and an important finding of this study, is that concentrations of PFAS in earlier ponding events are higher than those in subsequent ponding events. Consecutive ponding in a short timeframe (24 h interval between ponding events) may have reduced the
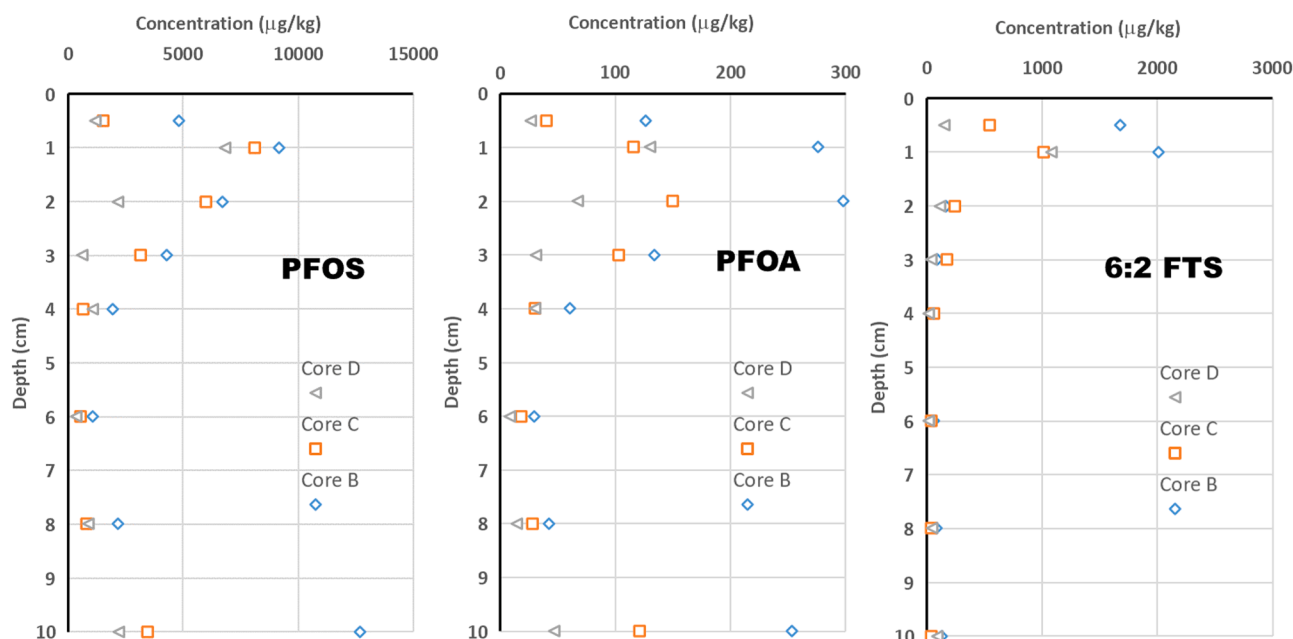
Fig. 1. Vertical profiles of PFOS, PFOA, and 6:2 FTS in three different concrete cores (note the different scales of the x axis).
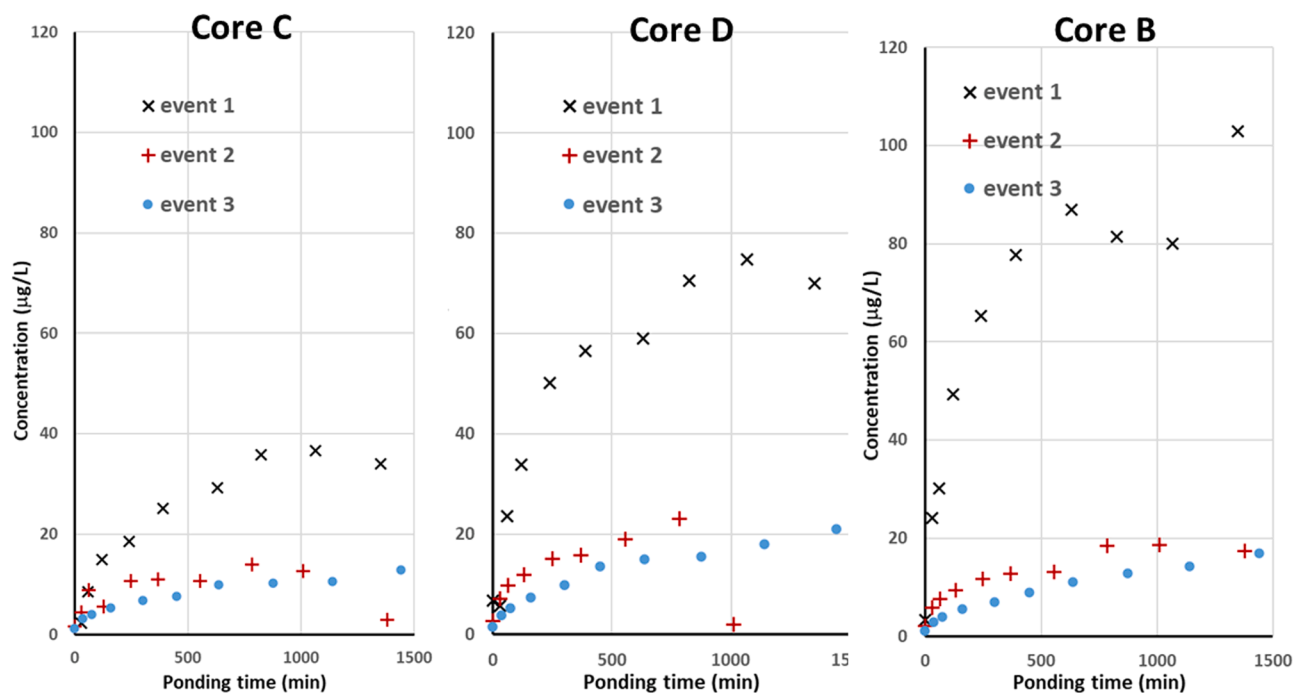

