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Are Geotextiles Silent Contributors of Ultrashort Chain PFASs to the Environment?

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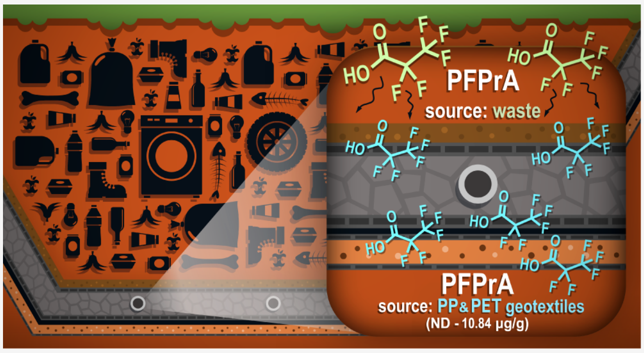

ABSTRACT: We investigated the presence of per- and poly fluoroalkyl substances (PFASs) in woven and nonwoven polypropylene geotextiles and four nonwoven polyester geotextiles commonly used in modern geosynthetic composite lining systems for waste containment facilities such as landfills. Targeted analysis for 23 environmentally significant PFAS molecules and methods for examining "PFAS total" concentrations were utilized to assess their occurrence in geotextiles. This analysis showed that most geotextile specimens evaluated in the current investigation contained the ultrashort chain PFAS compound pentafluoropropionic acid (PFPrA). While the concentrations ranged from nondetectable to 10.84 μg/g, the average measured concentrations of PFPrA were higher in polypropylene than in polyester geotextiles. "PFAS total" parameters comprising total fluorine (TF) and total oxidizable precursors (TOPs) indicate that no significant precursor mass nor untargeted intermediates were present in geotextiles. Therefore, this study identified geotextiles as a possible source of ultrashort PFASs in engineered lined waste containment facilities, which may contribute to the overall PFAS total concentrations in leachates or liquors they are in contact with. The findings reported for the first time herein may lead to further implications on the fate and migration of PFASs in geosynthetic composite liners, as previously unidentified concentrations, particularly of ultrashort-chain PFASs, may impact the extent of PFAS migration through and attenuation by constituents of geosynthetic composite liner systems. Given the widespread use of geotextiles in various engineering activities, these findings may have other unknown impacts. The significance of these findings needs to be further elucidated by more extensive studies with larger geotextile sample sizes to allow broader, generalized conclusions to be drawn.

KEYWORDS: *geosynthetics, geotextiles, pentafluoropropionic acid, ultrashort-chain PFAS, waste containment facilities, landfills*

INTRODUCTION

Per- and poly fluoroalkyl substances (PFASs) constitute a category of anthropogenic organic compounds used in various industrial processes and commercial products since the 1940s.[1] Both polymeric and nonpolymeric forms of PFASs exist, possessing unique physical and chemical characteristics attributed to their molecular structures. Nonpolymeric PFASs often comprise a fluorinated hydrophobic and lipophilic portion with variable carbon chain length attached to one or more hydrophilic and lipophobic terminal functional groups.[2] Polymer PFASs often possess a carbon-only or carbon and oxygen polymer backbone, with fluorine atoms attached to the carbon atoms or fluorinated side chain branches attached to the polymer backbone.[1] Due to their amphiphilic properties, low molecular polarity, and high thermal and chemical resistance, PFASs have been used extensively in the manufacture of textiles and leather, carpets and furniture, and aqueous film-forming foams (AFFFs), metal plating processes, fluoropolymer production, and paper products for food packaging.[3,4]

The widespread use and long-term persistence of PFASs have resulted in ubiquitous environmental pollution, and concern has been raised regarding their mobility, potential for bioaccumulation, and toxicity.[4] Perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), and perfluorohexanesulfonic acid (PFHxS), the three most widely investigated and debated perfluoroalkyl acids (PFAAs) were incorporated into the annexes of the Stockholm Convention in 2009, 2019, and 2022, respectively, as persistent organic pollutants (POPs), restricting their manufacture and use.[5−7] The regulatory restriction of PFOS, PFOA, and PFHxS led to their phase-out and replacement with short-chain (4−7 fully fluorinated carbon atoms) PFASs for commercial and industrial

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production.[4] Despite the industrial transition toward shorter-chain homologues, the fundamental knowledge required for determining their occurrence, fate, transport, and toxicity remains limited.[8] Additionally, the current uses of short-chain PFASs are seldom reported. To date, no public information is available on the use of ultrashort-chain (1−3 fully fluorinated carbon atoms) PFASs in manufacturing processes.

Short- and ultrashort PFASs were ubiquitous in the global environment prior to the phase out of production and use of long-chain PFAAs, occurring as unintended byproducts formed during manufacturing of long-chain PFAAs or as environmental degradation products of longer-chain PFAA compounds.[9,10] For example, ultrashort compounds such as perfluoropropionic acid (PFPrA) and trifluoroacetic acid (TFA) can be formed via atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).[11,12] Ultrashort PFAAs may also be produced by thermolysis of fluorinated polymers and atmospheric oxidation of precursor compounds.[1,13] However, measurements of short- and ultrashort PFAAs in the environment imply that the concentrations observed cannot be solely attributed to degradation and residual formulation. This is mainly due to the reported shift in some industries toward short-chain PFASs as replacement compounds for the long-chain analogues,[113−115] increased detection frequency of short- and ultrashort PFAAs in consumer products,[59,75,78] generally increasing temporal trends in environmental concentrations of short- and ultrashort congeners,[14,15,18−21,106,107] and their elevated concentrations in leachates from younger landfills[16,17,22,25,105,108,116] (particularly landfills that accept construction and demolition (C&D) wastes). Thus, it is inferred that short- and ultrashort PFAAs are likely to be used extensively in the modern manufacturing of consumer and industrial products.

