

ABSTRACT

LANG, JOHNSIE RAY. Per- and Polyfluoroalkyl Substances in Municipal Solid Waste and Landfill Leachate. (Under the direction of Dr. Morton A. Barlaz.)

Landfills are the final stage in the life cycle of many products containing per- and polyfluoroalkyl substances (PFASs), but the mass release to U.S. landfill leachate is not known. The primary objective of this study was to evaluate the processes occurring within landfills that result in PFAS release and the relative importance of solid waste as a source of PFASs to wastewater treatment. Aqueous phase concentrations of PFASs released from carpet and clothing over time (>500 days) were monitored in anaerobic model landfill reactors operated under biologically-active and abiotic conditions. Leachate PFAS concentrations were characterized in a representative survey of U.S. landfills operated in different climates and contain refuse of different ages for calculating a national inventory. Aqueous phase PFAS concentrations in anaerobic model landfill reactors were quantified under live and abiotic conditions from three separate MSW samples, in an effort to evaluate sample to sample variability and to differentiate between physical leaching and release due to biodegradation.

For anaerobic model landfill reactors filled with carpet, total PFAS release was greater in live than abiotic reactors, with an average of 8.5 nmol/L and 0.62 nmol/L after 552 days, respectively. Release in live carpet reactors was primarily due to 5:3 fluorotelomer carboxylic acid (FTCA – 3.9 nmol/L) and perfluorohexanoic carboxylic acid (PFHxA – 2.9 nmol/L). For clothing, release was more dependent on sample heterogeneity than the presence of biological activity, with 0.63, 21.7, 2.6, and 6.3 nmol/L for two live and two abiotic reactors after 519 days, respectively. Release in the clothing reactors was largely due to perfluorooctanoic carboxylic acid (PFOA), with low relative concentrations of measured biotransformation precursors (FTCAs). For carpet and clothing reactors, the majority of PFAS release was not measured until

after day 100. Results demonstrate that carpet and clothing are likely sources of PFASs in landfill leachate.

The mass flow estimates of measured PFASs from U.S. landfill leachate to wastewater treatment plants are estimated to be between 854 and 1,055 kg for 2013. Mass flows were estimated by coupling measured concentrations for the 23 PFASs where more than 50% of samples had quantifiable concentrations with climate specific estimates of annual leachate volumes. Releases of long chain perfluoroalkyl carboxylates ($\geq C8$ PFCAs) and known precursors (8:2 and 7:3 FTCAs - 125 kg/yr) were less than short chain PFCAs ($< C8$) and known precursors (6:2 and 5:3 FTCA - 634 kg/yr). In the majority of landfill leachate samples, 5:3 FTCA was dominant and variations in concentrations by climate and waste age affected total measured concentrations. Measured concentrations of C11-C18 PFCAs, C9-C10 perfluoroalkyl sulfonates (PFSAs), fluorotelomer mercaptoalkyl phosphate esters (FTMAPs), di-substituted polyfluorinated phosphate esters (diPAPs), and di-substituted perfluoroalkyl phosphinic acids (PFPIs) were less than the limit of quantification (LOQ) in over 80% of samples.

Two classes of PFASs dominated total, measured concentrations in both landfill leachate and anaerobic model landfill reactors filled with MSW (i.e. short chain PFCAs and FTCAs). For short chain PFCAs, concentrations were similar in live and abiotic MSW reactors, which corresponds to their physical release from MSW. The other major contributing PFAS class, FTCAs, demonstrated higher concentrations in live compared to abiotic reactors with implications that release from MSW is dependent on biological activity. Results from anaerobic model landfill reactors demonstrated a significant lag period before the majority of measured PFAS release occurred in live reactors. The significant lag time before appearance in the aqueous

phase implies that these compounds were not used directly on products, but instead are present in the aqueous phase as a result of precursor transformation.

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Per- and Polyfluoroalkyl Substances in Municipal Solid Waste and Landfill Leachate.

by
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DEDICATION

I would like to dedicate this work to the hardest working man I know, Dr. Morton A. Barlaz.

BIOGRAPHY

Johnsie Ray Lang was born and raised in North Carolina (NC). She graduated from high school in Wilmington, NC before attending two years of college at East Carolina University. She later received her Associate of Science degree from Wake Technical Community College. Johnsie received her Bachelor of Science degree in Environmental Engineering from North Carolina State University (NCSU) in 2007 and began her consulting career with HSMM/AECOM (Hickory, NC), where she was an Engineer in Training (E.I.T. – Passed 2007). Her consulting work consisted of design, bidding, and construction management of drinking water distribution and wastewater collection systems for public municipalities. In 2009, Johnsie returned to NCSU to work on a Master of Science degree in Environmental Engineering under direction of Dr. Morton Barlaz. She defended her Master's thesis in 2012, with sulfate leaching from construction and demolition (C&D) fines as the topic.

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CHAPTER 1 - INTRODUCTION

PFASs are used on a large variety of products as surfactants, where they repel both oil and water.¹ Since producers are not required to report the presence of many PFASs on products sold in the U.S., the total amounts and primary usages are not known. Several previous publications reported the presence of PFASs on outdoor clothing, carpet, leather, outdoor awnings, microwave popcorn bags and food wrappers.²⁻⁵ While total mass flows of PFASs to the environment are unknown, usage and release are large enough that several PFASs have been detected at points far from areas of manufacture and use.⁶ In addition, PFASs have been reported to be present in large portions of human serum from the general U.S. population.⁷⁻⁸

In the U.S., the majority of consumer products are disposed of in landfills at the end of their useful life but estimates of the PFASs mass flows to the environment in landfill leachate are not included in global models of release. Such models do not calculate releases from specific sources, but instead assume environmental releases are solely due to residual non-polymerized PFASs (3% of manufacture by weight).⁹⁻¹⁰ In the case of PFAS mass flows in U.S. landfill leachate, models must make assumptions because overall release has not been previously estimated. For the U.S., both variables needed to calculate PFAS mass flows in landfill leachate (i.e. PFAS concentrations in landfill leachate and the volume of leachate release to wastewater treatment plants (WWTPs) in the U.S. annually) were previously unknown. Landfills and their leachates could represent a long-term source of PFASs and the mass of PFASs associated with leachates could prove a significant component of overall release models.

Several previous studies report on the presence of PFASs in landfill leachate,¹¹⁻¹⁴ Variations in concentrations are large enough that overall averages cannot be computed. For example, Allred et al. (2014) reported PFOA concentrations in seven U.S. landfill leachate

samples ranged from 0.15 to 9.2 µg/L. The range of previously reported PFAS concentrations in landfill leachate is not surprising given the heterogeneity of waste and variability in PFAS content on products.²⁻⁵ To accurately estimate mean PFAS concentrations, a large number of leachate samples from a variety of U.S. landfills is required.

Previous publications implicate short chain perfluorocarboxylic acids (PFCAs) and perfluorobutane sulfonic acid (PFBS), as the largest contributors to total, measured PFAS concentrations in landfill leachate from North America.¹¹⁻¹⁴ Some have suggested that the dominance of short chain PFASs compared to long chain compounds is due to their higher aqueous solubility and lower sediment-water partition coefficients.¹⁴ There are no known previous works conducted to assess the mechanisms for PFAS release from municipal solid waste (MSW) in landfills or from the surface of specific products exposed to simulated landfill conditions.

Previous reports on PFASs in landfill leachate focused on perfluorinated compounds, with only limited attempts to measure polyfluorinated compounds. For example, only two of the previous reports on PFAS concentrations in landfill leachate analyzed fluorotelomer carboxylic acid (FTCA) concentrations, with only six target analytes. Buck et al. (2011) identified the three classes of perfluorinated compounds measured in this study as surfactants used on products, while the polyfluorinated compounds are generally listed as intermediate environmental transformation products.

The first objective of this study was to measure aqueous phase concentrations of 70 PFASs released from carpet and clothing over time (>500 days) in anaerobic model landfill reactors operated under biologically-active and abiotic conditions. The second objective of this study was to characterize leachate PFAS concentrations in a representative survey of U.S.

landfills operated in different climates and containing refuse of different ages for calculating a national inventory. Mean concentrations were coupled with estimates of leachate volume to estimate the mass flow of PFASs from U.S. landfills. Temporal variability was examined using samples collected from two landfills five times over a two-year. The final objective of this study was to quantify aqueous phase PFAS concentrations in anaerobic model landfill reactors under live and abiotic conditions from three separate MSW samples, in an effort to evaluate sample to sample variability and to differentiate between physical leaching and release due to biodegradation.

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**CHAPTER 2 – PHYSICAL AND BIOLOGICAL RELEASE OF POLY- AND
PERFLUORINATED SUBSTANCES IN LABORATORY-SCALE ANAEROBIC
BIOREACTORS FILLED WITH CARPET AND CLOTHING**

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INTRODUCTION

In the United States (U.S.), the majority of textiles (i.e. carpet and clothing) are disposed in landfills at the end of their useful lives.¹ Since the turn of the century, the contribution of carpet and rugs to the total mass of municipal solid waste (MSW) discarded in the U.S. has increased from 1.3% (2.23 Tg) to 2.1% (3.25 Tg).¹ Discards include the mass landfilled plus the mass combusted for energy, but approximately 80% of discards are disposed in the ~1900 landfills in the U.S.¹ Increases in the contribution of clothing and footwear to discards have also been reported, with 3.2% (5.05 Tg) in 2000 and 5.7% (8.64 Tg) in 2013.¹ Current recycling of carpet and clothing is estimated at only 6.3 and 14.4% of total waste generation, respectively, and there are limited recycling alternatives.¹ Thus, a majority of carpet and clothing is likely to be disposed in landfills for the foreseeable future.

Per- and polyfluoroalkyl substances (PFASs) are anthropogenic compounds that are used in many applications in which they impart stain and water repellency.² PFASs are primarily applied to textiles during production, but post-consumer fabric treatments are also reported.²⁻⁵ PFASs are also reported to be applied to “virtually all residential nylon carpet sold” in the U.S., although the specific composition of the applied PFASs is not known.² PFASs are present on textiles in two forms, as non-polymerized compounds that can be washed out or evaporated, or as a molecule integrated into a fluorine free polymer network via covalent bonds.⁵

Perfluorinated chains were previously shown to be resistant to degradation pathways including hydrolysis, photolysis, and biological metabolism, and some are considered to be bioaccumulative.^{4,6-7} Recent reports indicate potential links between perfluorooctanonate (PFOA) and multiple types of cancer in humans living near manufacturing plants.⁸ Concerns over the bioaccumulation, toxicity, and persistence of PFOA and perfluorooctane sulfonic acid (PFOS) led the European Union to limit their levels to 1 µg/m² on textiles and other coated products.⁹⁻¹⁰

End of life management is an important stage of a product's life cycle that should be considered when assessing the potential for PFASs release to the environment. A product disposed in a U.S. landfill will be exposed to both physical leaching through infiltration of precipitation, as well as to anaerobic biodegradation. Leachate is the contaminated water that infiltrates through the waste mass in landfills, and is required by regulation to be collected and treated.¹¹⁻¹⁴ Landfill leachate was previously identified as an environmental source of PFASs, with short chain perfluorocarboxylic acids (PFCAs) as the most significant contributor to total PFASs.¹⁵⁻¹⁸ Although leachate is treated, attenuation during wastewater treatment will vary by PFAS and many are not attenuated.^{3,19}

In a landfill, anaerobic conditions begin shortly after waste burial, once entrained oxygen is consumed by aerobic metabolism. Biodegradation of organic solids under anaerobic conditions involves several trophic groups of microorganisms working in syntrophic assemblages. Cellulose and hemicellulose from paper, yard and food waste are the primary organic solids available for biodegradation in landfills.¹⁴ Initially after burial, disproportional activity of the microorganisms converting cellulose/hemicellulose to carboxylic acids, relative to the microorganisms that convert these acids to final products (i.e. methane and carbon dioxide) results in acidic leachate

(5.0 – 6.0). Most solids degradation occurs once the activity of the microbial populations is balanced and the pH increases to circumneutral.¹⁴

While earlier research confirmed PFASs are present in landfill leachate, there is little research identifying sources or the mechanisms for transfer of PFASs from disposed materials to leachate. Allred et al. (2015) was the first to study PFAS release from a mixed MSW sample in laboratory-scale landfill reactors and reported significantly higher release in biologically-active reactors relative to killed controls (abiotic). Short-chain mono-substituted compounds, specifically fluorotelomer carboxylic acids (FTCAs) and PFCAs were the dominant classes of PFASs in both the live and abiotic systems.²⁰ Kim et al. measured leaching of Σ PFAS (10 PFCAs & 4 PFSAs) from carpet to be 10.28 ng/L in short-term (24 h) experiments at 308 K with landfill leachate as the medium.²¹ No previous literature was identified that examines PFASs release from textiles during exposure to landfill conditions.

The objective of this study was to measure aqueous phase concentrations of 70 PFASs released from carpet and clothing over time (>500 days) in anaerobic model landfill reactors operated under biologically-active and abiotic conditions.

EXPERIMENTAL METHODS

Sample Collection, Preparation and Methane Potential. Carpet and clothing samples were obtained in a form representative of materials ready for disposal in a landfill. The carpet sample was obtained from a local carpet installer and included used carpet and new carpet scraps generated during installation. Two ~50 L bags of clothing were obtained from a second hand clothing store and comprised over 20 garments. A visual inspection of the clothing sample revealed no high performance, water-proof clothing (e.g., rain jackets), which were previously

reported to contain PFCAs and fluorotelomer alcohols (FTOHs).²² Water-proof clothing was not intentionally excluded from the sample, but was not present as this type of clothing is a small portion of annual clothing discards.

Since clothing and carpet are largely comprised of synthetic polymers that do not biodegrade, copy paper (Office Depot Bright White Laser Print Paper) was added to simulate anaerobic biodegradation in the reactors as it would occur in a landfill. The anaerobic biodegradability (i.e. methane potential) of each material was assessed using a biochemical methane potential (BMP) test.²³ In this test, 160 mL microcosms were incubated with biological growth medium, a methanogenic inoculum, and a test substrate ground to pass a 1 mm screen (e.g. carpet) for 60 days to establish the methane potential of the substrate.

The carpet, clothing, and copy paper samples were cut into approximately 5 x 15 cm strips, separately, with methanol-rinsed scissors for sample homogenization and to allow for filling of 8 L reactors. Each sample was stored, before and after shredding, separately, in a clean, methanol-rinsed, 30 L high density polyethylene (HDPE) bin at room temperature. Whole carpet strips (i.e. fibers and backing) were added to reactors.

Reactor Construction and Operation. Reactors were operated with the objective of exposing the test materials to simulated landfill conditions, using the methods presented in Allred et al. (2015). Reactors were filled with the sample (carpet or clothing), copy paper (1:1 paper:sample by weight), an anaerobic methane-producing consortium (1 L), synthetic leachate (1 L), and deionized (DI) water. Duplicate reactors were operated under both biologically-active and abiotic conditions. Streptomycin (0.34 g) and 2,2-dibromo-3-nitrilopropionamide (DBNPA – 10 g) were added to suppress biological activity in the abiotic treatments. Two reactors filled with copy paper only were also monitored to measure PFAS contamination from all aspects of

the reactor system. The complete contents of each reactor are presented in Table S1 of the Supporting Information (SI).

The anaerobic methane-producing consortium used to inoculate the reactors was generated from a methanogenic culture grown on residential MSW and transferred regularly for over 15 years.²³ This mixed methanogenic consortium was used because it is the best known representation of the microbial community that decomposes waste in municipal landfills. To avoid PFAS contamination of the consortium, copy paper was used as the sole carbon source for at least three transfers prior to reactor inoculation. Synthetic leachate was used to mimic organic matter present in landfill leachate, without introducing PFAS contamination.²⁰ The synthetic leachate consisted of humic matter (1.203 g/L - Sigma Aldrich Inc.), acetic acid (0.37 g/L – Sigma Aldrich Inc.), propionic acid (0.185 g/L – Thermo Fisher Scientific) and butyric acid (0.185 g/L – Sigma Aldrich Inc.) and was adjusted to pH 7. After loading, all reactors were sparged with nitrogen (N₂) and sealed to prevent oxygen intrusion. Leachate was recirculated once per week, at a minimum, to create leachate movement across the product surface and simulate flow through a landfill.