Fig. 2. Release kinetics of PFOS in 3 consecutive ponding events on 3 different concrete cores.

availability of PFAS on or near the surface of concrete for release into the aqueous phase. Further, maximum PFAS concentrations achieved in the first ponding event are much higher than those achieved in the second ponding while there is less difference between the second and the third ponding events. An estimation of the PFAS released during each ponding event found that all cores released 3–4-fold more PFAS mass during the first ponding event compared to the second and third which were similar (Table S1).

3.3. Release kinetics from rainfall simulations

The concentration profile of PFOS, representing the target PFAS, in runoff water samples collected from core D during the rainfall simulations are presented in Fig. 3. Profiles of the other PFAS in cores D and A are presented in the Supporting Information (Fig. S3). All five target PFAS were detected in runoff water at the beginning of the rainfall simulations with magnitudes of concentration in the following order: PFOS > 6:2 FTS > PFHxS > PFHxA > PFOA. The concentrations of all five target PFAS decreased rapidly during the first 20 mm of rainfall. The rate of decrease became slower toward the end of the rainfall simulation.

The runoff profiles of PFAS observed in this study resemble those profiles of dissolved contaminant runoff over impervious surfaces as described previously, e.g., by Zhang et al. (2020), as concentrations of PFAS in runoff water continually decrease, approaching the limit of
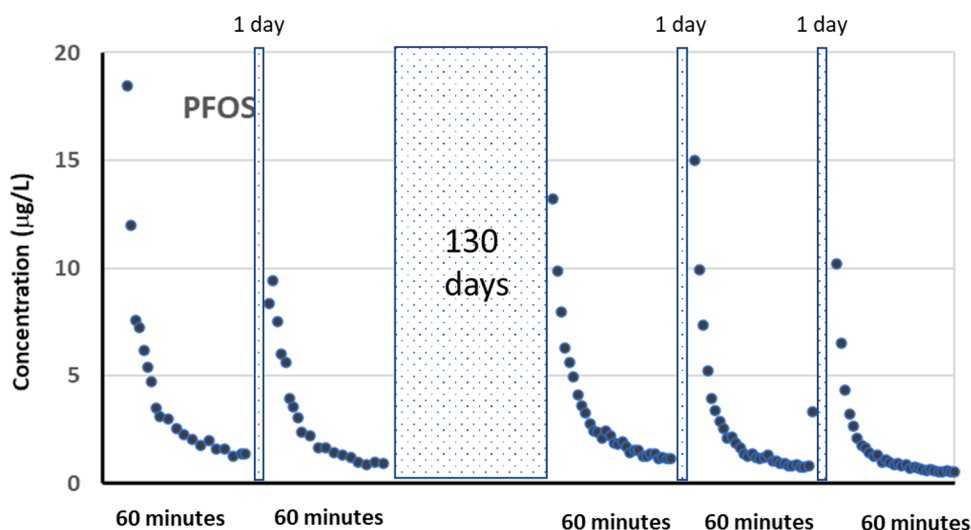
Fig. 3. Concentration response of PFOS in runoff water during rainfall simulations (core D).