The environmental levels of ultrashort-chain PFAAs are typically higher than those of longer-chain PFAAs, occurring at concentrations ranging from ng/L to μg/L in rain precipitation, snow, groundwater, surface water, and drinking water.[15,18−21] Furthermore, PFAAs have been widely identified in landfill leachates, with short-chain PFAAs contributing substantially to the overall PFAA leachate levels.[22−26,105] Ultrashort-chain PFAAs, such as TFA and PFPrA, have been reported in leachate (up to 8.07×10^4 ng/L) from municipal solid waste disposal facilities and were found to dominate over longer-chain PFAAs.[25] Notably, long-chain PFAAs are typically primary contributors to the total PFAA leachate concentrations in older landfills. Conversely, shorter-chain PFAAs tend to dominate in leachate from younger landfills, consistent with the phasing out of longer-chain PFAAs and replacement with shorter-chain congeners.[16,17]

Geotextiles made from synthetic polymeric fibers, such as polyester, polyethylene, and polypropylene, are used in relatively large quantities in engineering activities due to their versatility, ease of manufacture, and relatively low cost.[27] Their characteristic properties, such as high tensile strength and durability, render them suitable for various built environments, including agricultural, mining, civil, geotechnical, and geoenvironmental engineering applications. An example of such use is in geosynthetic composite liners, often employed in modern waste containment facilities to preclude or slow the flow of fluid and contaminants into the surrounding environment.[28−30] These lining systems commonly incorporate various nonwoven and woven geotextiles for separation, filtration, hydraulic retention, and protection function purposes.

In general, nonwoven geotextiles are produced through web formation (transforming the fibers into layers of loosely arranged webs) and bonding the fibers, typically by mechanical means via needle-punching.[31] The needle-punching process involves the repeated penetration of barbed needles, fixed on a board, into the fibrous web to produce a nonwoven fabric.[32] In contrast, woven geotextiles are manufactured using large industrial looms that interweave horizontal and vertical threads to form fabrics with planar structures.[32]

Fiber materials in technical textiles, such as geotextiles, may undergo chemical processing before converting these constituent materials into a fabric.[33] Scouring is generally employed to remove undesired content from the fiber, including dust and oils.[33,34] Dyeing can be conducted at any stage of the textile product form, such as the fiber form.[33,35] Furthermore, a finish/lubricant may be applied to fibers to dissipate static electricity generated and reduce fiber to metal friction during fiber processing or needle punching.[36]

Fluorochemicals carrying perfluoroalkyl groups are widely used in various industrial and commercial applications to impart resistance to heat, water, oil, and soil to various products and improve the processing characteristics of manufacturing stages.[73] Although there is no publicly available information on using PFASs in geotextile production (i.e., in fibers), inferences can be drawn from the manufacturing of textile fabrics, in which scouring, dyeing and/or finishing steps may involve using ultrashort chain PFAAs. Nonpolymeric PFASs are used in industry as processing aids in scouring and dyeing processes, and additives to lubricants applied to fibers to reduce friction and static during processing into fabrics.[4,37−43] If PFASs are used in geotextile manufacturing steps and retained on the final product, geosynthetic composite lining systems that employ geotextiles would potentially pose as additional sources of PFASs in lined waste containment facilities. The total PFAS mass, if present, in the geotextile components of geosynthetic composite lining systems is anticipated to increase the total PFAS concentrations in landfill leachate.

Although geosynthetic composite liners are engineered to prevent or mitigate the release of waste and contaminants into the surrounding environment,[44−48] most geosynthetic composite liners have not been designed to prevent or limit the migration of emerging contaminants, such as PFASs, to the environment.[49,50] Knowledge of contaminant migration through constituents of a composite liner is currently limited mainly to volatile organic compounds, metals, phenolic substances, and aromatic hydrocarbons.[51−56] Research efforts have only recently focused on examining the potential impact of PFASs on geosynthetics engineering performance.[49,50,57,58] However, further information is required in the literature regarding the interactions between ultrashort chain PFAAs and geotextiles or other geosynthetics. Given the widespread use of geotextiles in waste containment facilities, PFAA concentrations associated with geotextiles in leachate can lead to unknown implications on the fate and transport of PFASs in geosynthetic composite lining systems.

Hence, this study examines the presence of PFASs in polypropylene woven and nonwoven geotextiles and four polyester nonwoven geotextiles commonly used in modern geosynthetic composite lining systems. Targeted PFAS analysis for 23 environmentally significant PFASs and methods for

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assessing "PFAS total" concentrations comprising total fluorine (TF) and total oxidizable precursor (TOP) assay were utilized to determine the occurrence of PFASs in geotextiles. The TOP assay provides a means of quantifying PFAA precursors that may degrade in the environment to terminal products such as perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs),[69,93] while TF analysis quantifies the total levels of fluorine in a sample and therefore includes known and unknown PFASs and other chemicals containing fluorine. By comparing the concentrations of TOP and TF with the total PFAS measured in a sample by targeted analysis, the fractions of known and unknown fluorine substances can be quantified and summed to derive "PFAS total" concentrations, noting that this approach takes the conservative assumption that all measured fluorine is present as PFASs.