Reactors were incubated in a room maintained at 37°C throughout their operation to mimic typical mesophilic landfill conditions. The extent of anaerobic biodegradation in each reactor was assessed by measuring the volume of gas collected in gas bags (SKC, Inc.) and the corresponding methane composition. All gas data were corrected to standard temperature and pressure. The pH was monitored periodically and initially neutralized in the biological reactors to promote methanogenic activity. Leachate samples for PFAS analysis were collected weekly for the first two months, and bi-weekly thereafter. Two (10 mL) sub-samples were frozen

immediately after collection (-4°C) and shipped from North Carolina State University to Oregon State University overnight on ice for analysis. Reactor operation was terminated after ~500 days.

Micro-Liquid-Liquid Extraction (Micro-LLE) and Liquid Chromatography

Tandem Mass spectrometry (LC-MS/MS). A subset of the collected leachate samples were selected for PFAS analysis based on methane production trends in the reactors. Selected samples were analyzed for the leachate concentrations of 70 PFASs (Table 1), using the previously described methods for leachate analysis by LC/MS/MS.^{20,24} Briefly, leachate samples were centrifuged, titrated to pH 7-8, and extracted with trifluoroethanol and ethyl acetate.²⁴ Then 900 µL of the extract was injected, using orthogonal column chemistries to separate classes of compounds and tandem mass spectrometry for individual compound detection and identification.²⁴ For frontend separation, a modified Agilent 1100 series high pressure liquid chromatograph (HPLC) was used with two Zorbax zirconium modified diol guard columns in series with a Zorbax Eclipse Plus C18 column. The HPLC was coupled with a TQ detector operated under negative electrospray ionization and multiple reaction monitoring (MRM) mode. Analytes were chosen based on their association with commercial products that contribute to solid waste in landfills. Mono-alkyl phosphates were excluded due to their strong adsorption to the zirconium modified columns used.

For 18 PFASs analyzed, both analytical and isotopically labeled internal standards were available (Table S2).²⁴ There were 19 PFASs analyzed where analytical standards were available but no internal standard, 15 analytes where only a commercial reference material was available, and 18 analytes without any reference material.²⁴ Single samples were analyzed for each time point, but the accuracy of the method and whole-method precision were previously determined to be 81–120% and 5.5–33 %, respectively.²⁴ Method performance was robust and was verified

previously in both synthetic refuse leachate and in culture media as matrices.²⁴ Leachate from the clothing and carpet reactors was similar to that of refuse, as indicated by conductivity. Leachate PFAS concentrations were normalized to the initial reactor leachate volume, accounting for volume changes over the course of reactor operation.²⁰

Quality control measures were performed as described previously.²⁰ Briefly, method blanks were extracted and analyzed with every analytical sequence. Signals for PFASs were expected to have signal-to-noise (S/N) values of ≤ 3 prior to the analysis of actual reactor samples. An analytical sequence consisted of calibration curve standards, 24 or fewer samples, a method blank, and a standard split used to insure between day calibration accuracy. Replicate calibration standards and solvent blanks were run at least every 8 samples to track continued calibration performance over the course of the analytical sequence. Within an analytical sequence, a single sample was analyzed in triplicate to show that precision fell within reported method performance values. To test reactor sampling variability, duplicate reactor samples were analyzed for 27% of the total project samples and the variability was determined to be less than 20% for all analytes.

RESULTS AND DISCUSSION

Anaerobic Biodegradation in Laboratory Reactors. The methane potentials of the copy paper, carpet, and clothing samples, as measured in the BMP test,²³ were 199.2, 1.3, and 66.2 mL CH₄/g, respectively. The methane produced in each sample is consistent with the high cellulose content of copy paper, the presence of some natural fibers in clothing, and carpet comprised of synthetic non-biodegradable materials. All live reactors demonstrated significant conversion of the copy paper to methane and carbon dioxide (Figure 1). The lack of biological

activity in the abiotic carpet and clothing reactors was confirmed by the lack of measurable methane production during the >500 day operation. The live carpet reactors demonstrated higher methane yields than the live clothing reactors, which was surprising given the lack of biodegradability of the carpet and the presence of a degradable fraction in the clothing. The shape of the methane generation curve for live clothing reactors may be indicative of the biodegradation of two substrates with different decay rates (i.e. copy paper and clothing). Based on methane production rates in the live reactors, four phases of methane generation were defined for purposes of data interpretation; (I) lag phase, (II) exponential methane phase, (III) stationary phase, and (IV) stabilization phase. The pH in the reactors is presented in Figure S3 and shows conditions were suitable for methane generation in all of the live reactors.

Quality Control. The majority of total measured PFASs were attributed to compounds with both analytical and internal standards (>95% for carpet reactors and >73% for clothing reactors - Table S4). Most of the results for analytical, process and solvent blanks were non-detect or less than the limit of quantification (LOQ). Low levels (<5 ng/L) of 6:6 diPAP were detected in the culture and process blank for the carpet abiotic 1, clothing live 2, and clothing abiotic 1 reactors. In addition, <5 ng/L of 5:3 FTCA, PFOA, and MeFBSAA were present in the solvent blanks and PFHpA in the process blank for the copy paper reactors.

Copy Paper Control Reactors. Copy paper-only reactors, operated to measure potential PFAS background concentrations from the complete reactor system, resulted in a maximum of 0.11 nmol/L total PFASs, with PFCAs as the largest contributing class (Table 2). For the day 0 leachate samples, the measured concentrations of all PFASs analyzed were <LOQ (Table S3). Low PFAS levels in the copy paper controls indicate that the reactor system was operated with minimal background contamination introduced by the culture, copy paper substrate, and reactor

system components. Given the low levels of PFASs present in the copy paper-control reactors compared to the live carpet and clothing reactors (Table 2), carpet and clothing reactor PFAS concentrations were not corrected for background concentrations. In cases where PFASs in the carpet or clothing reactors were at similar concentrations in the copy paper reactors, no conclusions were drawn.

Carpet Reactors. Total PFAS concentrations at the final sampling point (day 552) in the live carpet reactors (avg. = 8.5 nmol/L) were an order of magnitude higher than in the abiotic reactors (avg. = 0.62 nmol/L), indicating biological processes were primarily responsible for PFAS transfer to the leachate (Table 2). In live carpet reactors, the release of PFASs was not attributable to substrate degradation, as the sample was not biodegradable (BMP of 1.3 mL CH₄/g). While the total PFAS concentration in abiotic carpet reactors over time remained similar to day 0 concentrations (avg. = 0.33 nmol/L), live carpet reactors demonstrated increases from day 0 concentrations (avg. = 0.82 nmol/L - Table S3). In both live and abiotic carpet reactors, day 0 PFAS concentrations were greater than the total concentrations in copy paper controls (Table S3), indicating PFASs released at day 0 were likely present on the carpet initially. In both abiotic and live carpet reactors, day 0 concentrations were primarily attributed to PFCAs (avg. = 0.51 nmol/L), with only minimal contribution of polyfluorinated compound classes (avg. < 0.12 nmol/L – Table S3). The major PFASs that accumulated were short-chain PFCAs (C4 – C7) and FTCAs, at an average of 54.7% and 35.8% of the total PFASs at the final sampling point, respectively (Table 2). The reason for the dominance of short chain PFASs is not clear, but may reflect the switch to production of shorter chain PFASs, differences in solubility and volatility,² and/or differences in microbial biodegradation. In addition to PFCA/FTCA release, live carpet reactors also demonstrated release of N-methyl fluoroalkyl sulfonamido acetic acids

(MeFASAAs) at low relative concentrations, with concentrations primarily due MeFBSAA (Table 2). In both live and abiotic carpet reactors, concentrations of larger, di-substituted PFASs were below the LOQ (FTMAPs, SAmPAPs, diPAPs, and PFPis), with the exception of low level di-substituted polyfluorinated phosphate esters (di-PAPs - Table 2). The absence of di-substituted compounds indicates that carpet is not a source of these compounds in landfill leachate.

Since the duplicate live carpet reactors were comparable in both PFAS leachate concentrations and in the level of anaerobic biodegradation, additional discussion of PFAS release is focused on live reactor 2. PFAS concentrations in carpet live 2 fluctuated during the lag and exponential methane phases (I/II), but release was not significant as total PFASs measured on day 0 (0.97 nmol/L) were approximately equal to day 56 levels (0.99 nmol/L) (Figure 2). Methane was generated prior to day 56 (Figure 2), but the substrate in these reactors (copy paper) did not release nearly enough PFASs on its own (Table 2) to account for the levels observed in live carpet reactors. If residual PFASs were present, they were likely released to the aqueous or gas phase before day 80, as approximately 90 L of biogas was generated in live carpet reactors and leachate was recirculated weekly. The notable lag in PFASs release could have been due to the lag time required for microbial enzyme production,²⁵ slow degradation rates of precursors,²⁶ or that a precursor did not release until a critical dispersion point.²⁷ The scenario of sudden release of FTOH at critical dispersion points, as opposed to a smooth dispersion through time, was previously shown in fluorotelomer polymer experiments and attributed to abiotic hydrolysis.²⁷

The majority of PFASs release in live carpet reactors occurred during the stationary methane phase (III – days 111 to 251) and was attributed primarily to 3 of the 70 compounds

measured (6:2 FTCA, 5:3 FTCA, and PFHxA - Figure 2). The dominance of 5:3 FTCA and PFHxA at the final time point suggest that unmeasured C6 telomer precursors may have contributed to the relative abundance of these two compounds. Around the day 211 sample, concentrations of 6:2 FTCA peaked, followed by a decrease and corresponding peak in the 5:3 FTCA concentration in the day 357 sample (Figure 2). The transformation of 6:2 FTCA to 5:3 FTCA was reported previously in the anaerobic degradation of 6:2 FTOH, with 6:2 FTUCA as a rapidly transforming intermediate.²⁶ Zhang et al. (2013) indicated that 5:3 FTCA was an anaerobic end-product of the 6:2 FTUCA, but live carpet 2 demonstrated decreases in the 5:3 FTCA concentrations and corresponding increases of PFHxA during the stabilization phase (IV - Figure 2). Gas phase PFAS releases were not measured, which is important because many PFASs are semi-volatile and have been documented in ambient air.²⁷⁻²⁹

The live carpet results contrast Zhang et al. (2013), who reported that PFCAs would not be generated from 6:2 FTUCA under anaerobic conditions. The monitoring period for the work by Zhang et al. (2013) was less than 200 days while the increases of PFHxA in the present study were not detected until day 447 (Figure 2). Additionally, the use of different inocula (i.e. inoculum grown on MSW vs. digester sludge) may have resulted in different products, abundance ratios, and transformation rates. Total PFASs in solution declined during the stabilization phase (IV – Figure 2). There was no apparent reason for the decrease in total PFAS concentrations, but similar decreases were observed in the aerobic degradation of acrylate-linked fluoropolymers.²⁵ Washington et al. (2009) suggested that the drop in PFAS concentration was due to the transformation of n:2 FTCAs to n:3 FTCAs, which were not measured. However, the n:3 FTCAs were measured in this present study and PFASs decreased nonetheless.

While the initial PFAS composition of the carpet tested here was not determined, recently published data on the PFAS composition on carpet provides further evidence that the release observed in this study cannot be attributed to the residual fraction. For perfluorohexanoic carboxylic acid (PFHxA) concentrations, average release in the abiotic carpet reactors (9 nmol/g fiber) was comparable to the maximum extractable concentration previously published for 8 carpet fibers (3 nmol/g fiber).⁵ Concentrations were converted assuming 0.1 g fiber/g carpet. In contrast, PFHxA concentrations in live, carpet reactors exceeded the maximum, chemically extracted concentrations by more than a factor of 10 (110 nmol/g fiber).⁵ This suggests that the elimination of extractable residuals on carpet, as a means to reduce PFCA concentrations in the environment, will not eliminate release during anaerobic conditions after landfill disposal.

Clothing Reactors. Clothing reactors demonstrated high variability in total PFAS release, with live 1 and live 2 demonstrating the lowest (0.63 nmol/L) and the highest (21.7 nmol/L) final concentrations of any treatment, respectively (Table 2). In the abiotic reactors, clothing demonstrated 4 to 9 times higher total PFASs concentrations than abiotic carpet or mixed MSW reactors and was similar to live carpet reactor concentrations (Table 2). The elevated PFAS release in abiotic clothing reactors indicates that the release processes for clothing differ from processes associated with carpet and mixed MSW reactors, where release in abiotic reactors was minimal. Clothing live 2 demonstrated higher initial of PFASs (day 0 total = 4.84 nmol/L - Table S3) compared to day 0 release in all carpet reactors, further demonstrating differences in processes of release. The initial PFAS release in clothing live 2 was primarily attributed to PFCAs (2.28 nmol/L), but FTCAs (0.56 nmol/L) and FTSAAs (1.95 nmol/L) were also present at considerable levels (Table S3). For the other clothing reactors, initial releases were low, similar to initial releases in carpet (Table S3).

The major PFASs that accumulated were short chain PFCAs, PFOA, and 8:2 fluorotelomer sulfonate (FTSA – Figure 3), a unique composition relative to the major compounds leached from carpet and MSW (Table 2).²⁰ Clothing live 2 demonstrated long chain PFCA release (9.93 nmol/L) at concentrations comparable to short chain PFCAs (8.33 nmol/L), which contrasts to the other treatments (i.e. carpet and MSW) where long chain PFCA release was less than 1.0 nmol/L (Table 2). In live clothing 2, PFCAs were present without detection of FTCA precursors at similar concentrations. The lack of FTCAs does not exclude the possibility that other unmeasured PFCA precursors were the source of the increase in PFCAs. Since biological activity was shown to be a requirement for transformation of several PFCA precursors,^{26,28} the presence of PFOA in abiotic clothing 2 (Figure S6) suggests that biological transformation of precursors was not the only source of PFOA.

Clothing reactors lacked significant concentrations of larger, di-substituted PFASs (FTMAPs, SAmPAPs, diPAPs, and PFPis – Table 2), with the exception of di-PAPs in clothing live 1. At the final sampling point, the sum of the diPAP concentrations was 0.24 nmol/L in clothing live 1 (Table 2), which represents 39.5% of the total measured PFAS concentrations and the highest diPAP levels for any reactor. For clothing live 1, concentrations of diPAPs and PFCAs increased concurrently without detection of FTCAs at similar levels (Figure S5). The transformation of diPAPs to PFCAs was expected as the microbially mediated biodegradation of diPAPs to PFCAs has been previously reported in aerobic microcosm experiments, with FTCAs as biotransformation intermediates.²⁹

With the exception of live clothing reactors 1 and 2, PFAS concentrations in all MSW²⁰ and carpet reactors are lower than average concentrations previously reported for 5 landfill leachate samples (PFOA: 4.13 nmol/L, 8:2 FTSA 0.17 nmol/L, and \sum diPAPs: 0.08 nmol/L).²⁴ In

contrast, the final leachate concentrations of PFOA (9.93 nmol/L) and 8:2 FTSA (3.02 nmol/L) in live clothing 2 and diPAPs in clothing live 1 are higher than average concentrations for these 5 landfill leachate samples. The higher concentrations in the clothing reactors may indicate a significant contribution to landfill leachate concentrations from clothing for PFOA, 8:2 FTSA, and diPAPs. It is also noteworthy that the clothing sample did not visually contain water-proof garments, which are reported to carry high concentrations of PFASs²² and therefore may contribute even higher concentrations of PFASs to landfill leachate.

The initial release in clothing live 2 was followed by a lag period where PFAS concentrations in the reactor were relatively constant, and then increasing release beginning with the day 169 sample (Figure 3). In contrast to carpet live 2, total PFAS release in clothing live 2 reactor followed a linear trend beginning after the exponential methane phase (Figure 4). The constant PFAS generation in clothing live 2 indicates that release was independent of the amount of PFASs present in the reactor and raises the possibility that concentrations would have continued to rise if the reactors had remained in operation. In clothing live 2, the concentrations of 8:2 FTSA and PFCAs rose concurrently, suggesting the release was simultaneous, not consecutive. Low level transformation of 6:2 FTSA to PFCAs was previously reported in aerobic biotransformation experiments,³⁰ but FTSAAs were reported to persist for decades in groundwater.³¹ The data presented here cannot be used to conclusively show the presence of biological activity on the degradation of 8:2 FTSA.