detection (LOD).

A novel finding of the rainfall simulations presented here is the similarity of the PFAS concentration profiles of five successive rainfall simulations, notwithstanding an extended resting period. Rainfall and its runoff is usually thought to dissolve/desorb/wash-off or otherwise remove pollutants from field surfaces, including low permeability surfaces such as concrete. Previous rainfall simulation studies either had to rely on the particle phase of the runoff (Thai et al., 2015) or on re-loading the dissolved contaminant on the surface before simulation (Xiao et al., 2017) to maintain the contaminant concentration in the collected runoff water. The results presented here strongly support the hypothesis that concrete infrastructure in FTGs are potentially a secondary source of PFAS. After decades of repetitious surface releases of AFFF solution, the associated PFAS residues within the concrete matrix may impact runoff associated with rainfalls or with water from ongoing training activities for an extended period.

The observations of similar initial PFAS concentrations in the five successive rainfall simulations (Fig. 3) and the vertical PFAS mass distribution within the concrete cores (Fig. 1) suggest that the presence of water on the surface of the concrete encourages dissolution of PFAS and the extraction of PFAS from the sub-surface layers to the surface. Further, the 24 h drying of the core followed by a repeated 60 min rainfall simulation shows that the drying period was sufficient to obtain a new release of PFAS from the core that is essentially the same as the first one. The drying period results in a replenishment of the PFAS that becomes available in the next rainfall event and suggests the evaporation of water on the surface may lead to a "wicking" effect, facilitating the transport of PFAS from a subsurface layer where it is not readily available to the surface where it will be released during the next surface water runoff event. The resultant simulated runoff concentrations support a lasting potential source of PFAS retained within concrete released at concentrations in the micrograms per liter [μg/L] range.

We acknowledge that there were some limitations in the design of our rainfall simulations. First, there was no raindrop and thus minimal kinetic energy that could affect the mechanism by which PFAS are released from the concrete into the runoff water. Second, the concrete surface was not exposed to sunlight (high heat) during the drying of after each rainfall simulation, which would have more accurately represented field conditions and additional environmental fate and transport mechanisms. However, our experimental conditions provide one of the first detailed studies into the fate of PFAS within concrete during rainfall events.

3.4. Mass release of PFAS through runoff water

The cumulative PFAS mass into runoff water during the five 60 mm rainfall simulations (Fig. 3) are presented in Fig S6. The PFAS release was normalized to the surface area (1 m^2) for ease of comparison.

The range of cumulative mass released for the five targeted PFAS analyzed in this study is 7.5 ± 1.8 μg/m^2 (for PFOA) to 541 ± 217 μg/m^2 (for PFOS), with the total cumulative mass released from Core D and Core A being 431 ± 92 μg/m^2 and 850 ± 290 μg/m^2, respectively. The difference of estimated mass released between Core D and Core A highlight the variability across a given concrete pad, which inhibits the direct prediction of PFAS mass released from other concrete pads. For example, the average cumulative PFOS mass release calculated for Core D and Core A is approximately 170 ± 46 μg/m^2 and 540 ± 216 μg/m^2, respectively, representing an approximate 3 times difference over the same concrete pad. It is noted that these calculations represent site-specific PFAS mass release estimates and the data was generated from a relatively small area of the entire concrete pad (e.g., concrete core to concrete pad area ratio). Further, for site-specific applicability, the contributing PFAS mass released from a FTG concrete pad would need to be considered, estimated, or measured within the entirety of the captured flow and associated runoff.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2022.100050.

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