■ MATERIALS AND METHODS

Geotextiles. Six different commercially available geotextiles in Australia were used in the current study. They were manufactured between 2020 and 2022 and sourced from local manufacturers and suppliers. These geotextiles were selected based on the functions (i.e., separation/filtration, protection, and hydraulic retention) they must fulfill in waste containment facilities and the corresponding specifications enforced by environmental authorities or agencies. They are extensively employed in the lining systems of waste containment facilities and other engineering applications.[28,44,50] A summary of their characteristics is presented in Table 1. They include polypropylene woven and nonwoven geotextiles, denoted as GTX A and GTX B, respectively, two polyester nonwoven geotextiles with low mass per unit areas, referred to herein as GTX C and GTX D, and two polyester nonwoven geotextiles with larger mass per unit areas, denoted as GTX E and GTX F.

Table 1. Geotextile Properties

geotextile	description	average mass/unit area (g/m^2)[a]
GTX A	woven polypropylene	110
GTX B	nonwoven polypropylene	250
GTX C	nonwoven polyester	240
GTX D	nonwoven polyester	250
GTX E	nonwoven polyester	870
GTX F	nonwoven polyester	860

[a] As measured in the laboratory.

Chemicals and Reagents. For the TOP assay and targeted analysis of geotextile samples, 23 PFASs and 16 mass-labeled internal standards were measured. The analytes and corresponding CAS numbers are provided in Table S-1. PFAS internal standards (in methanol, 1 μg/mL) were acquired from Wellington Laboratories Inc., Canada, while analytical PFAS standards (in methanol, 2 μg/mL) were obtained from Novachem, Australia. High-performance liquid chromatography (HPLC) grade methanol (≥99.9%), sodium hydroxide (≥98%), potassium persulfate (>99%), and Supelclean ENVI-Carb solid-phase extraction (SPE) tubes were purchased from Sigma-Aldrich, Australia. All deionized (DI) water (>18 MΩ) used was sourced from an in-house purification system from the Department of Civil Engineering, Monash University, Australia.

The PFAS compounds assayed were selected based on: a) typical constituents detected in landfills, different aqueous environments, textiles and other consumer products, and drinking water,[15,21,22,24,59] b) their diversity in physicochemical properties, and c) the available analytical techniques.

Sample Preparation. This study used methanol as a solvent for extraction. Methanol has been routinely used to extract PFAAs from various matrices.[60,61] including textiles.[62−64] The methods employed by the above-mentioned studies, which rely on sequential solvent extraction cycles with methanol, were found to limit matrix effects and provide reproducible recoveries of PFASs.

The analytes were extracted from the geotextile specimens using sonicator-assisted extractions to ensure thermodynamically favorable conditions in separating the solvent from the solute.[65] Sonicator-assisted extractions are a commonly employed technique that utilizes ultrasonic waves to produce a rapid micromovement of solvents, leading to higher mass transfer.[66] Variables such as extraction temperature, ultrasonic power, and sonication time can be altered to achieve optimal extraction for the required application.[66] Several studies have reported using a sonicator at elevated temperatures (approximately 60 °C) and an optimal time of roughly 20 min to sufficiently extract trace organic compounds, including PFASs, from animal and plant tissues, and soils.[67,68]

In this study, a 40 mg geotextile specimen was cut in one piece using scissors and weighed into a 50 mL polypropylene centrifuge tube. A 40 mg specimen was found to be the minimum amount required to ensure that PFPrA concentrations in most specimens (>70% from each geotextile type) can be measured with statistical rigor, reducing the amount of laboratory-produced waste requiring disposal/destruction. Each tube containing the specimen was fortified with internal standards (1 mL, 100 nM) and suspended in 20 mL of methanol on an orbital shaker (NB-101M, N-Biotek) for 8 h. A 1 min equilibration time was allowed between adding the internal standard and methanol. The specimens were immersed in a water bath (UB-405 Thermoline) at 60 °C for 20 min. The resulting extract was transferred to a 50 mL polypropylene tube after sonication. This extraction procedure was repeated twice. The concentration of PFASs in the methanol extract was evaluated using liquid chromatography tandem mass spectrometry (LC-MS/MS). Method blanks were incorporated in each experimental run.

Three samples for each geotextile type were chosen for the TOP assay to examine the presence of PFAA precursors. The TOP assay methodology was based on a study by Houtz and Sedlak,[69] with additional adaptations and refinements. Each tube was amended with 300 μL of a 10 M sodium hydroxide (NaOH) solution and filled up to 10 mL with a solution containing 120 mM potassium persulfate ($K_2S_2O_8$) in DI water. A 10 mL aliquot of the sample extract, not spiked with internal standards, was added to the tube, and the sample was placed in a preheated bath for a reaction at 85 °C for 6 h. The sample was subsequently cooled to room temperature, spiked with internal standards, and cleaned using Supelclean SPE cartridges to reduce the elevated salt concentration for more accurate quantification of PFAAs by LC-MS/MS. Method blanks were included with each experiment.