The unequal distribution of PFASs on the clothing garments (i.e. sample heterogeneity), is one possible explanation for the high variability in total PFASs released in the clothing reactors. If for example, PFASs were not distributed equally to all clothing, then variability would be expected based on which and how much of each clothing garment was included in each

reactor. The addition of samples strips during reactor filling was randomized and no more than 5 strips (~10 gm/strip) of any one clothing type was added to a reactor such that no one material represented more than 8% of the total clothing mass added to a reactor.

After the heterogeneity in the live clothing reactor leachate was detected, individual clothing garments were analyzed using the recently defined particle induced gamma-ray emission (PIGE) method,³² which is described in the SI. Using PIGE, fluorine was detected on only one of the 17 garments added to the reactors, providing some level of confirmation that heterogeneity in the live clothing reactor leachate concentrations was due to the uneven presence of PFASs on the garments added to each reactor.

ENVIRONMENTAL IMPLICATIONS

Previous attempts to evaluate global environmental PFAS releases from products have neglected release during the disposal phase.⁴ While the levels of release to the environment need further exploration, this study demonstrated PFASs release from landfilled carpet and clothing in anaerobic model landfills. Hence, estimates of global PFASs release should include release during the disposal phase for products (e.g. carpet). There was a lag period (>100 days) before the majority of PFAS release, indicating that the source of release may not be limited to residual unbound PFASs. Future work analyzing PFAS release from products should be done in biologically active systems with relatively long monitoring periods.

Biotransformation precursor compounds were major contributors to PFAS release from carpet in landfills, as PFCAs and FTCAs represented an average of 43% and 55% of total PFAS accumulation in leachate, respectively. In contrast, Zhang et al. (2013) suggested that PFAS release from landfills is generally due to direct PFCAs release from products. While the

accumulation of biotransformation intermediates over time comprised a significant fraction of the total PFASs in leachate, the initial PFAS content on the carpet and clothing was not determined in this study. Future work to determine parent compounds and release mechanisms is needed to determine whether PFAS release was due to compounds entrapped in the matrix or on the surface. The levels of FTCAs versus PFCAs released from landfills in leachate is important as FTCAs were previously determined to have a toxicity thresholds 100 times lower than PFCAs for a fresh water microorganism.³³ Future efforts to characterize PFASs release from landfills should include releases due to PFCA precursor compounds, as they likely play an important role in overall release.

Ultimately, it would be useful to have an estimate of PFAS release from U.S. landfills. The test system used here was a batch system in which leachate remained in the reactor for extended periods of time and the majority of the release did not occur until >200 days of operation. In contrast, leachate is continuously removed from landfills and typically transported to a wastewater treatment plant. Thus, the releases measured here may not be perfectly representative of landfills. A study to estimate national mass release is in progress and is based on measured leachate composition at landfills coupled with estimates of leachate generation as a function of rainfall.

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Table 1. Acronyms and structures of PFAS compound classes analyzed. Adapted from Allred et al. (2014).

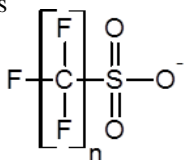
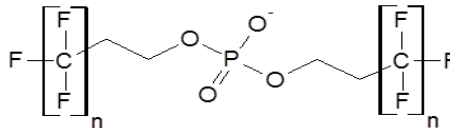
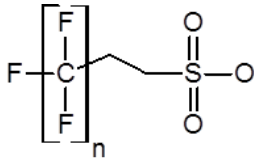
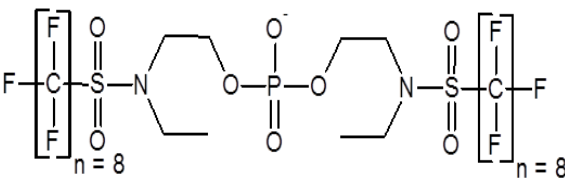
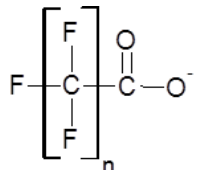
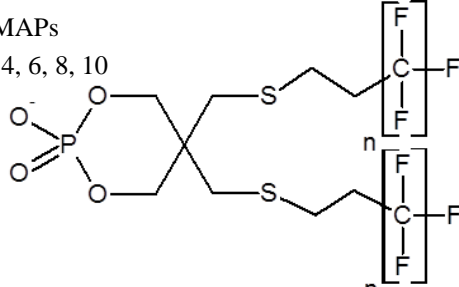
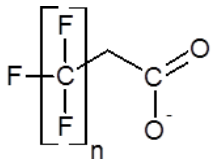
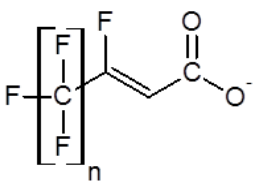
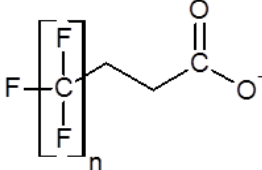
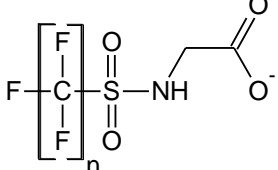
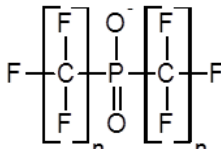
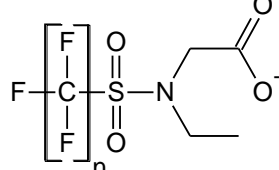
<p>Perfluoroalkyl sulfonic acids PFASs n = 4-10</p> 	<p>Di-substituted polyfluorinated phosphate esters DiPAPs n = 4, 6, 8, 10</p> 
<p>Fluorotelomer sulfonic acids n:2 FTSAs n = 4, 6, 8</p> 	<p>Bis(N-ethyl perfluoroalkylsulfonamidoethane) phosphate DiSAmPAP</p> 
<p>Perfluoroalkyl carboxylic acid PFCAs Short Chain n = 4-7 Long Chain n = 8-18</p> 	<p>Fluorotelomer mercaptoalkyl phosphate esters FTMAPs n = 4, 6, 8, 10</p> 
<p>Fluorotelomer carboxylic acids FTCAs n:2 FTCA n = 4, 6, 8, 10</p>  <p>n:2 FTUCAs n = 4, 6, 8, 10</p>  <p>n:3 FTCA n = 3, 5, 7, 9</p> 	<p>Fluoroalkyl sulfonamido acetic acids FASAAs n = 4-8</p> 
<p>Disubstituted perfluoroalkyl phosphinic acids PFPIAs n = 4, 6, 8</p> 	<p>N-ethyl fluoroalkyl sulfonamido acetic acids EtFASAAs n = 4-8</p> 

Table 2. Concentration ranges of PFAS classes in anaerobic reactors at the final time point. See Table 1 for specific analytes included in each PFAS compound class. ^{a, b}

nmol/L			Σ C4-C7 PFCAs (n = 4) ^c	Σ C8-C16 PFCAs (n = 9)	Σ FTCA s (n = 10)	Σ FTSA s (n = 2)	Σ DiPAP s (n = 5)	Σ PFSA s (n = 6)	Σ Me-FASAA s (n = 4)	Σ Et-FASAA s (n = 3)	Di-SAmPA P (n = 1)	Σ PFAS s (n = 70)
Copy Paper												
Only	Live	1	0.04	0.02	0.02	<LOQ ^d	ND ^e	0.01	<LOQ	<LOQ	ND	0.11
Day 525		2	0.03	0.03	0.03	0.01	<LOQ	<LOQ	0.01	ND	ND	0.11
	Live	1	2.02	0.31	4.91	<LOQ	0.01	0.02	0.12	<LOQ	<LOQ	7.40
Carpet		2	4.25	0.96	4.12	<LOQ	0.02	0.05	0.20	<LOQ	ND	9.59
Day 552	Abiotic	1	0.17	0.10	0.23	<LOQ	0.03	0.02	0.01	ND	ND	0.57
		2	0.44	0.10	0.01	<LOQ	ND	0.08	0.03	ND	ND	0.67
	Live	1	0.16	0.16	<LOQ	0.02	0.24	0.04	<LOQ	0.01	ND	0.63
Clothing		2	8.33	9.93	0.35	3.02	0.02	0.06	<LOQ	<LOQ	ND	21.73
Day 519	Abiotic	1	0.63	0.74	0.42	0.65	0.03	0.06	0.10	<LOQ	ND	2.63
		2	3.34	2.36	0.35	0.19	<LOQ	0.03	<LOQ	ND	ND	6.28
	Live	1	0.84	0.33	1.60	0.02	0.05	0.04	0.02	0.02	0.01	2.96
MSW^f		2	1.09	0.43	7.31	0.02	0.03	0.12	0.17	0.07	<LOQ	9.24
Day 273	Abiotic	1	0.87	0.19	0.02	0.02	0.03	0.05	0.01	<LOQ	<LOQ	1.19
		2	0.77	0.17	0.03	0.02	0.01	0.05	0.02	<LOQ	ND	1.08

- The following were not presented because the measured concentration in all reactors was non-detect: Σ FTMAPs (n=5), Σ FASAAAs (n=5), Σ PFPIAs (n=5), C17-C18 PFCAs, 4:2 FTSA, 4:2/4:2 diPAP, 4:2/6:2 diPAP, PFNS, MeFHxSAA, EtFHxSAA, EtFHpSAA, FBEA, and FBUEA
- Single samples were analyzed for each time point, but the accuracy of the method and whole-method precision were previously determined to be 81–120% and 5.5–33%, respectively
- The number (n) of analytes included in each PFAS compound class
- All signals for analytes in compound class were less than the LOQ, refer to Allred et al. (2014) for limit of quantification (LOQ) by specific PFAS compound
- All signals for analytes in compound class were non-detect (ND), refer to Allred et al. (2014) for limit of detection by specific PFAS compound
- Data adapted from Allred et al. (2015)

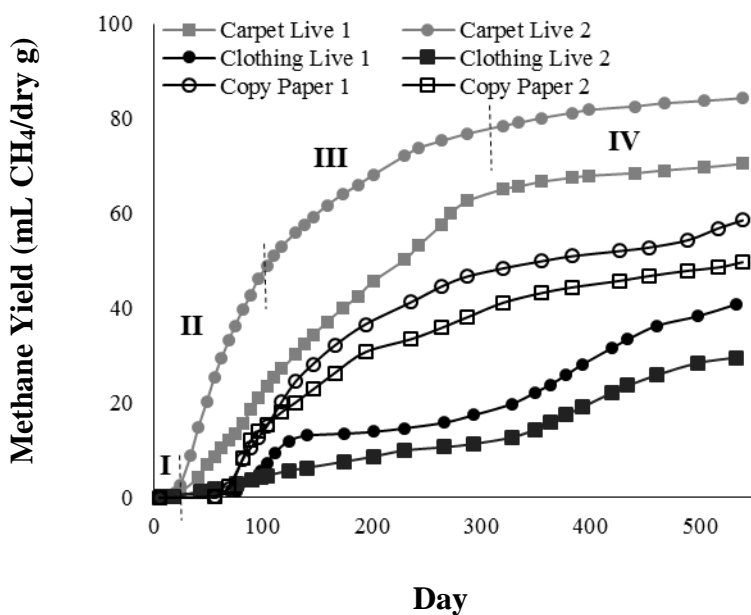


Figure 1. Methane yields in the live copy paper, clothing, and carpet reactors per total mass added to each reactor.

Methane yields in abiotic carpet and clothing reactors are not presented as they were negligible. Phases for carpet live 2 presented [(I) Lag Phase, (II) Exponential Methane Phase, (III) Stationary Phase, and (IV) Stabilization Phase] were determined graphically using Figure S2.

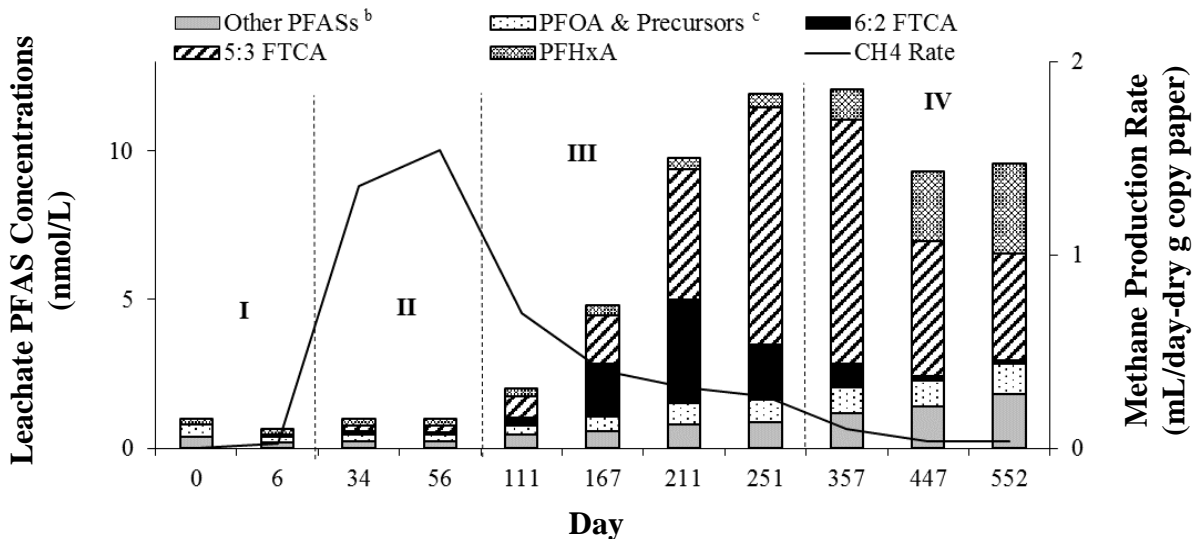


Figure 2. PFAS release from carpet live 2 presented as total concentrations at each sampling point.

Methane (CH₄) measurement from the previous sampling point was presented if a measurement was not made on the same day as PFAS samples. PFAS release from carpet live 1 is presented in Figure S4. Note the non-linear x-axis. Whole method variability for 6:2 FTCA, 5:3 FTCA, PFHxA, and PFOA was 20%, 20%, 20%, and 12%, respectively. Other PFASs includes the sum of concentrations for all other measured compounds (n = 59). PFOA & Precursors includes the sum of concentrations for PFOA, 8:2 FTCA, 8:2 FTUCA, 7:3 FTCA, 8:2 diPAPs, and 8:2 FTSA

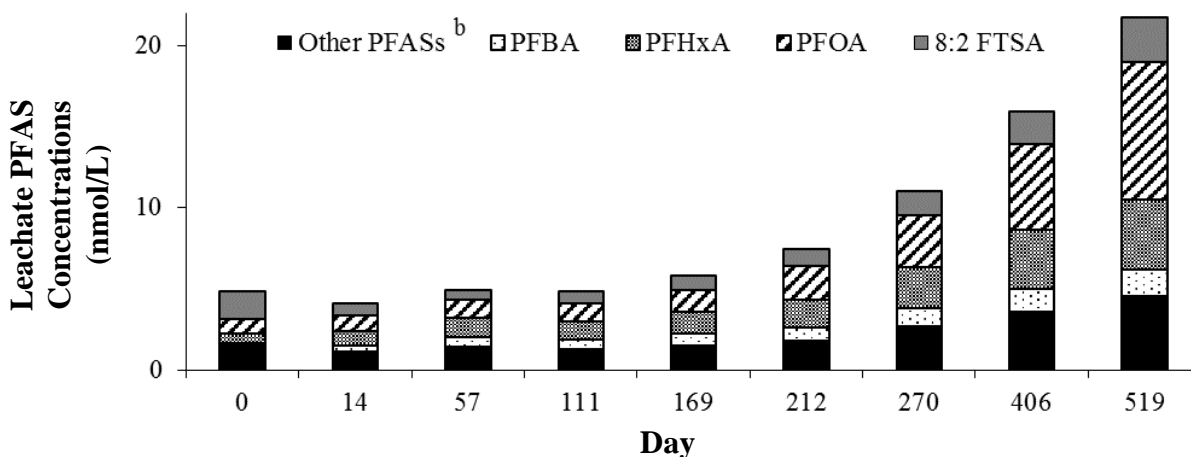


Figure 3. Leachate PFAS concentrations in clothing live 2. Final concentrations for each PFAS compound class are shown in Table 2.