TF quantification was conducted in a NATA Accredited (ISO/IEC 17025) commercial laboratory (Eurofins Scientific), and 20 × 20 cm geotextile specimens for each geotextile type were shipped to the laboratory for this purpose. A Metrohm combustion ion chromatography (CIC) system was used for TF analysis. Samples were placed in ceramic boats and subjected to pyro-hydrolysis in a furnace at temperatures

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Table 2. Detection Frequencies and Concentrations of PFPrA in Geotextiles[b]

specimen ID	detection frequency (%) (n = 10)[a]	concentration range (μg/g)	average concentration (μg/g)	median concentration (μg/g)	std. dev. (μg/g)
GTX A	100	0.2 − 6.73	2.18	1.34	2.04
GTX B	100	0.70 − 10.84	4.48	3.52	3.35
GTX C	80	ND − 0.98	0.45	0.41	0.29
GTX D	100	0.28 − 1.27	0.62	0.49	0.30
GTX E	70	ND − 1.16	0.43	0.47	0.36
GTX F	90	ND − 2.21	0.73	0.64	0.60

[a] n = number of specimens tested per geotextile type. [b] ND results were treated as zeros in the calculations.

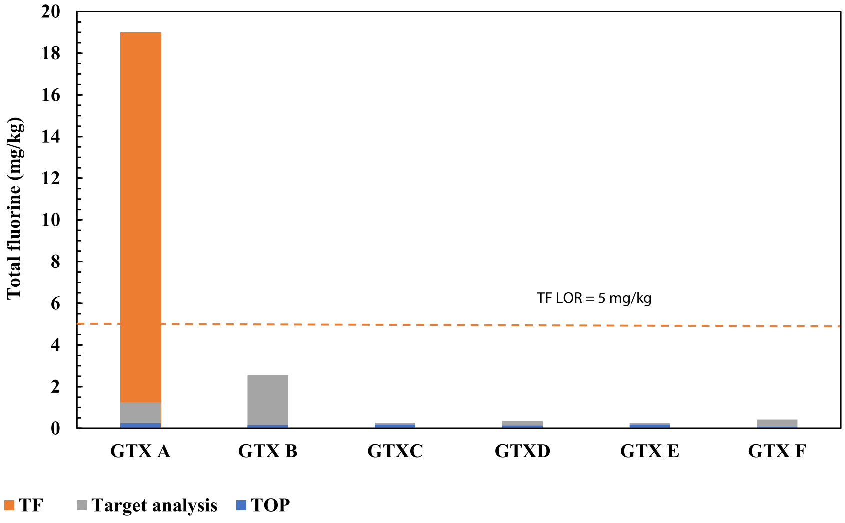

Figure 1. Total fluorine concentrations measured in TF analysis, PFAA target analysis following the original extraction and TOP assay. PFPrA contributed 100% to the total concentrations measured from target analysis following the original extraction and TOP assay.

ranging from 900 to 1000 °C in a humid, oxygen-rich environment. Under these conditions, the samples underwent oxidation to break the strong carbon−fluorine bond, and vapors were sparged through an absorbing solution. The hydrofluoric acid (HF) generated through the combustion of organic fluorine dissociates into H$^+$ and F ions within the absorption solution, which contains an internal standard for calibrating the analytical results. The analysis of fluoride in aqueous samples was undertaken using ion chromatography (IC). The above-mentioned method can measure the levels of total fluorine (both inorganic and organic). However, when applied to textiles, it is presumed that the influence of inorganic fluorine is negligible.[117,118]

PFAS Analysis. Ultrahigh-definition liquid chromatography-quadrupole time-of-flight tandem mass spectrometry instrument (LC-Q-TOF-MS/MS, Agilent 6540) was employed for determining PFAS concentrations in extracts. Detailed instrumental parameters are provided in the Supporting Information. Internal standard calibration was used to quantify PFASs. Internal standards used to calculate PFAS concentrations are shown in Table S-2. All the standard curve correlation coefficients (R^2) were >0.99. Mass-labeled standard recoveries ranged between 62% and 120%. The method detection limit (MDL), which represents the minimum concentration of a chemical that can be measured and reported with 99% confidence that the concentration is distinct from method blank results,[70] was determined based on a signal-to-noise ratio of 3:1. The limit of quantification (LOQ), defined as the minimum analyte concentration for accurate detection and quantification with statistical rigor,[71] was established from a signal-to-noise ratio of 10:1. Table S-3 provides MDL and LOQ values for the PFAAs.

Quality Assurance and Control. Targeted PFAS analyses included 10 replicates conducted in 3 batches for each geotextile type. For each geotextile type, the 10 specimens were taken randomly from different areas of a large 1 × 5 m geotextile roll to account for inhomogeneity. Before initiating the experiments, thorough cleaning of all tubes and HPLC vials was conducted using DI water and HPLC grade methanol to minimize PFAS contamination. To avoid adding PFASs during analyses, no fluorinated materials were used in the experiment. The cleanliness of the LC-MS/MS instrument was assessed using instrumental blanks consisting of methanol/DI water. Method blanks containing only methanol or oxidants and bases were subjected to the same analytical procedures as the geotextile samples to monitor and detect contamination and potential interferences arising from sample manipulations, laboratory equipment, and the overall laboratory environment.

Target analytes were not detected in the method and instrumental blanks, confirming that contamination was not introduced during extraction experiments and LC-MS/MS processing.

Fluorine Equivalency Determination. Fluorine mass balance analysis was performed by comparing measured concentrations of target PFASs and TF. For this comparison, concentrations of target PFASs from the original extraction and TOP assay were converted to fluorine equivalency concentrations using the following equation:

$$C_F = C_{PFAS}(n_F AW_F / MW_{PFAS}) \qquad (1)$$

where C_F is the calculated fluorine concentration (ng F/g), C_{PFAS} is the concentration (ng/g) of each PFAS, n_F represents the number of fluorine atoms on each PFAS, AW_F denotes the atomic weight of fluorine (18.998 g/mol), and MW_{PFAS} is the molecular weight of each PFAS (g/mol).

RESULTS

Targeted PFAS Analysis. The results of the targeted PFAS analysis showed that most geotextile specimens contained PFPrA, ranging in concentration between nondetectable (ND) and 10.84 μg/g (Table 2). No other PFAS assayed in this study was detected in any specimen. The detected concentrations of an ultrashort chain PFAS, PFPrA, may be attributed to the recent reorientation of manufacturers toward using nonlegacy shorter-chain and unknown fluorinated compounds for commercial production.[4] Although source data for ultrashort-chain PFASs are currently limited, there is evidence to establish that PFPrA is likely used extensively in industrial processes and consumer products, as PFPrA has been identified in drinking water, rain, surface water, wastewater, and landfill leachate.[20,21,25,72]

TOP Assay/TF Analysis. To enable comparison with TF measurements, concentrations of target PFASs from the original extraction and TOP assay were converted to fluorine-equivalency concentrations (see eq 1). In this study, the fluorine equivalency of the sum of targeted long and short-chain PFASs following the TOP assay was 0 mg/kg in all samples, implying that oxidizable precursors were likely insignificant in these samples. The average fluorine equivalency concentration of the ultrashort-chain PFAS, PFPrA, decreased moderately after the TOP assay in all six samples (see Figure 1). Hence, it is inferred that the quantitative analysis of PFPrA was hampered by the high ionic strength of the TOP assay reaction mixture. Applying the TOP assay produces considerable amounts of sodium sulfate and potassium sulfate via the reduction of oxidizing agent potassium persulfate. This impedes the subsequent quantitative analysis of ultrashort PFAAs due to signal suppression during LC-MS/MS analysis or interference with the SPE process for PFAAs.[93] Alternatively, ultrashort PFAAs may decompose after applying the TOP assay, becoming undetectable by the available analytical techniques. Hence, most previous studies excluded PFPrA from their analyses. While recent efforts to include shorter chain PFASs in the TOP assay protocol have been successful, these studies show relatively low recovery of PFPrA.[93] This demonstrates the need for an improved TOP assay protocol extended toward more mobile PFASs, such as PFPrA, to avoid excluding a portion of the PFAS load.

The fluorine equivalency of the sum of other targeted ultrashort chain PFASs (excluding PFPrA) was 0 mg/kg before and after the TOP assay for all six geotextiles. Notably, low concentrations and/or similar results before and after oxidation indicate an absence of substantial precursors.[101] While the TOP assay may underestimate concentrations of ultrashort PFASs, there were no detections of other targeted ultrashort compounds (excluding PFPrA) above the limit of reporting (LOR). Hence, the results suggest that significant precursor mass was unlikely to be present in geotextiles.

The fluorine equivalency average concentrations of the targeted ultrashort-chain PFAS, PFPrA, was below the LOR (5 mg/kg) for TF assessment for all geotextiles (see Figure 1). Therefore, it is unsurprising that TF concentrations were below the reporting limit for five out of six geotextiles. TF analysis is a less sensitive measurement technique than LC-MS/MS for discrete PFAS parameters and thus has a relatively higher LOR.[101] Therefore, limitations of the reporting limit likely resulted in excessive censoring of data below the LOR. However, the low/ND TF concentrations in the geotextiles of this study imply that it is unlikely large quantities of other PFASs, if any, were present in the geotextile samples.

Moreover, the fluorine equivalency average concentration of PFPrA (1.25 mg/kg) from the target analysis following the original extraction was less than the measured TF concentration for GTX A (19 mg/kg) (see Figure 1). The minor divergence between the concentration of fluorine from TF and target analysis following the original extraction (<100 mg/kg)[102] indicates that this difference is likely attributed to the variation in PFPrA distribution between different specimens of the same geotextile.

In summary, "PFAS total" parameters comprising the TF and TOP assay were found to provide an incomplete picture of PFAS concentrations in geotextiles by excessively censoring data below the LOR and insufficiently capturing ultrashort-chain PFASs. Furthermore, the results indicate no significant precursor mass and untargeted intermediates were present in geotextiles. Thus, the discussion below primarily relates to the findings of the targeted PFAS analysis from the original extraction.

DISCUSSION

PFAS in Geotextile Manufacture. PFAS chemicals have been used to manufacture nonstick and water-repellent products and AFFFs, and in various industrial processes.[74−77] While certain industries have disclosed some level of information regarding the use of PFASs, others have reported minimal, if any, information.[103,104] Furthermore, no information is available in the current literature on using PFASs in the manufacturing process of geotextiles. However, research has shown that textile fabrics impregnated with chemical coatings may contain variable concentrations of a range of PFASs. Knepper et al.[78] investigated the total concentrations of PFASs found in outdoor jackets and reported a range varying from 5 to 719 μg/m^2. Notably, most of the PFASs detected were PFCAs. The dominant PFCAs were the long-chain compounds PFOA and perfluorodecanoic acid (PFDA).