PFAS release in clothing live 1 is presented in Figure S5. Note the non-linear x-axis. The whole method variability for PFBA, PFHxA, PFOA, and 8:2 FTSA was 20%, 20%, 12%, and 20%, respectively. Other PFASs includes the sum of concentrations for all other measured compounds (n = 66)

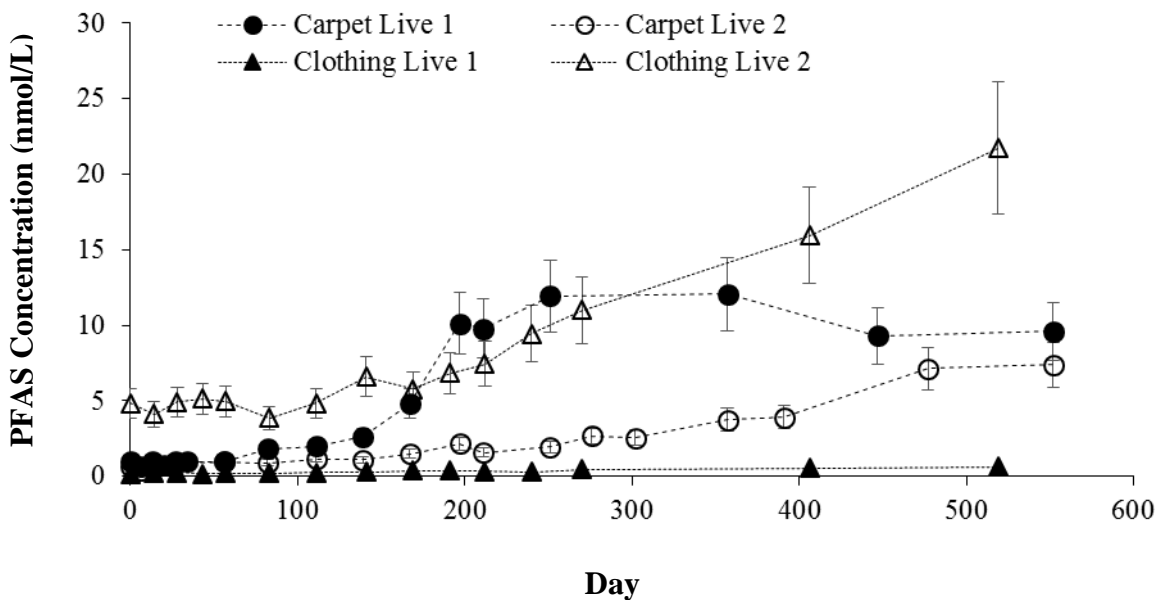


Figure 4. Total PFASs concentrations for all measured compounds (n = 70) as a function of time in live carpet and clothing reactors.

The whole method variability for individual analytes ranges from 12% - 20%, error bars represent the greatest variability (20%)

**CHAPTER 3 – NATIONAL INVENTORY OF PER- AND POLYFLUOROALKYL
SUBSTANCES (PFAS) IN U.S. MUNICIPAL LANDFILL LEACHATE RELEASES OF
PER- AND POLYFLUOROALKYL SUBSTANCES TO U.S. MUNICIPAL LANDFILL
LEACHATE**

INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are used in many consumer products including baking papers, microwave popcorn bags, carpet, upholstery, medical garments, food contact paper, non-stick cookware, dental floss, and outdoor clothing.¹⁻⁴ Many of these products are disposed in landfills at the end of their useful life and the presence of PFASs in landfill leachate is well documented, though the range of concentrations varies widely.⁵⁻¹⁰ For example, the reported range of perfluorooctanoic acid (PFOA) concentrations in U.S. landfill leachate (n = 13) was 0.15 to 9.2 µg/L.^{6,9} For Chinese landfill leachate, concentrations of PFOA have been reported to be as high as 214 µg/L.⁵ The range of reported PFAS concentrations in landfill leachate is not surprising given the heterogeneity of municipal solid waste (MSW)¹¹ and the range of PFAS content on various products.^{1-4,12}

The mass release of PFASs from landfills to wastewater treatment plants (WWTPs) is of interest as the U.S. EPA recently established advisory levels for perfluorooctanesulfonic acid (PFOS) and PFOA of 0.07 µg/L in drinking water.¹³⁻¹⁴ Since WWTPs are not known to attenuate PFOA and PFOS,¹⁵ PFASs in landfill leachate could be released to surface water. The mass of PFASs in collected leachate sent to WWTPs is a function of both leachate concentrations and leachate volume. Leachate volume will depend on the climate (i.e. rainfall rates, evapotranspiration) as precipitation is the major source of infiltration to landfills.

Given the heterogeneity of waste disposed in landfills, there are many potential sources of variability in leachate PFAS concentrations. Concentrations could be influenced by infiltration volume (i.e. climate) as well as waste age and seasonal variability in infiltration. In addition, some landfills accept WWTP biosolids that have been reported to contain PFASs.¹⁶ Previous studies on PFASs in leachate did not assess variations in concentrations based on the climate of the landfill.⁵⁻¹⁰ The potential for leachate PFAS concentrations to change with time as concentrations of phased-out PFASs decrease (i.e., PFOA- and PFOS-based products) has not been evaluated. Benskin et al (2012) demonstrated temporal PFAS concentration variations for a single landfill with one average waste age, with variations largely attributed to increases of C5, C6, C8, and C10 PFCAs and 8:2 fluorotelomer carboxylic acid (FTCA) during the spring months. However, no studies identified have evaluated the effect of climate or waste age on PFAS concentration.

The objective of this study was to characterize leachate PFAS concentrations in U.S. landfills operated in different climates and containing MSW of different ages, and to use concentration data with independent estimates of leachate volumes to estimate the mass of PFASs released from U.S. landfills. In addition, temporal variability was examined using samples collected from two landfills that were sampled five times over two-years.

EXPERIMENTAL METHODS

Site Selection and Descriptions. Prior to selecting a landfill for inclusion, landfill operators completed a questionnaire with information on waste sources and waste age, operating characteristics, and potential sample locations. Landfills were selected to include sites in different climates and containing refuse of different ages. Climate categories were adopted from

the U.S. EPA which categorizes landfills based on annual precipitation: arid (<38 cm), temperate (38 – 75), and wet (>75).¹⁷ The average waste age associated with a leachate sample (Table 1) was calculated from the mean of the date of initial waste placement and the sampling date (2013). This calculation of average waste age is imperfect because it assumes equal waste placement annually, but it allows for some analysis of the effect of waste age.

All participating landfills were publicly owned, the implication of which is that they were receiving primarily MSW and in some cases biosolids, but were less likely to accept a range of industrial wastes relative to privately owned facilities. Ultimately, 95 samples were collected from 18 landfills (Table 1), either directly from a valve after flushing, or using a polyethylene baler for leachate obtained from manholes, lagoons, and ponds. Most landfills were sampled twice, but two landfills (T and U) were sampled five times over a two-year period to examine temporal variability.

The primary focus of the sampling strategy was to collect leachate as it leaves the landfill for offsite treatment at a WWTP. At some landfills, leachate was collected at additional locations to obtain samples from individual landfill cells to increase the size of the data set and/or to obtain waste-age specific leachate samples. To insure that all landfills were weighted equally, all data from cells of the same waste age was averaged so that only one value is reported for each landfill at each time point.

Sample Collection and Storage. Landfill operators were provided with self-contained sampling kits with return shipping instructions. Sample collection took place from February 2013 to December 2014, with the majority of sample collection in 2013. Leachate was collected in a 1-L HDPE container and then partitioned into two 50 mL sample tubes, sealed with parafilm squares, and frozen overnight onsite when possible. After freezing, samples were shipped on ice

overnight to Oregon State University (OSU) for analysis. For Landfill O, the samples were shipped the same day as a freezer was not available.

For quality control, each sample kit included duplicate field and trip blanks (i.e. sampling containers with DI water only). Trip blanks remained sealed during sampling while field blanks were opened during sample collection to assess potential background contamination during sampling.

Micro-Liquid-Liquid Extraction (Micro-LLE) and Liquid Chromatography Tandem Mass spectrometry (LC-MS/MS). Samples were analyzed for the aqueous concentrations of 70 PFASs comprising 14 compound classes (Table S1) using previously described methods for leachate analysis by LC/MS/MS.⁶ Briefly, leachate samples were centrifuged, titrated to pH 7-8, and extracted with trifluoroethanol and ethyl acetate. Then, 900 μ L of the extract was injected, using orthogonal column chemistries to separate classes of compounds and tandem mass spectrometry for individual compound detection and identification. Method detection limits were at low to sub-ng/L levels. Analytes were divided into four tiers based on the availability of standards: quantitative (Qn), semi-quantitative (Sq), screening (Sc), and qualitative (Ql). Quantitative (Qn) analytes (n = 29) had analytical standards, the measured accuracy fell within 90 – 110%, and precision was $\leq 20\%$ RSD. Semi-quantitative (Sq) analytes (n = 7) had analytical standards, but the measured accuracy did not fall within 90-110% and/or the precision was $\geq 20\%$ RSD. Only a commercial reference material was available for qualitative (Ql) analytes (n = 16). No reference material was available for screening (Sc) analytes (n = 18) but whose composition fell within homologous series of compounds that differed only in chain length. For PFASs in the Sc and Ql categories, concentrations were estimated assuming equal

molar response factors to structurally similar, quantifiable PFASs. Leachate samples were analyzed concurrently with samples presented in Allred et al. (2015) and Lang et al. (2016).

Quality Control. Concentrations in all 69 trip and field blanks were less than the limit of quantification (<LOQ) for all 70 PFASs measured, except for low level contamination in one field blank sample, from the first sampling event at Landfill Q (< 3 ng/L for all compounds). The absence of quantifiable levels of PFASs in the blanks indicates that concentrations measured in the samples were attributable to the leachate and not background contamination.

Data Analysis of PFAS Concentrations. For the national inventory, the 70 PFASs were categorized into three groups based on the number of samples with concentrations above the LOQ. This grouping was implemented because a large number of PFAS concentrations were <LOQ. Individual PFASs were assigned to group 1 if over 50% of all samples were >LOQ. Mean concentrations were calculated for group 1 PFASs, as a majority of concentrations were at quantifiable levels. PFASs were assigned to groups 2 or 3 if the fraction of samples >LOQ was 20 - 50% or <20%, respectively. To evaluate the contribution of group 2 PFASs, maximum likelihood concentrations were calculated as outlined in Gibbons and Coleman (2001), with the equation in the SI. Group 3 compounds are presented graphically in the SI, but a mean was not calculated.

Leachate PFAS concentrations were analyzed to evaluate whether there were significant differences attributable to climate or average waste age (greater than or less than 10 years). For waste age evaluation, an average waste age of ten years was selected because this value divided the landfill samples into two groups with similar numbers of samples in each group. To estimate national release, a separate mean concentration was used for each climate and waste age category for each PFAS.

Estimate of Mass Flow of PFASs in U.S. Landfill Leachate. Equation 1 was used to estimate the mass release of individual PFASs in leachate from U.S. landfills in wet climates. This equation was repeated for landfills in temperate and arid climates, with the sum of the three climates equal to the total mass release for an individual PFAS in U.S. landfill leachate.

$$M_{p,wet} = (\bar{x}_{p,<10,wet} \times WIP_{<10,wet} + \bar{x}_{p,>10,wet} \times WIP_{>10,wet}) \times LG_{wet} / SA \quad (1)$$

where, $M_{p,wet}$ is the mass release of PFAS p from landfills in wet climates (kg/yr), $\bar{x}_{p,a,wet}$ is the average concentration of PFAS p for the set landfills with average waste age a, (i.e. >10 years or <10 years) from landfills in wet climates, $WIP_{a,wet}$ is the total mass of waste contained in U.S. landfills in Tg (1 Tg = 10⁶ kg) from landfills in wet climates with waste age a, LG_c is the leachate generation rate for landfills in wet climates (m³/ha-day), and SA is average mass of waste per surface area for U.S. landfills (Tg/ha). PFAS mass release was estimated for 2013, which was the year when most leachate samples were collected. The leachate generation rate was derived for three climate categories, as leachate generation varies with precipitation. SA was calculated for all U.S. landfills as it was not expected to vary with climate.

The probable range for the national release of total PFASs calculated here was estimated using a Monte Carlo analysis, which reflects uncertainties in PFAS concentrations and in predictors of leachate volume (LG_c and SA). For the Monte Carlo analysis, the total mass release of group 1 PFASs in U.S. landfill leachate was estimated as the sum of Equation 2, repeated for landfills in wet, temperate, and arid climates. Group 1 PFASs defined as screening (Sc) or qualitative (Ql) in the LC-MS/MS method were not included in equations 2 and 3. Group 2 PFASs were not included in the total release, as their average concentrations are only maximum likelihood estimates.

$$M_{T,wet} = (\bar{x}_{T,<10,wet} \times WIP_{<10,wet} + \bar{x}_{T,>10,wet} \times WIP_{>10,wet}) \times LG_{wet} / SA \quad (2)$$

where, $M_{T,wet}$ is the total PFAS mass released to WWTP from landfills in wet climates, and $\bar{x}_{T,a,wet}$ is the average of the total measured group 1 PFAS concentrations for the set of n landfills in wet climates and each waste age (equation 3).

There are two methods that can be used to calculate the total, average PFAS concentration for a given climate and waste age category (\bar{x}_T). One alternative is the average of the total PFAS concentration from each landfill, which is not the same as the sum of the average concentration for each PFAS. To calculate M_T in equation 2, the sum of the group 1 PFAS concentrations from each landfill was used as in equation 3. This is because the total measured PFASs at each landfill was judged to be a more accurate estimate of total release than summing the average concentrations of individual PFASs.

$$\bar{x}_{T,a,c} = \frac{\sum_l \sum_p x_{l,p,a,c}}{n_{a,c}} \quad (3)$$

where, $\bar{x}_{T,a,c}$ is the average of the sum of the measured group 1 PFAS concentrations for the set of n landfills in climate c and waste age a, $\sum_l \sum_p x_{l,p,a,c}$ is the sum of the total group 1 PFAS concentrations from landfill n in climate c with waste age a, and $n_{a,c}$ is the number of landfill samples analyzed in climate c with waste age a.

The Monte Carlo analysis was conducted with 10 variables including the total PFAS concentration for waste that is less than and greater than 10 years in age in each of three climates (6), the leachate generation rate in each climate (3) and the waste mass per surface area (1). To ensure model convergence, 10,000 realizations were conducted on the total PFAS mass flow (equation 2).

For estimates of the total mass of waste in U.S. landfills, 1980 was selected as the base year given the assumption that waste disposed after 1980 was managed in engineered landfills, which include leachate collection systems, though some landfills were operated without liners

through the early 1990s.¹⁷ Previous estimates for annual waste disposal in U.S. landfills demonstrate considerable variability, with annual disposal estimates varying from 150 to 284 Tg in 2013 (Figure S1).^{11,21-23} The Powell et al. (2015) estimate for annual disposal was adopted here as it is the most recent and is the only one that utilizes certified reports from landfill operators for the majority of the data. For the years prior to 1990, the Powell et al. (2015) estimate was decreased at the rates described by the U.S. EPA.¹¹ For years after 1990, the Powell et al. (2015) estimate was assumed to be linear between the years where the mass was provided. The fraction of waste generated in each climate region was adopted from published estimates of disposal rates for each region (Figure S2).

For landfills in wet climates, leachate generation rates (Figure S3) were estimated using data from annual landfill operating reports to state agencies (n = 27), published data (n = 12), data provided by some of the landfills that participated in this study (n = 7) and data obtained from a consulting engineer (n = 6).²⁴⁻²⁵ While it is possible that variability in leachate generation rates is due to the low number of samples, the wide distribution of leachate generation rates is likely due to variability in landfill geometry and operating conditions, which are known to affect the infiltration into a landfill. Leachate generation rates for temperate and arid climates are summarized in Table S2.