Similarly, Dreyer et al.[75] examined the total concentrations of PFASs found in outdoor jackets and gloves and observed a slightly different trend. Consistent with Knepper et al.'s[78] study, PFCAs were the prominent group of PFASs, although short-chain PFASs were more dominant. In contrast, the long-chain compounds represented only a small portion of the total PFAA concentrations. The total concentrations of PFCAs were similar to those reported in Knepper et al.'s[78] study. However, PFOA was the dominant PFCA in only 53% of samples. In 27% of samples, perfluorohexanoic acid (PFHxA) was the predominant PFCA, and in 20% of samples, perfluorobutanoic acid (PFBA) was detected at the highest concentration. In the present study, the presence of a PFCA compound corroborates the findings of the aforementioned previous studies; however, the results indicate a further shift from long and short-chain PFAAs toward ultrashort-chain homologues. Hence, investigations that are several years old may not represent current PFAS uses/trends when assessing manufactured products.

In a more recent study, Xia et al.[59] assessed 72 children's textile products from Canadian and American stores, predominantly school uniforms, to evaluate if clothing may be a significant source of exposure to PFASs. PFASs were found in all samples from both countries, with the highest PFAA concentration reported for PFPrA (45.9 ng/g). These results corroborate the findings of the present study, wherein PFPrA was either the dominant or the only PFAS compound detected in geotextiles. Notably, the Xia et al.[59] study identified that items containing elevated concentrations of PFASs were weather-proof articles, where PFASs were added to impart water resistance to the textile fibers.

PFASs are used in consumer products for their functional use or as processing aids during manufacturing. The presence of PFASs in the textiles examined by the above-mentioned studies[59,75,78] was attributed primarily to the intentional application of polymeric PFASs that impart oil and water repellency to the fibers. The concentrations of total fluorine reported in these studies significantly exceeded those obtained through targeted PFAS analysis, likely since the PFAS content was in a polymeric form. Conversely, the low TF concentrations detected and the variability in PFPrA concentrations among the geotextiles studied herein imply that PFAS-based surfactants were likely applied during manufacturing and remained on fibers as unintended residues.

The constituent fiber materials used in geotextile manufacture may require a series of chemical processing steps prior to converting them into a geotextile.[27] Although there is no publicly available information on the use of PFASs in geotextile production, inference can be drawn from the manufacturing of other textile fabrics, which often require several chemical treatment stages that may involve using PFAAs as surfactants in scouring, dyeing, and lubrication or as fluorinated polymers in durable water/stain repellent finishes.[42] Heydebreck et al.[41] reported the presence of PFASs in wastewater, air, airborne particles, and settled dust samples taken along the textile manufacturing chain, indicating that they may be used as surfactants in scouring, dyeing, and/or finishing agents. Textile mills have been shown to use PFAS-based surfactants to increase the cleanability of fabrics, as wetting agents for dyeing processes and as lubricants in various production steps.[4,40−43] Additionally, several patents mention PFASs and/or fluorinated compounds for use in textile fiber production.[37−39,79,80] Below, we explore the geotextile manufacturing steps in which PFAA-based surfactants may be applied and what functionality may be associated with their use.

Processing aids, such as surfactants, are used to improve the processing characteristics of the aforementioned manufacturing stages. Analogous to textiles, the fiber materials in geotextiles may undergo scouring, dyeing, and finishing processes, prior to converting them into geotextiles.[36,81] Scouring is the process where the impurities in the fibers are removed by washing to achieve even and reproducible results in the dyeing and finishing processes.[34] The key ingredients of scouring agents are typically amphiphilic surfactants (such as PFASs), which comprise hydrophilic and lipophilic portions and form surfactant micelles in the aqueous solution.[42,82] The lipophilic group in the surfactant molecule orients toward oil attached to the fiber and applies an emulsifying function. Moreover, due to the presence of hydrophilic moieties, the oil molecules incorporated into the micelle are dispersed in the solution to remove oil stains on the fibers.[82] Furthermore, during the dyeing process, synthetic fibers require surfactants containing both hydrophilic and hydrophobic groups, such as PFASs, to ensure that the dye is homogeneously distributed in the media and the dyeing solution is impregnated into the fiber matrix.[4,40,83] Notably, surfactants applied during the scouring and dyeing processes are not intended to remain on the fibers.

After the scouring operation, impurities in the initial fiber mass are eliminated. Surfactants (also known as fiber finishes) are typically applied to fibers to dissipate any static electricity generated during processing.[84,85] Excessive static can create conditions in which fibers adhere to equipment. Surfactants act as lubricants, surface conditioners, or softeners.[86] Lubrication is very important in needle-punching and weaving operations.[87] Point contact exists between needles and fibers during needle punching when preparing nonwoven geotextiles and between fibers at crossover points during the stretching and bending of woven geotextiles. Hence, an additional function of a lubricant is to reduce friction during fiber processing, a function that assumes greater importance as fiber production speeds rise[87,88] because excess heat generated by friction can cause softening or even melting of the fibers.[85] Additionally, a finish that provides low fiber to metal friction for easy release of fibers from manufacturing equipment enables more efficient processing on high throughput web-forming equipment and minimizes wear of the reverse-barbed needles during needle punching to prolong the lifespan of the needles.[84]