The mass of waste contained per landfill surface area was estimated using landfill operating reports to state agencies (n = 18)²⁵ and data obtained from a consulting engineer (n = 95 - Table S3). The mass of waste contained per surface area is not expected to vary with climate, so data were aggregated (Figure S4).

RESULTS AND DISCUSSION

The results for group 1 PFASs are presented first, as these were the only data used quantitatively for the national inventory. Results for group 1 PFASs are followed by the results for group 2 and 3 PFASs. As presented below, group 2 PFASs were less <1% of the total estimated PFAS release to landfill leachate.

PFASs Present above the Detection Limit in >50% of Samples (Group 1). The PFASs assigned to group 1 (i.e. >50% of samples exhibited quantifiable concentrations) belong to the PFCAs, FTCAs, PFSAs, fluorotelomer sulfonic acid (FTSAs), n-methyl fluoroalkyl sulfonamido acetic acids (MeFASAAs) and n-ethyl fluoroalkyl sulfonamido acetic acid (EtFASAAs) compound classes (Table 2). The widespread presence of C4 - C10 PFCAs and C4, C6, and C8 PFSAs in the sampled leachate is consistent with previous observations of these PFASs in leachate⁵⁻¹⁰ and as residuals on PFAS-treated products.^{1-4,12} The presence of FTSAs, FTCAs, EtFASAA, and MeFASAAs in leachate is less well-documented. With the exception of FTSAs, these polyfluorinated substances are described as “intermediate environmental transformation products,” as opposed to surfactants used on products.¹²

The mean concentrations for group 1 PFASs are presented in Table 3. The standard deviations are often greater than the mean and reflect considerable variability in each sample population (Table 3). Given the heterogeneity of landfills and the numerous factors that influence PFAS release to leachate (e.g., sorption, preferential flow paths of leachate through waste, uneven distribution of PFAS-containing products in landfills), this is not surprising.

Of the 19 group 1 compounds quantified, there were four for which all concentrations were >LOQ (i.e. C6-C8 PFCAs and PFHxS). For the remaining 15 compounds, the mean concentration across all landfill samples was essentially the same whether a value of the LOQ,

50% of the LOQ or 0 was used to calculate the mean (Table S4). To calculate a mean concentration for cases in which samples were < LOQ, the concentration was assumed to be 50% of the LOQ.

PFAS Concentration Variations with Waste Age. Analysis of variations in PFAS concentrations as a function of average waste age was examined for the 19 group 1 PFASs defined as quantitative or semi-quantitative in the LC/MS/MS method (Table 2). For this analysis, data from all climates was combined. There were nine PFASs that demonstrated significantly different means ($P < 0.05$) for older waste compared to younger waste (MeFBSAA, PFBS, 6:2 FTCA, 8:2 FTCA, 5:3 FTCA, 7:3 FTCA, PFHpA, PFNA, and PFDA - Table S5), with higher concentrations in leachate from younger waste in all cases. This could be due to decreases in concentrations with time or to changes in the types of PFASs used on products. For example, manufacture of PFBS and PFNA based products increased as alternatives to PFOS and PFOA products, and both PFBS and PFNA were higher in younger leachate.¹²

PFAS Concentration Variations with Climate. When mean group 1 PFAS concentrations were compared using analysis of variance (ANOVA), no means were statistically different based on climate in the location of the landfill (Table S6). While variability with climate would be expected, the large variability in the measured concentrations likely masked any potential effect of climate on PFAS concentration.

Volume of Leachate Released from U.S. Landfills in 2013. For 2013, the estimated total volume of leachate generated in the U.S. was 74.1 million m³/yr (Table 4). Landfills in wet climates generated the majority of leachate in the U.S. (82%), even though only 47% of the waste is generated in this climactic region (Table 4). It is recognized that this estimate of leachate volume does not consider leachate that is recirculated to the waste and not sent off-site

for treatment. Estimates of total leachate recirculation were not available but judged to be on the order of 10 - 20% of leachate generation in wet climates.

Annual PFAS Mass Release in U.S. Landfill Leachate. The national inventory of PFAS mass release based on equation 1 is given in Figure 1. The majority of estimated PFAS mass release was attributable to PFCAs (401 kg/yr) and FTCAs (380 kg/yr), with lower releases of PFSAAs and their precursors (116 kg/yr). Both 5:3 FTCA and 6:2 FTCA were previously identified products of anaerobic 6:2 FTOH degradation.²⁶ While Buck et al. (2011) lists FTCAs as biotransformation intermediates, a recent publication demonstrates that FTCAs were present on Japanese consumer products.²⁷ PFAS release from arid climates was <1% of the total mass release. Although mean PFAS concentrations were statistically similar in different climates, the low leachate volume in arid climates resulted in low mass release (Figure 1). Total release of the seven group 1 PFASs defined as qualitative and screening was estimated to be ~74 kg PFAS/yr, but these compounds were not included in Figure 1 or the national release model as concentrations were not quantitative..

A Monto Carlo analysis was conducted to evaluate the uncertainty associated with the point estimate developed using equation 1. Model parameter distributions are described in Table S7. The 90 percentile range for total group 1 PFASs of 854 to 1,055 kg/yr (~900 to ~1,000 kg/yr with one significant figure - Figure 2). Since total oxidable precursor assays or total fluorine analyses were not completed in the current study, the actual inventory of PFASs in U.S. landfill leachate is likely higher than presented here, due to the presence of unmeasured PFASs.

PFASs Present above the Detection Limit in 20 - 50% of Samples (Group 2). Eleven PFASs were placed in group 2 (Table 2). The two classes of PFASs with the largest representation in group 2 were FASAAs and long chain FTCAs, but one PFSA, one unsaturated

fluorotelomer carboxylic acid (FTUCA) and one FTSA were also present. The presence of a compound in group 2 indicates that the PFAS could be present in landfill leachate, but its presence is not widespread. Maximum likelihood estimates for group 2 PFASs that were quantifiable (10:2 FTCA, 8:2 FTUCA, and 4:2 FTSA - Table 5) are low relative to concentrations for group 1 PFASs (Table 3). The inclusion of group 2 PFASs added only ~1 kg/yr to PFAS mass flows (Figure 1).

Long chain FTCAs are less likely to be present in leachate compared to their more soluble, shorter chain homologues, which were present in >50% of the leachate samples (group 1 – Table 2). FASAs were present in a lower number of samples (group 2) compared to MeFASAs and EtFASAs, which were present in the majority of samples (group 1 – Table 3). This is consistent with the lower production and use of FASAs relative to the production of N-MeFASAs and N-EtFASAs derivatives.²⁸

PFASs below the Detection Limit in the Majority of Samples (Group 3). There were 32 PFASs defined as group 3 PFASs because they were present in less than 20% of leachate samples (Table 2). Data for group 3 PFASs are only presented graphically (Figure S5) because the fraction of results that were quantifiable was too low for a mean to be calculated. Long chain PFCAs (>C11), diPAPs, and PFPis were present at quantifiable levels in <20% of landfill leachate samples. One explanation for this is the sorption of these PFASs to several materials known to be present in MSW.²⁹ Since diPAPs were previously identified on food contact paper,² a product that is typically landfilled in the U.S., their absence in the majority of landfill leachate does not imply that they are not entering landfills, but rather that they are not being released to the aqueous phase. Allred et al. (2015) reported that diPAPs were present in the leachate in anaerobic laboratory scale landfill reactors filled with a single MSW sample, but concentrations

were depleted by day 200 in both live and abiotic reactors. The PFPis are less likely to be present in MSW initially, as their primary use is pesticides.¹²

Temporal PFAS Concentration Variations. Five samples were collected over 17 months at Landfills T and U to evaluate temporal variability. The variability illustrated in Figure 3 is useful when considering the degree to which PFAS concentrations are representative of a landfill. At both Landfill T and U, variations appeared to be consistent with time across the landfill cells. For example, the March 2013 samples had the lowest group 1 PFAS concentrations in both Cells A and B, although the cells were physically separate, and Cell A had not accepted waste since 1990 while Cell B was accepting waste when sampled (Figure 3). Similar variations in PFAS concentrations in separate cells suggest that climate (i.e. rainfall) as opposed to internal processes in the buried waste was responsible for variations in concentrations (Figure 3). This contrasts the conclusion presented above that PFASs concentrations were not statistically different based on the climate of the landfill sampled (Table S6). Benskin et al. (2012) also noted temporal changes for one landfill with increases over time in most of the PFASs analyzed as part of that study. The coefficients of variation ($CV = \text{std. dev.}/\text{mean}$) for total PFAS concentrations in leachate from Cells A and B at Landfill T and Cells A to E at Landfill U were 53, 46, 37, 13, 33, 30 and 27%, respectively. In general, these values are lower than the variability in leachate samples between landfills (Table 3).

IMPLICATIONS

The estimate of total PFAS mass release in landfill leachate developed here (~1000 kg/yr – Figure 2) represents the mass of PFASs sent to wastewater treatment in 2013. This estimate is a significant fraction of the reported emissions to all media for companies participating in the EPA

PFOA Stewardship Program which was 2,090 kg in 2013.³⁰ These values should not be compared directly given that our estimate incorporates waste buried since 1980 while the EPA Stewardship only reports releases for products manufactured in 2013. However, the method used here will project a release of ~1000 kg PFASs/yr in landfill leachate annually. In addition, products manufactured in 2013 will continue to release PFASs to landfill leachate for many years. Since 5:3 FTCA was a major contributor to overall PFAS release in leachate, future work is needed to identify FTCA precursors in landfills and to estimate the attenuation of FTCAs during wastewater treatment.

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Table 1. Site Characteristics for U.S. landfills sampled

Landfill ^a	Number of Sampling Events	Total Samples Collected	Climate ^b	Years of Waste Disposal	Average Waste Age ^c (Years)
K	2	10 ^d	Arid	1996 – Present	9
L	2	2	Arid	1970 – Present	22
M	2	2	Arid	1966 – Present	24
E	2	2	Temperate	1988 – Present	13
F	2	4 ^e	Temperate	1993 – 2001	10.5
G	2	8 ^f	Temperate	1999 - Present	7.5
T	5	10 ^g	Temperate	1975 – Present	19.5
B	2	2	Wet	1981 – Present	16.5
H	2	2	Wet	1998 – Present	8
I	2	2	Wet	1989 – Present	12.5
J	2	2	Wet	1996 – Present	9
N	1	1 ^h	Wet	1998 – Present	8
O	2	4 ⁱ	Wet	1970's – Present	>15
P	2	4 ^j	Wet	1970's – Present	>15
Q	2	2	Wet	2001 – Present	6.5
R	2	8 ^k	Wet	1977 – Present	18.5
S	2	4 ^l	Wet	1997 – Present	8.5
U	5	26 ^m	Wet	1980 - Present	17
Total		95			

- a. Landfills A, C, and D are not shown because these landfills were closed before 1980 and the data were not included in the national inventory.
- b. 'Arid' < ~38 cm of precipitation a year, 'Wet' >~75 cm a year, and 'Temperate' precipitation between 38 and 75 cm a year as in reference 23.
- c. Average waste age was calculated as 2013 minus the initial waste placement date divided by two
- d. For Landfill K, the average concentration of the five cells at each time point were used in the national inventory model
- e. For Landfill F, the average concentration of the two cells at each time point were used in the national inventory model
- f. For Landfill G, the average concentration of the four cells at each time point were used in the national inventory model
- g. For Landfill T, only the four samples collected in March and October 2013 were used in the national inventory model
- h. For Landfill N, concentrations for the single sample were entered twice in the national inventory model
- i. For Landfill O, the average concentration of the two cells at each time point were used in the national inventory model
- j. For Landfill P, the average concentration of the two cells at each time point were used in the national inventory model
- k. For Landfill R, only the samples collected from the onsite lagoon were used in the national inventory model
- l. For Landfill S, the average concentration of the two cells at each time point were used in the national inventory model
- m. For Landfill U, only the samples collected from the onsite tank collected in February and October 2013 were used in the national inventory model

Table 2. Per- and polyfluoroalkyl substances grouped based on the percent of total samples analyzed above the LOQ. Full compound names and their abbreviations are listed in Table S1.

Percent of Samples >LOQ	
>50% n = 27	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, 6:2 FTCA, 8:2 FTCA, 3:3 FTCA ^b , 5:3 FTCA, 7:3 FTCA, PFBS, PFPS ^b , PFHxS, PFOS, 6:2 FTSA, 8:2 FTSA ^c , MeFBSAA ^c , MeFPeSAA ^d , MeFHxSAA ^d , MeFHpSAA ^d , MeFOSAA, EtFBSAA ^d , EtFPeSAA ^d , EtFHxSAA ^d , EtFOSAA
20 - 50% n = 11	10:2 FTCA, 6:2 FTUCA, 8:2 FTUCA, 9:3 FTCA ^d , PFHpS ^b , 4:2 FTSA ^c , FBSAA ^d , FPeSAA ^d , FHxSAA ^d , FHpSAA ^d , EtFHpSAA ^d
<20% n = 32	PFUnDA, PFDoDA, PFTriDA, PFTeDA ^c , PFPeDA ^b , PFHxDA ^c , PFHpDA ^b , PFOcDA ^c , 4:2 FTCA ^d , 4:2 FTUCA ^d , 10:2 FTUCA ^d , PFNS ^b , PFDS, FOSAA ^c , 4:4 PFPIA ^d , 4:6 PFPIA ^b , 6:6 PFPIA, 6:8 PFPIA, 8:8 PFPIA, 4:4 diPAP ^d , 4:6 diPAP ^d , 6:6 diPAP, 6:8 diPAP ^b , 8:8 diPAP, 8:10 diPAP ^b , 10:10 diPAP ^b , 6:2 FTMAP ^b , 6:2/8:2 FTMAP ^b , 8:2 FTMAP ^b , 8:2/10:2 FTMAP ^b , 10:2 FTMAP ^b , 8:8 SAmPAP ^b

- PFASs defined in Allred et al. (2014) as quantitative based on standard availability unless otherwise specified (n = 29).
- PFASs defined in Allred et al. (2014) as qualitative based on standard availability and therefore not included in the national release model (n = 16)
- PFASs defined in Allred et al. (2014) as semi-quantitative based on standard availability (n = 7)
- PFASs defined in Allred et al. (2014) as screening based on standard availability and therefore not included in the national release model (n = 18)

Table 3. Mean concentrations ($\mu\text{g/L}$) for group 1 PFASs used in the mass release model.^{a, b}

$\mu\text{g/L}$	Wet		Temperate		Arid	
	<10 yrs. (n = 14)	>10 yrs. (n = 12)	<10 yrs. (n = 2)	>10 yrs. (n = 6)	<10 yrs. (n = 2)	>10 yrs. (n = 4)
PFBA	0.9 \pm 1	1 \pm 0.9	0.3 \pm 0.01	1 \pm 0.9	1 \pm 0.3	0.3 \pm 0.2
PFPeA	1 \pm 1	0.8 \pm 0.8	0.2 \pm 0.01	0.9 \pm 0.9	0.9 \pm 0.04	0.3 \pm 0.1
PFHxA	2 \pm 2	1.8 \pm 1.9	0.5 \pm 0.1	2 \pm 2	3 \pm 0.1	0.6 \pm 0.3
PFHpA	0.8 \pm 0.8	0.6 \pm 0.6	0.2 \pm 0.04	0.6 \pm 0.4	1 \pm 0.1	0.1 \pm 0.1
PFOA	1 \pm 2	1 \pm 1	0.2 \pm 0.001	0.7 \pm 0.6	1 \pm 0.05	0.1 \pm 0.04
PFNA	0.1 \pm 0.1	0.1 \pm 0.	0.01 \pm 0.002	0.02 \pm 0.01	0.1 \pm 0.002	0.005 \pm 0.003
PFDA	0.1 \pm 0.1	0.05 \pm 0.1	0.005 \pm 0.003	0.01 \pm 0.01	0.02 \pm 0.001	0.003 \pm 0.004
6:2 FTCA	0.9 \pm 0.5	0.6 \pm 0.7	1 \pm 0.5	0.5 \pm 0.4	3 \pm 1	0.1 \pm 0.1
8:2 FTCA	0.2 \pm 0.2	0.1 \pm 0.2	0.1 \pm 0.03	0.1 \pm 0.1	0.4 \pm 0.01	0.01 \pm 0.01
5:3 FTCA	4 \pm 6	3 \pm 3	4 \pm 0.9	4 \pm 3	15 \pm 1	0.4 \pm 0.4
7:3 FTCA	0.9 \pm 1	0.4 \pm 0.6	0.1 \pm 0.02	0.2 \pm 0.2	0.9 \pm 0.4	0.03 \pm 0.03
PFBS	0.5 \pm 0.8	0.3 \pm 0.5	0.02 \pm 0.005	0.03 \pm 0.02	0.3 \pm 0.04	0.01 \pm 0.01
PFHxS	0.3 \pm 0.3	0.4 \pm 0.2	0.1 \pm 0.01	0.3 \pm 0.2	0.5 \pm 0.005	0.02 \pm 0.01
PFOS	0.1 \pm 0.2	0.1 \pm 0.1	0.01 \pm 0.001	0.1 \pm 0.1	0.2 \pm 0.05	0.003 \pm 0.003
6:2 FTSA	0.2 \pm 0.1	0.3 \pm 0.6	0.03 \pm 0.003	0.1 \pm 0.1	0.3 \pm 0.01	0.005 \pm 0.009
8:2 FTSA	0.1 \pm 0.	0.03 \pm 0.05	0.001 \pm 0.0002	0.03 \pm 0.1	0.1 \pm 0.05	0.0003 \pm 0.0005
MeFBSAA	0.6 \pm 0.6	0.4 \pm 0.6	0.4 \pm 0.1	0.2 \pm 0.2	0.8 \pm 0.01	0.04 \pm 0.06
MeFOSAA	0.2 \pm 0.3	0.2 \pm 0.	0.005 \pm 0.003	0.1 \pm 0.2	0.04 \pm 0.01	0.001 \pm 0.002
EtFOSAA	0.1 \pm 0.2	0.1 \pm 0.2	0.0003 \pm 0.0004	0.1 \pm 0.3	0.04 \pm 0.01	0.001 \pm 0.001
Total	15 \pm 16	11 \pm 12	7 \pm 1	11 \pm 9	29 \pm 1	2 \pm 0.8

a. One standard deviation is presented for each mean concentration

b. Climates: ‘arid’ less than \sim 38 cm of precipitation a year, ‘wet’ above \sim 75 cm a year, and ‘temperate’ annual precipitation between 38 and 75 cm a year

Table 4. Mean values for leachate generation and the mass of waste per surface area, total waste in place for United States landfills, and the estimated volume of leachate generated in 2013

	Leachate Generation (m³/ha-day)^a	Mass per Surface Area (Tg/ha)^a	Total Waste in Place^b (Tg)	Volume of Leachate for 2013 (million m³/yr)
Arid	0.04 ± 0.03	0.14 ± 0.098	1,492	0.10
Temperate	2 ± 3	0.14 ± 0.098	2,602	13
Wet	7 ± 14	0.14 ± 0.098	3,648	61
Total				74.1

a. One standard deviation is presented for leachate generation and mass of waste per surface area

b. Waste disposed from 1980 – 2013

Table 5. Concentration ranges and maximum likelihood estimates for group 2 PFASs (20 - 50% of the results were >LOQ).

µg/L	Concentration Ranges	Maximum Likelihood Estimate^a
10:2 FTCA	ND – 0.3	0.004
8:2 FTUCA	ND – 0.2	0.005
4:2 FTSA	ND – 0.02	0.001

a. Maximum likelihood estimate calculated using methods outlined in Gibbons & Coleman (2001) using all samples (n = 95)

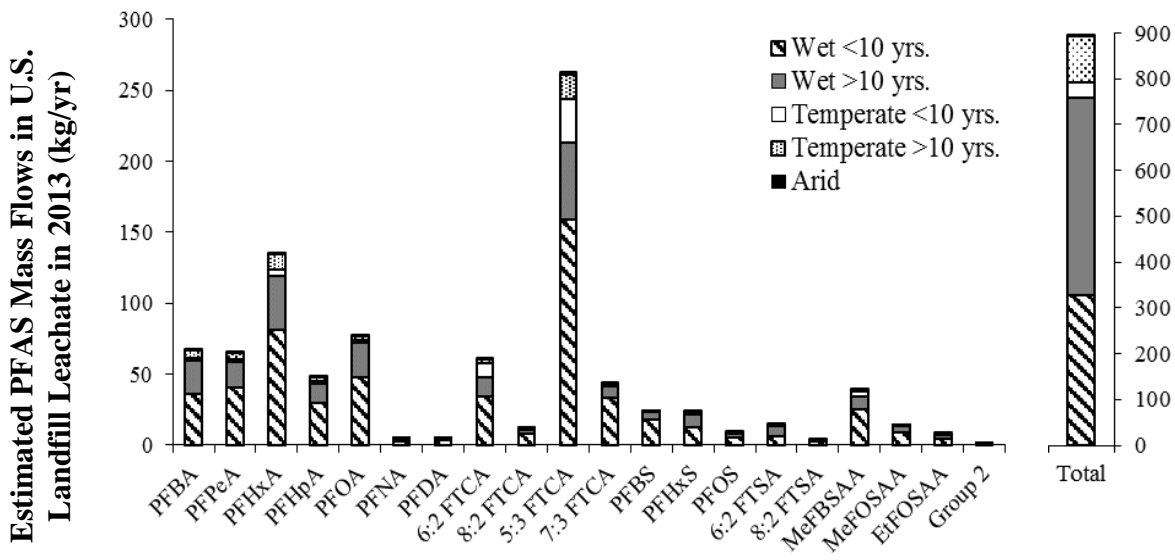


Figure 1. Group 1 PFAS release in U.S landfill leachate for 2013 demonstrating a dominance of compounds with five fluorinated carbons (PFHxA and 5:3 FTCA). Releases were calculated from mean concentrations in each climate and age category (Table 3). The individual columns are based on eq. 1 while the total is based on eq. 2

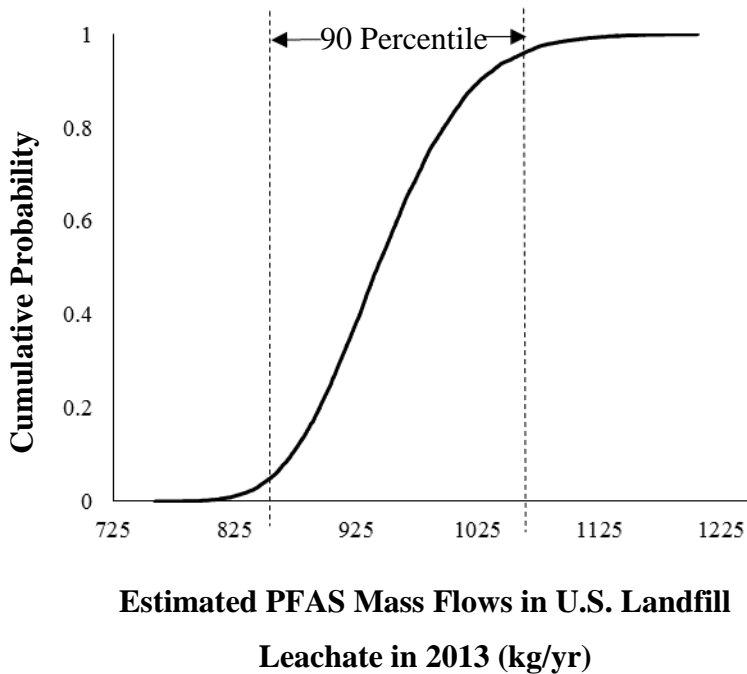


Figure 2. Distribution for total PFAS release in 2013 created using a Monte Carlo analysis with eq. 2 and the distributions in Table S7.

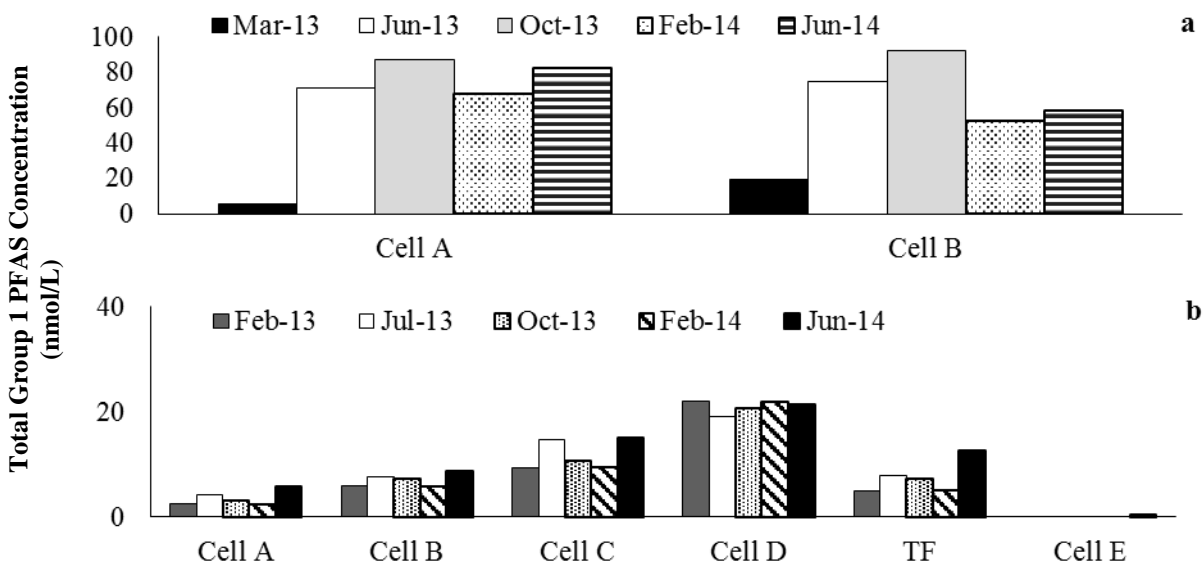


Figure 3. Total group 1 PFAS concentrations measured at (a) Landfill T and (b) Landfill U. The maximum whole method variability for the compounds in group 1 PFASs was 20%. For Landfill T, leachate was collected from two distinct areas with waste placement dates of 1975-1990 (Cell A) and 1990-present (Cell B). For Landfill U, Cell A contained the oldest waste (1980-1988) with each subsequent cell containing younger waste (Cell B: 1988-1993, Cell C: 1993-1998, Cell D: 1999-2014, and Cell E: 2014-present). Samples were also collected from a tank farm (TF), which collects and stores all leachate from Cells A – E prior to discharge for wastewater treatment. The leachate flows for Landfill U during the sampling period are presented in Figure S6.

**CHAPTER 4 – VARIATIONS IN PER- AND POLYFLUOROALKYL SUBSTANCE
(PFAS) RELEASE FROM MUNICIPAL SOLID WASTE (MSW) IN ANAEROBIC
MODEL LANDFILL REACTORS**

INTRODUCTION

Many products known to contain per and polyfluoroalkyl substances (PFASs) are disposed in landfills at the end of their useful life, including outdoor clothing, leather, carpet and upholstery, with total concentrations of perfluorocarboxylic acids (PFCAs) and fluorotelomer alcohols (FTOHs) reported up to 47,100 ng/g.¹⁻² Lang et al. (2016) demonstrated that PFCAs and fluorotelomer carboxylic acids (FTCAs), which are FTOH degradation products, are released from mixed carpet and clothing samples in model anaerobic landfill reactors, with total measured PFAS releases of 14.2 and 23.7 ng/g, respectively.

For U.S. landfill leachate, the annual mass release of PFASs to wastewater treatment plants was estimated to be 854 to 1,055 kg/yr in 2013.⁴ This estimate was based on 93 leachate samples collected from 18 landfills and was higher than previous mass release estimates for German landfill leachate (<0.4 kg/yr in 2010) due to larger annual leachate volumes (i.e. 74 vs. <5 million m³/yr). The PFASs previously reported to be dominant in North American landfill leachate are 5:3 fluorotelomer carboxylic acid (FTCA) and short chain PFCAs.^{4,7-10}

While the transfer of PFASs from products to leachate is occurring, little is known about the mechanisms of PFAS release from products in anaerobic landfills. There are two possible mechanisms for PFAS release. The first is physical release of PFASs present directly on products, which should occur relatively rapidly and correspond to the extractable content. The second possible mechanism for release is a biological mechanism for cleavage of PFASs bound to the surface of products, which would occur relatively slowly compared to physical

mechanisms. This could occur due to degradation of the PFASs present on the surface of the product or due to degradation of the product.

An understanding of PFAS release mechanisms will assist with our overall understanding of global PFAS releases to the environment. Published global release models estimate the mass of PFASs released from products following manufacture are equal to the mass of PFAS release that can occur via physical release. Zhang et al. (2013) reported that transformation of precursors in landfills does not contribute to overall PFCA release, but this assessment was based on FTOH degradation experiments, not actual waste samples.

Allred et al. (2015) reported PFAS release from one municipal solid waste (MSW) in anaerobic model landfill reactors, with a relatively rapid release of short chain PFCAs in live and abiotic reactors, as well as FTCA release in live reactors after significant operation times (>200 days). While these results indicate both physical and biological release mechanisms are occurring in landfills, it is difficult to make conclusions on release mechanisms based on one MSW sample due to the heterogeneity of PFAS content on disposed products.

The objective of this work was to compare concentrations of 70 PFASs in anaerobic models landfill reactors in three separate samples of MSW operated under live and abiotic conditions in order to assess PFAS release mechanisms from solids waste during disposal.

MATERIALS AND METHODS

MSW sample collection and preparation

MSW samples from residential collection vehicles were collected from a local waste transfer station in November 2012, May 2013, and August 2013. Waste samples would have included any item that can be disposed in household waste containers, but did not include bulky

waste items such as large sections of carpet and furniture. For each sample, approximately 35 bags of waste were collected at random from the transfer station floor. The entire sample was shredded (ShredPax. Corp., AZ-7H, Wood Dale, Illinois) to decrease particle size for homogenization and filling of the 8-L model landfill reactors. After shredding, samples were stored in methanol rinsed, high density polyethylene (HDPE) storage bins at 4°C.

Reactor operation, characterization, and sampling

Reactors were constructed, filled, and operated using the methods presented in Allred et al. (2015). Replicate live and abiotic reactors were operated with each MSW sample. Reactors were filled with ~1.3 kg of the shredded MSW, an anaerobic culture which served as an inoculum, synthetic leachate and deionized (DI) water (Table S1). The anaerobic consortium used to inoculate reactors was acclimated to the conversion of solid refuse to methane and was grown and maintained on laser print paper, with 30% recycled content to eliminate background PFAS present in MSW. DI water was added to create sufficient volumes of leachate for sampling. The synthetic leachate mimicked dissolved organic matter present in leachate and included humic matter (1.203 g/L), acetic acid (0.37 g/L), butyric acid (0.185 g/L), and propionic acid (0.185 g/L). Streptomycin (0.34 - 0.50 g) and 2,2-dibromo-3-nitrilopropionamide (DBNPA – 10 - 12.5 g) were added to suppress biological activity in the abiotic reactors, although only DBNPA was added to the first set of reactors (Table S1).

After reactors were filled, they were sealed to prevent gas leakage and nitrogen was flushed through the system to remove residual oxygen. Gas produced during decomposition was collected in gas bags (SKC Inc.) and analyzed for the gas volume and methane concentration. Leachate samples (5 mL) were removed for pH measurement and leachate was neutralized with

sodium hydroxide (NaOH) as necessary to until the reactor pH stabilized around neutral as required for methane generation. To correct measured PFAS concentrations for the addition of NaOH or DI water to the reactors, all concentrations were corrected back to the initial leachate volume as described in Allred et al. (2015).

Leachate samples were collected weekly for the first two months, and bi-weekly thereafter. Centrifuge vials (50 mL) were used for sample collection and storage. Samples were frozen immediately after collection and shipped over night on ice to Oregon State University (OSU) for analysis. Leachate samples were selected for PFAS analysis based on the CH₄ production rate in the live reactors so that leachate samples were analyzed through the lag phase, exponentially increasing methane generation phase and the phase in which methane generation exhibited an asymptotic decrease.