The levels of PFPrA in polypropylene versus polyester geotextiles varied. PFPrA was measured at the highest concentrations in polypropylene woven and nonwoven geotextiles, with average concentrations of 2.18 and 4.48 μg/g, respectively. Polyester geotextiles with low mass per unit areas, i.e., GTX C and GTX D, contained PFPrA at average concentrations of 0.45 and 0.62 μg/g, respectively, while average concentrations detected in polyester geotextiles with larger mass per unit areas, GTX E and GTX F, were 0.43 and 0.73 μg/g, respectively. The observed variance in PFPrA concentrations between polypropylene and polyester geotextiles may be attributed to the variability in their surface morphologies and PFAA sorption affinities. Polypropylene fibers exhibit a rough surface texture (Figure 2a) that increases fiber to metal friction during fiber processing. Polyester fibers have smooth outer surfaces (as shown in Figure 2b) and are not as prone to friction at interfaces. Hence, smooth polyester fibers typically require no lubrication compared to rough polypropylene fibers. A rougher surface can also have advantages in retaining lubricants/surfactants as their pores and indents can act as lubricant/surfactant holding pockets.[89]

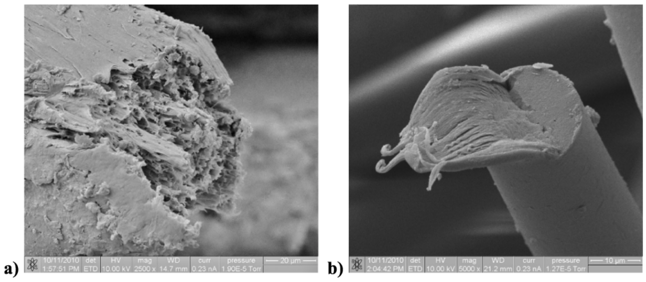

Figure 2. a) Scanning electron microscopy (SEM) image of the polypropylene fiber surface (scale bar 20 μm) (left). b) SEM image of the polyester fiber surface (scale bar 10 μm) (right).

Furthermore, it is well-known that amphiphilic surfactants (such as PFASs) are adsorbed on polyester and polypropylene fibers in contact with an aqueous surfactant solution. Liu et al.[90] observed a strong correlation between the adsorption affinity of amphiphilic silicone-based surfactants containing methylated siloxane hydrophobic groups attached to one or more hydrophilic groups and the hydrophobicity of the fiber. The sorption of these silicone-based surfactants was higher on more hydrophobic surfaces, which was attributed to increased hydrophobic interactions. Moreover, an extensive body of research literature has focused on examining the potential mechanisms governing the sorption of PFAAs with various chain lengths and terminal functional groups on polymers.[109−112] These investigations have suggested that the adsorption of anionic PFAAs is influenced by various forces acting between the solute and surfaces, the dominant mechanism being hydrophobic interactions with the fluorinated tail.

Polypropylene comprises repeating propylene monomer units ($-CH_2(CH_3)CH_2$).[91] Polyester comprises recurring units of terephthalic acid (TA) and ethylene glycol monomers.[92] Ethylene glycol contains two hydroxyl (OH) groups, and TA comprises a large, six-sided carbon ring and two carboxyl (CO_2H) groups. Due to heat and catalytic effects, the hydroxyl and carboxyl groups react, forming ester (CO−O) groups.[92] Thus, polyester exhibits higher hydrophilicity than polypropylene due to the presence of more polar ester groups in the former. Polypropylene, being purely a hydrocarbon polymer, does not contain such groups and, therefore, is more hydrophobic. Consequently, amphiphilic surfactants such as PFASs are likely to be more strongly attracted to polypropylene than polyester geotextiles, the former being more hydrophobic; albeit shorter chain length PFASs tend to be more soluble in water and likely have a lower potential for sorption than the longer-chain analogues.[112] Notably, surfactant adsorption onto fiber surfaces is often reversible, and the surfactant can desorb when the surfactant solution is replaced by water during textile rinsing processes. The extent to which this may occur may be governed by the sorption affinity of the surfactant to the fiber or application of any surfactant anchoring processes, wherein the fabric is heated to bond the adsorbed surfactant to the fiber surface thereby inhibiting its desorption.[37,94,95]

Moreover, our investigation has shown that PFPrA concentrations vary over a wide range within different specimens of the same geotextile, as shown in Table 2. Some were close to the detection limit, while some specimens contained higher levels. This is similar to Brigden et al.'s[96] study, wherein differences in PFAS levels were measured for varying sections of individual clothing articles. Quality control checks confirmed that these differences reflected factual discrepancies in concentrations within the clothing. Thus, the reported variations are characteristic of textile products treated with PFASs. Since the fibers may be manufactured in different batches, inter- and intrageotextile variability is expected. Furthermore, the application method may yield an uneven distribution and incomplete/uneven surfactant coverage of the fibers.