Micro-Liquid-Liquid Extraction (Micro-LLE) and Liquid Chromatography Tandem Mass spectrometry (LC-MS/MS)

Single leachate samples were extracted and analyzed for each time point using procedures described Allred et al. (2014). Briefly, samples were centrifuged, titrated to pH 7-8, and extracted with trifluoroethanol and ethyl acetate. The extract (900 µL) was analyzed using an adapted Agilent 1100 Series high pressure liquid chromatograph (HPLC) coupled with a TQ Detector MS/MS system. The HPLC was equipped with two Zorbax Zirconium modified diol guard columns in series with a Zorbax Eclipse Plus C18 column. The MS/MS system was operated under negative electrospray ionization and multiple reaction monitoring (MRM) mode. Solvent and method blanks were analyzed daily. Method blanks were extracted and analyzed with every analytical sequence. Replicate calibration standards and solvent blanks were run at

least every eight samples to track continued calibration performance over the course of the analytical sequence.

The PFASs analyzed were divided into four tiers based on the availability of standards: quantitative (Qn), semi-quantitative (Sq), screening (Sc), and qualitative (Ql).⁶ Quantitative (Qn) analytes (n = 29) had analytical standards, the measured accuracy fell within 90 – 110%, and precision was $\leq 20\%$ RSD. Semi-quantitative (Sq) analytes (n = 7) had analytical standards, but the measured accuracy did not fall within 90-110% and/or the precision was $\geq 20\%$ RSD. Only a commercial reference material was available for qualitative (Ql) analytes (n = 16). No reference material was available for screening (Sc) analytes (n = 18).⁶ For PFASs in the Sc category, concentrations were estimated assuming equal molar response factors to structurally similar, quantifiable PFASs. Leachate samples were analyzed concurrently with samples presented in Allred et al. (2015) and Lang et al. (2016).

RESULTS AND DISCUSSION

MSW samples were collected in November, May and August. Methane generation in the three samples is compared first, followed by comparison of PFAS release in live and abiotic reactors operated with each sample.

Reactor characterization and anaerobic degradation

Methane was produced in all live reactors, consistent with anaerobic biodegradation of organic solids (Figure 1). Peak methane production in the live reactors occurred between 60 and 120 days of operation, except for November live 2 which exhibited an extended lag phase

(Figure 1). The methane production rate in all abiotic reactors remained less than 0.1 mL/day-dry g throughout operation, indicating that the biological inhibitors added were effective.

Initially, the leachate in all reactors was acidic (pH < 6.5), corresponding to carboxylic acid accumulations in the aqueous phase during the initial phase of anaerobic decomposition (Figure S1). The pH in live reactors increased from < 6.5 to 7.0 due to leachate neutralization and remained between 7 and 8.2 throughout the decomposition cycle as is typical of refuse methanogenesis. The pH in the abiotic reactors remained <7.1 in all reactors throughout operation (Figure S1). Leachate pH in the abiotic reactors was allowed to remain acidic because it helped to inhibit methane production.¹⁸ To test the effect of pH on PFASs release in abiotic reactors, the leachate pH in November abiotic 1 was increased on the last day of operation (Day 627 – Figure 1) and results are reported below.

QA/QC

Lang et al (2016) demonstrated that the reactor system did not contribute significant concentrations of PFASs (<0.15 nmol/L) during anaerobic decomposition of a PFAS free paper. All solvent and method blanks were non-detect (ND) for all PFASs analyzed, except for low level (<4.4 pmol/L) 6:2 di-substituted polyfluorinated phosphate ester (diPAP) contamination in the method blank for May live 2. The ND results for the majority of the results indicate that the PFASs measured in the reactor leachate samples were attributed to the sample and not to background contamination. No conclusions were drawn for the diPAP concentrations in the May live 2 reactor.

Final PFAS concentrations

Based on final concentrations of the four PFAS classes present in the greatest abundance, it appears that both physical and biological release of PFASs from solid waste is occurring in the anaerobic landfill system (Table 1). Short chain PFCA release was likely due to a physical release of compounds present directly on products, as release occurred relatively rapidly and was similar in live and abiotic reactors (Table 1). In contrast, release of FTCAs to leachate from solid waste was likely due to biological mechanisms, as release occurred relatively slowly and was higher in live compared to abiotic reactors (Table 1).

Short chain PFCAs

Short chain PFCAs (<C8) were present in all reactors at concentrations between 220 and 1,460 pmol/L throughout operation (Table 2, Figures 1 and 2). Initially, short chain PFCAs were the most abundant PFAS class measured in the reactor leachate (Table 2). Their presence in both the abiotic and live reactors indicates that biological processes are not solely responsible for their transfer to the aqueous phase. Thus, biotransformation of precursors or degradation of parent materials (i.e. paper or clothing) did not control the transfer of short chain PFCAs to the leachate. While final short chain PFCA concentrations were greater than initial (Table 2), the majority of these increases occurred relative rapidly (<60 days – Figures 1 and 2). The rapid release in both the live and abiotic reactors suggests the direct presence of unbound, short chain PFCAs on products.¹⁹⁻²⁰

Short chain PFCA release from MSW was not likely affected by leachate pH, as live and abiotic reactors demonstrated similar release (Table 2) despite differences in pH during operation (Figure 1 and S1). The concentration of long chain PFCAs present in a solution containing

organic matter was previously demonstrated to be pH dependent, but the pH dependence of short chain PFCAs has never been tested.¹⁴ Longer chain, hydrophobic PFCAs bind inside large organic matter at lower pHs, but are released when carboxylic acids on the organic matter are deprotonated and the molecule spreads out, no longer providing a center region for hydrophobic molecules. Increases in short chain PFCAs were not observed during the period of rapid pH neutralization in November abiotic 1 (Day 627 - Figure 2). Shorter chain PFCAs are less hydrophobic so their sorption may not be dependent on pH.

Concentrations of short chain PFCAs with even chain lengths (i.e. PFHxA and PFBA) were present at greater concentrations relative to short chain PFCAs with odd chain lengths (i.e. PFPeA and PFHpA). Previous research examining the PFCAs content on 116 consumer products found similar concentrations of extractable PFCAs for C5-C12 chain lengths on carpet, carpet care liquids, and treated fabrics, but reported even chain length short chain PFCAs at greater concentrations than odd chain in the case of food contact paper.¹¹ Lang et al. (2016) demonstrated short chain PFCAs with even chain lengths at greater concentrations than odd chain lengths for carpet and clothing reactors. Further work is needed to determine the parent products in MSW that contain short chain PFCAs.

FTCAs

While FTCAs were not present at significant concentrations ($\sum\text{FTCA} < 100$ pmol/L) in any reactor initially, n:3 FTCAs were the most abundant PFAS class measured at the final time point in several of the live reactors (Table 2). In abiotic reactors, FTCA concentrations remained negligible throughout operation ($\sum\text{FTCA} < 100$ pmol/L), indicating biological processes were primarily responsible for their presence in the leachate (Table 2). The near absence of FTCAs in

initial leachate samples is consistent with Buck et al. (2011), who reported FTCA were environmental transformation intermediates and not surfactants used on products.¹²

The FTCA detected at the highest concentration in live reactors was 5:3 FTCA (Figure 1). Zhang et al. (2013) previously identified 5:3 FTCA as the stable anaerobic by-product of 6:2 fluorotelomer alcohol (FTOH). 6:2 FTCA, a previously defined intermediate of 6:2 FTOH transformation, was the next most abundant PFAS measured at the final sampling point in all live reactors. In live reactors, aqueous phase accumulations of 6:2 FTCA and 5:3 FTCA were measured following peak methane production, with only minimal detection in earlier samples, which is consistent with the role of biological activity in FTCA accumulation (Figure 1).

Long Chain PFCAs

Initial concentrations of long chain PFCAs (<C8) were similar in live and abiotic reactors for each MSW sample (Table 2) but final long chain PFCA concentrations were greater than initial concentrations in live, but not abiotic reactors, suggesting that biological processes played a role in their release (Table 2). Increases were primarily attributed to PFOA, but \geq C13 PFCAs were detected in several of the live reactors (Figures 1, S5, S6, and S7). It was surprising to see \geq C13 PFCAs in solution given the presence of solids available for sorption, as the long chain PFCAs are likely to resorb to other MSW components. In all live reactors, the maximum long chain PFCA concentrations occurred before the final sampling point, but after peak methane production (Figures 1, S5, S6, and S7).

PFOA was the dominant long chain PFCA in all live and abiotic reactors, which corresponds to the higher historic production of C8 based products¹² In addition, since it was the shortest of the long chain PFCAs measured, it is was also the most soluble.¹⁴ Long chain PFCA

concentrations remained below short chain PFCA concentrations throughout operation. This trend is consistent with the previous reports of PFCA concentration distributions in North American landfill leachate^{1,3,4,6} and is consistent with the lower solubility of long chain compounds.¹⁴

One explanation for differences in the concentration of long chain PFCAs ($\geq C8$) in the live and abiotic reactors at the final time point (Table 2) is leachate pH (Figure S1) as the concentration of long chain PFCAs present in a solution containing organic matter was previously demonstrated to be pH dependent.¹⁴ At acidic pHs, organic matter functional groups are protonated and the large organic molecules are tightly bound, allowing sorption of hydrophobic PFASs. At basic pHs, organic matter functional groups lose their protons, causing the molecule to spread out, repel negatively charged compounds, and aqueous phase concentrations of hydrophobic PFASs increase. Since leachate contains organic matter, the higher concentrations of long chain PFCAs in live compared to abiotic reactors could have been attributed to differences in pH, as the abiotic reactors remained acidic throughout operation but final live reactor pHs were slightly basic. During the period of rapid pH neutralization in November abiotic 1, long chain PFCA concentrations did not exceed earlier concentrations observed in this reactor (Figure 2a). Thus the presence of $\geq C13$ PFCAs were present in live November reactors cannot be attributed to a pH effect.

FTSAs

Fluorotelomer sulfonic acid (FTSA) concentrations remained relatively constant in live and abiotic reactors throughout operation (Table 2). The detection of FTSAs in leachate initially corresponds to the direct release of these surfactants from products.¹² Since release was similar

in live and abiotic reactors, there are no indications of release being dependent on pH over the range occurring during methanogenic degradation. Concentrations of FTSA remained below 150 pmol/L throughout reactor operation for all MSW samples (Figures S9, S10, and S11) This is low relative to concentrations of the other measured fluorotelomer acid compound classes in live reactors (i.e. n:3 FTCA – Table 2). The major contributor to FTSA concentrations was 6:2 FTSA in all reactors, which corresponds to the previously reported dominance of 6:2 FTSA over 8:2 FTSA in ground water from air force bases.¹⁵ In the case of groundwater, the source is firefighting foams,¹⁵ which would not necessarily be present in MSW. Thus, the dominance of 6:2 FTSA suggests that it is present in other consumer products.

PFSAs

Both initial and final concentrations of PFSAs were low compared to PFCA concentrations (Table 2). Since release was similar in live and abiotic reactors, there are no indications of release being dependent on pH over the range occurring during methanogenic degradation (Table 2). Measured PFSA concentrations remained below 100 pmol/L throughout operation of all reactors, with no apparent trends (Figure S12, S13, and S14). The maximum PFSA concentrations occurred in the initial sample for December reactors (Table 2; 119-130 pmol/L), which may indicate that the presence of one material in the December waste sample contributed the bulk of the PFSAs.¹¹

FASAAs

For the three types of fluoroalkyl sulfonamido acetic acids (FASAAs) measured, n-methyl fluoroalkyl sulfonamido acetic acids (MeFASAAs) were measured in the greatest

concentrations (Table 2), which corresponds to the higher production levels for methyl based compounds compared to ethyl based.²⁵ For reactors with significant concentrations of MeFASAs, live reactors demonstrated higher concentrations compared to abiotic reactors, indicating biological mechanisms may be responsible for release (Table 2). For the majority of live reactors, the highest MeFASAA concentrations were measured at the final sampling time and release began following peak methane production (Figures S15, S16, and S17). The MeFASAA present at the highest concentrations was the C4 (MeFBSAA), which corresponds to the higher detection of C4 PFASs compared to C8 on products like carpet and leather.²⁰

diPAPs

DiPAPs were detected in the initial samples from all reactors, except for the November abiotic reactors (Table 2). Initial detection in the leachate corresponds to the direct use of diPAPs as surfactants on products.¹² The initial presence in both the live and abiotic reactors indicates that biological processes were not solely responsible for the release. The release of diPAPs from municipal waste is of interest as these compounds have recently been implicated as significant contributors to PFAS accumulations in arctic environments.⁹

DiPAPs disappeared slowly during reactor operation (Figures S18, S19, and S20), which could have been caused by sorption to other MSW components or by compound transformation. FTCAs are a known product of diPAPs in aerobic laboratory experiments.¹⁷ FTCAs do increase in all reactors, but the decreases in diPAPs (2 mols diPAP = 1 mol FTCA) do not account for the total FTCA increases and there are no data on anaerobic transformations. There were a few notable exceptions of diPAPs increases during operation and subsequent decreases during operation (Figure S18, S19, and S20).

8:8 SAmPAP

One n-ethyl perfluorooctane sulfonamido ethanol-based polyfluoroalkyl phosphate diester (SAmPAP) was included in the analytical methods, but the absence of standards for this compound did not allow for quantification. The presence of 8:8 SAmPAP was detected in the November reactors (Figure S21), which corresponds to their previously defined presence on products such as food contact paper.¹⁸

ENVIRONMENTAL IMPLICATIONS

In U.S. landfills, the release of short chain PFCAs, FTSAs, PFSAs, and EtFOSAs from MSW is likely governed by physical as opposed to biological processes and depends on the amount of compound present directly on the product at the time of disposal. The release of long chain PFCAs, FTCAs and MeFASAs is likely governed by the presence of biological activity, with sources being the transformation of precursors and not their direct use on products. Global release models should include the transformation of precursors due to biological release mechanisms in the calculation of total release.

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Table 1. Final concentrations of the major four PFAS classes present in the reactors. Only results for PFASs that were quantitative (Qn) or semi-quantitative (Sq) were included in the sum (Σ) for each class.

	Mean			Coefficient of Variation		
	Live	Abiotic	All	Live	Abiotic	All
PFCAs (<C8)	851 (235)	833 (260)	842 (230)	27.6%	31.3%	27.3%
PFCAs (\geqC8)	306 (224)	118 (71)	212 (184)	73.1%	60.5%	86.7%
n:2 FTCAs	455 (392)	<LOQ	228 (354)	86.2%	n/a	155.4%
n:3 FTCAs	2015 (1360)	11 (11)	1013 (1393)	67.5%	100.7%	137.5%
Total	3767 (1852)	1016 (264)	2392 (1914)	49.2%	26.0%	80.0%

Table 2. Initial (I) and final (F) average PFAS concentrations in each reactor treatment presented as the sum of concentrations in each compound class shown in Table S1. PFPIAs, FOSAA, and FTMAPs are not shown as they were less than the limit of quantification (<LOQ) for all samples. Only results for PFASs that were quantitative (Qn) or semi-quantitative (Sq) were included in the sum (Σ) for each class.

pmol/L		May		August		November		December ^a	
		Live	Abiotic	Live	Abiotic	Live	Abiotic	Live	Abiotic
Σ PFCAAs (<C8) (n = 4)	I ^b	528	419	459	302	628	504	457	479
	F ^c	967	1185	592	558	729	772	967	818
Σ n:2 FTCAAs (n = 3)	I	ND	ND	41	ND	ND	ND	67	54
	F	ND	ND	421	ND	425	ND	966	ND
Σ n:3 FTCAAs (n = 2)	I	13	17	8	8	13	ND	72	54
	F	265	ND	2042	9	2330	9	3486	26
Σ n:2 FTUCAAs (n = 2)	I	41	92	30	13	ND	ND	58	51
	F	ND	ND	1	ND	12	ND	29	ND
Σ PFCAAs (\geq C8) (n = 8)	I	90	86	62	63	179	184	201	188
	F	169	41	107	73	461	181	378	176
Σ FTSAAs (n = 3)	I	34	32	6	6	11	23	9	15
	F	66	46	14	7	10	2	18	17
Σ PFSAAs (n = 4)	I	28	26	12	14	25	21	130	119
	F	41	18	10	13	23	15	78	53
Σ MeFASAAs (n = 2)	I	5	ND	5	5	19	12	8	9
	F	38	ND	5	ND	96	11	83	11
EtFOSAA (n = 1)	I	3	4	3	ND	1	3	4	5
	F	3	ND	2	ND	1	ND	6	ND
Σ diPAPs (n = 2)	I	14	10	128	23	310	ND	124	140
	F	54	ND	2	8	19	ND	14	13
Total (n = 29)	I	756	686	753	435	1187	746	1130	1114
	F	1604	1290	3196	664	4106	983	6025	1114

a. Previous published in Allred et al. (2014)

b. Initial (I) sample collected on day 0

c. Final (F) sample collected on days 462, 384 and 649 for the May, August and November samples, respectively.