Environmental Implications of Our Findings. If released into the surrounding environment, PFPrA at the concentrations detected in geotextiles potentially poses a risk to the environment. Owing to these substances' high polarity and aqueous solubility, they are presumed to possess a lower bioaccumulation potential, as reported for the short-chain PFAS compound perfluorobutanesulfonate (PFBS).[97] Nonetheless, PFBS and PFBA have been detected in humans and wildlife species.[98] The extreme resistance of ultrashort-chain PFASs to degradation will lead to accumulation in surface water, groundwater, the atmosphere and dust, and contamination of drinking water resources, resulting in potential health hazards for aquatic species and higher levels of human exposure through contaminated food, water, and air.[99,100]

PFASs have been extensively detected in landfill leachate, attributed to their release from PFAS-containing consumer products.[22−26] However, the occurrence of PFPrA in geotextiles presents an additional source of PFASs in lined landfills, potentially exacerbating the overall PFAS concentrations in landfill leachate. Geotextiles may cover thousands of square meters when deployed on a large scale, often with multiple layers. Thus, to place the results of this study in a practical light, we considered a modern single geosynthetic composite bottom liner system in a municipal solid waste landfill, as presented by Gates et al.[49] Such a liner system would typically comprise several layers of geotextiles with functions including separation, filtration, and protection, as well as contributing indirectly to sealing functions. Assuming a landfill requires 10 000 m^2 of liner and that GTX A, GTX B, GTX C, and GTX E of this study are employed to perform the functions mentioned above, the total PFPrA mass associated with geotextiles in this liner system is anticipated to range between 1.97 and 46.95 g. Hence, the total PFAS mass (if present at the levels observed herein) in the geotextile components of geosynthetic composite lining systems is anticipated to increase the total PFAS concentrations in landfill leachate.

The method employed by this study relied on solvent extractions with methanol at a solvent to sample mass ratio of ≈2000:1 to limit matrix effects and provide reproducible recoveries of PFASs. The high methanol concentration employed in this study is not anticipated to reflect the concentrations present in landfill leachate. Therefore, directly comparing this study's results to PFPrA concentrations in landfill leachates is not completely relevant. Furthermore, the PFPrA concentrations associated with geotextiles in leachate are site-specific. They vary mainly depending on the size of the landfill, the type of geotextiles employed, the leaching rate, and the presence and mobility of water. Hence, estimating the concentration of PFPrA that may be present in leachate is difficult. Nonetheless, given the typical mass of geotextiles used in modern composite liners (29400 kg/Ha), these values, if achieved via interaction with landfill leachate, would represent a significant potential contribution of PFPrA concentrations in leachate (up to 29.85 μg/L after 1 year in a hypothetical liner system with a surface area of 10 000 m^2, assuming a leachate generation of 0.15 m/Ha/yr, a leachate volume in the leachate collection layer of 1500 m^3/yr, and a leakage rate of 73 m^3/Ha/yr, and that the entire PFPrA mass is leached from geotextiles [refer to Table S-4 for further detail]) compared to literature values (PFPrA levels up to 40 μg/L in municipal solid waste landfills).[25]

Elevated concentrations may directly impact the extent of PFAS migration through and attenuation by constituents of geosynthetic composite liner systems. Ultrashort-chain PFASs can pass through various environmental compartments and underlying manufactured barriers and ultimately enter drinking water sources where generic treatment methods do not adequately eliminate them.[20] As such, using ultrashort-chain PFASs in geotextiles may increase environmental pollution and human exposure if PFASs are emitted into the surrounding environment. The presence of PFASs in geotextiles and their subsequent release can potentially undermine the primary purpose of employing geosynthetic composite lining systems (to control contaminant migration) in landfill applications. Conspicuously, given the wide use of geotextiles in numerous civil, mining, geotechnical, environmental, and agricultural engineering applications, the implications of these findings not only are limited to landfills but can also be extended to other applications that utilize geotextiles.

While this study indicates that the materials used in modern composite geosynthetic lining systems may be sources of PFPrA in landfill leachate, such systems are an important defense against the environmental spread of contaminants from landfills. They will likely remain an important part of engineered hydraulic barriers for the foreseeable future. The significance of these findings needs to be elucidated through further studies with larger geotextile sample sizes to allow broader, generalized conclusions to be drawn, preferably leading to solutions for improved containment of PFAS.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c08987.

> List of PFAS analytes including abbreviation, CAS numbers (where available), and full names (Table S-1); internal standards used to calculate PFAS concentrations (Table S-2); MDLs and LOQs for the PFAAs used in this study (Table S-3); instrumental parameters of LC-MS/MS; concentration of PFPrA in leachate associated with geotextile calculation (Table S-4) (PDF)

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Notes

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■ ABBREVIATIONS

AFFF,, aqueous film-forming foam; C&D,, construction and demolition; CIC,, combustion ion chromatography; DI,, deionized; F,, fluorine; GTX,, geotextile; HCFCs,, hydrochlorofluorocarbons; HFCs,, hydrofluorocarbons; HPLC,, high-performance liquid chromatography; IC,, ion chromatography; LC-MS/MS,, liquid chromatography tandem mass spectrometry; LC-Q-TOF-MS/MS,, liquid chromatography-quadrupole time-of-flight tandem mass spectrometry; LOQ,, limit of quantification; LOR,, limit of reporting; MDL,, method detection limit; ND,, nondetectable; PFAAs,, perfluoroalkyl acids; PFASs,, per- and poly fluoroalkyl substances; PFBA,, perfluorobutanoic acid; PFBS,, perfluorobutanesulfonate; PFCAs,, perfluorocarboxylic acids; PFDA,, perfluorodecanoic acid; PFHxA,, perfluorohexanoic acid; PFHxS,, perfluorohexanesulfonic acid; PFOA,, perfluorooctanoic acid; PFOS,, perfluorooctanesulfonic acid; PFPrA,, pentafluoropropionic acid; PFSAs,, perfluorosulfonic acids; POPs,, persistent organic pollutants; SEM,, scanning electron microscopy; SPE,, solid-phase extraction; TFA,, trifluoroacetic acid; TF,, total fluorine; TOP,, total oxidizable precursor

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