PFBA
 PFPeA
 PFHxA
 PFOA
 6:2 FTCA
 5:3 FTCA
 8:2 diPAP
 Other PFASs
 CH₄ Rate

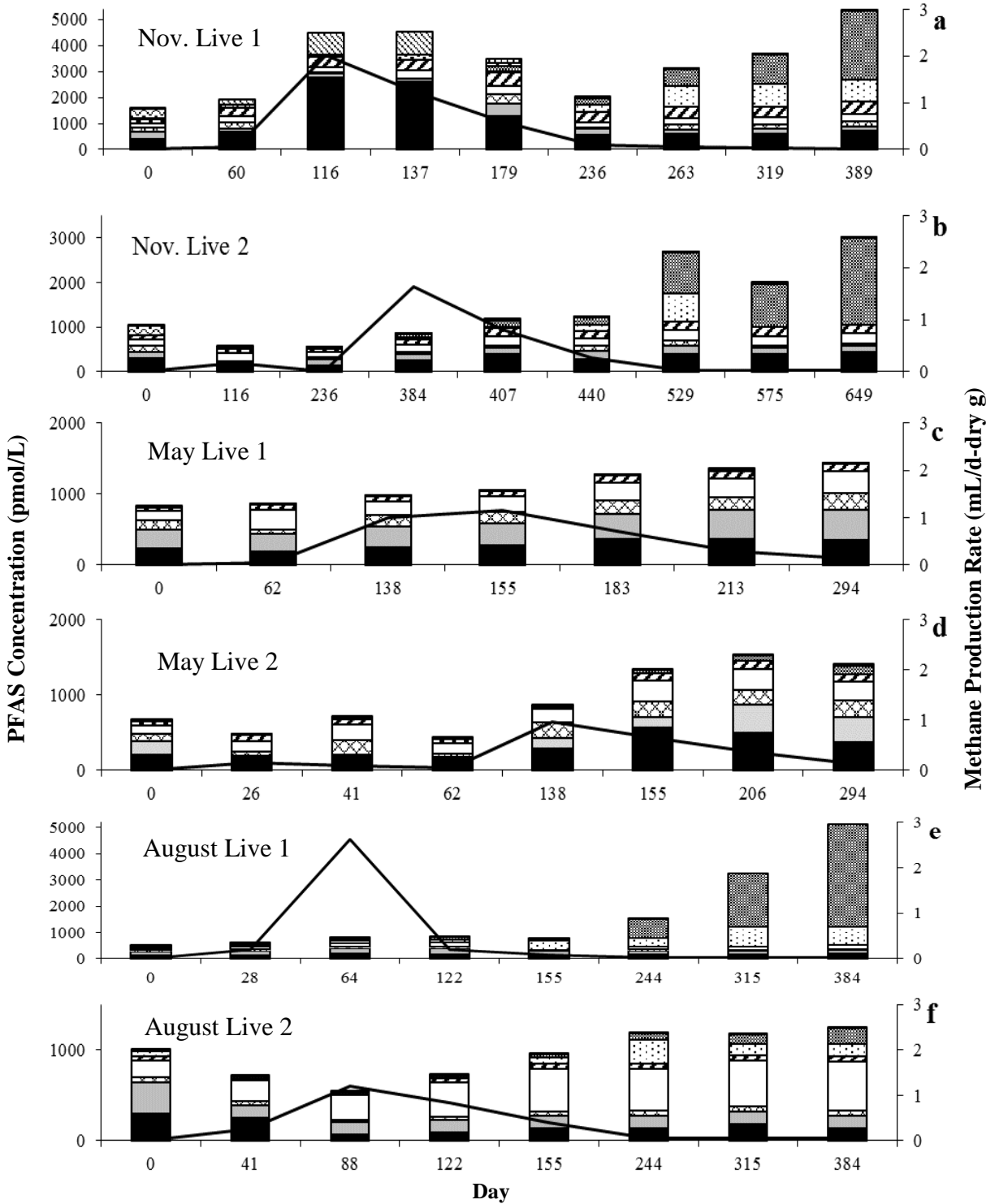


Figure 1. Concentrations of quantifiable and semi-quantifiable PFASs in live reactors: November (a) live 1 and (b) live 2, May (c) live 1 and (d) live 2, and August (e) live 1 and (f) live 2. The four PFASs present at the highest concentrations in each live reactor are presented individually. The total concentration of quantifiable and semi-quantifiable PFASs not individually represented were summed and represented as ‘Other PFASs.’ <LOQ results were included as ½*LOQ. Note varying y-axis and x-axis.

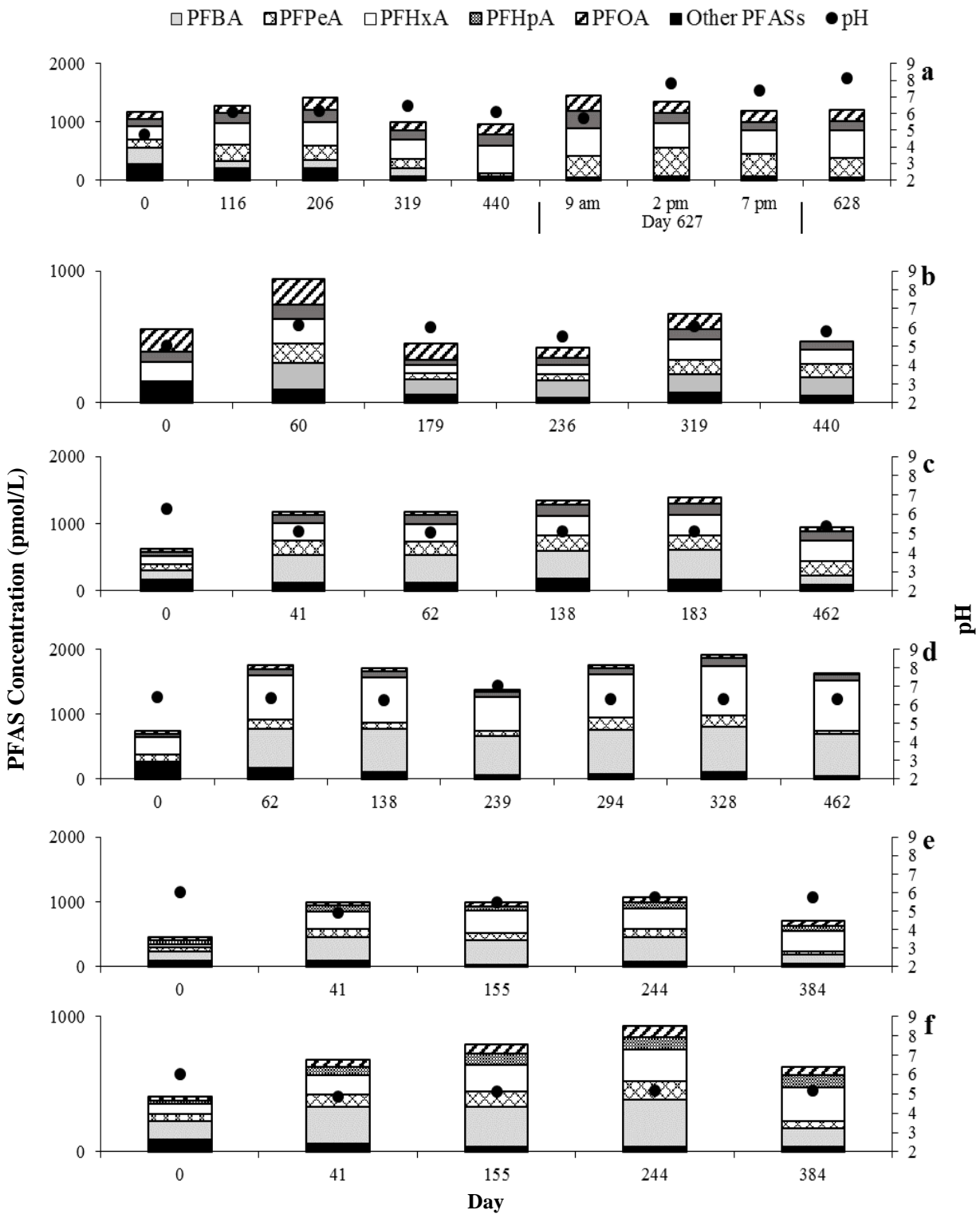


Figure 2. Concentrations of quantifiable and semi-quantifiable PFASs in abiotic reactors during operation: November (a) abiotic 1 and (b) abiotic 2, May (c) abiotic 1 and (d) abiotic 2, and August (e) abiotic 1 and (f) abiotic 2. The four PFASs present at the highest concentrations in each abiotic reactor are presented individually. The total concentration of quantifiable and semi-quantifiable PFASs not individually represented were summed and represented as ‘Other PFASs.’ Note varying y-axis and x-axis.

CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS

The total mass flow of measured PFASs in U.S. landfill leachate was estimated to be 854 to 1,055 kg/yr in 2013. This mass flow of PFASs represents a significant fraction of the reported emissions to all media for companies participating in the EPA PFOA Stewardship Program (2,090 kg in 2013).¹ These values are not directly comparable given that the estimate for mass flow in landfill leachate incorporates waste buried since 1980, while the EPA Stewardship only reports releases for products manufactured in 2013. Products manufactured in 2013 will result in releases to landfill leachate for many years in the future, as several measured PFAS concentrations in the landfill leachate demonstrated similar concentrations for waste masses with ages greater than and less than 10 years. In addition, the EPA PFOA Stewardship Program only estimates releases for long chain PFCAs and their known precursors, while estimates presented here incorporate more than five PFAS compound classes.

Two classes of PFASs dominated total concentrations in both landfill leachate and anaerobic model landfill reactors (i.e. short chain PFCAs and FTCAs). For short chain PFCAs, concentrations were similar in live and abiotic MSW reactors and were similar in leachate samples from waste masses with variable average waste ages or located in wet, temperate and arid climates. Short chain PFCAs have been documented as surfactants used directly on products,² which corresponds to their physical release from MSW. Implications are that short chain PFCA release from MSW is widespread, not dependent on the presence of biological activity, and may continue for many years following waste placement.

In both the anaerobic model landfill reactors and the landfill leachate samples, concentrations of short chain PFCAs with even chain lengths (i.e. PFH_xA and PFBA) were greater than concentrations of short chain PFCAs with odd chain lengths (i.e. PFP_eA and

PFHpA). A previous publication examining the PFCA content on 116 consumer products found similar concentrations of extractable PFCAs for C5-C12 chain lengths on carpet, carpet care liquids, and treated fabrics, but reported even chain length for short chain PFCAs at greater concentrations than odd chain on food contact paper.³ The results for carpet and clothing reactors are not consistent with the previous publication as they also demonstrated short chain PFCAs with even chain lengths at greater concentrations than odd chain lengths.

The other major contributing PFAS class, FTCAs, demonstrated higher concentrations in live compared to abiotic reactors and from waste that was more recently buried compared to older waste. Implications are that FTCA release from MSW is dependent on biological activity and will fluctuate following waste placement. In contrast to short chain PFCAs which are used as surfactants on products, FTCAs were previously identified as biotransformation intermediates.² Results from anaerobic model landfill reactors demonstrated a significant lag period before the majority of measured PFAS release occurred in live reactors, with carpet, clothing or MSW. The significant lag time before appearance in the aqueous phase implies that these compounds were not used directly on products, but instead are present in the aqueous phase as a result of precursor transformation. Future work should determine sources of FTCAs in leachate. Specifically, future work is needed to identify parent compounds and to determine whether PFAS release was due to compounds entrapped in the product matrix or on the surface. The precursor could be volatile (i.e. FTOH), so the gas phase release from landfills should be assessed.

FTSAs were present in live and abiotic MSW reactors and in leachate samples, but concentrations were low compared to the other fluorotelomer class measured (i.e. FTCAs). In clothing reactors, 8:2 FTSA contributed as much as 35% of the total measured PFASs and was present in both abiotic and live reactors. The large presence of FTSAs in clothing reactors, but

low presence in MSW and carpet reactors indicates clothing may be a significant source of FTSCAs in landfill leachate. FTSCAs are documented to be surfactants used on products and biotransformation intermediates.²

Measured concentrations of C11-C18 PFCAs, C9-C10 PFSAAs, FTMAPs, diPAPs, and PFPis were <LOQ in over 80% of the landfill leachate samples. The absence of long chain PFCAs in the landfill leachate samples may not indicate their absence in the landfill waste mass, as they fluctuated at low concentrations in reactors. Long chain PFCAs are known to be easily sorbed to sediments,⁴ so low level concentrations could easily be resorbed to other MSW components in the bulk waste mass. For PFDS, FTMAPs and PFPis, concentrations were also <LOQ in the reactors, indicating MSW is not a likely source of these PFASs to the environment. DiPAPs were present at fluctuating concentrations in several of the live and abiotic MSW reactors, but were largely absent in the carpet and clothing reactors. Transformation of diPAPs has been previously reported to be rapid.⁵ Detection in the MSW reactors and non-detection in the leachate could be attributed to rapid transformation or sorption to other MSW components in a landfill. Despite their absence in landfill leachate, diPAPs could still be a source of PFASs in landfill leachate.

Recommendations for future work

- 1) Determine which PFASs are the source of the FTSCAs shown to be present in landfill leachate. More specifically, future work should clarify if precursors are the residual fraction of PFASs on products or the polymerized fraction currently assumed to be recalcitrant.

- 2) The presence of FTCAs may be due to a volatile precursor (i.e. FTOH), so the gas phase PFAS release from landfills should be assessed.
- 3) Future work should estimate the attenuation of n:3 FTCAs during wastewater treatment as no previous evaluations were found and 5:3 FTCA contributed significantly to overall PFAS release in landfill leachate.
- 4) Model anaerobic model landfill reactors could be operated with single product types where the PFASs composition present on the material is known. The gas phase release of PFASs should be quantified during reactor operation.

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APPENDICES

Appendix A – Supporting information for Physical and biological release of poly- and perfluorinated substances in laboratory-scale anaerobic bioreactors filled with carpet and clothing

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PIGE Analysis of Reactor Solids. Individual clothing samples were analyzed with particle induced gamma-ray emission (PIGE) spectroscopy using a modified version of previously published methods to determine total F in biological and aerosol samples.¹⁻⁴ In brief, the presence of fluorine in a material was determined by the reaction of an accelerated beam of protons striking its surface. The excitation that occurs in ¹⁹F nuclei from interactions with the accelerated ion beam causes the emission of a series of characteristic gamma rays, which can be used to determine the quantity of ¹⁹F nuclei in the target material. For this analysis, a beam of 3.4 MeV protons from the Hope College Ion Beam Analysis Laboratory was extracted into air through a thin foil, and used to measure the fluorine content of solid materials placed in the beam. Typically ~2 μC of beam was delivered over 180 seconds to each target, and two characteristic ¹⁹F gamma rays (of 110 keV and 197 keV) were detected at an angle of 110° with respect to the beam by a high-purity Germanium detector (~20% efficiency). These peaks were integrated after background subtraction and used to provide a quantitative measure (in arbitrary units of counts/μC) of fluorine content in each sample. The absolute detection limit for fluorine is on the order of ppm for this technique on fabric samples, but absolute calibration with respect to external standards is still on-going. Reproducibility across the triplicate samples analyzed was better than 10%.

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Table S1. Masses and volumes of materials added to carpet, clothing, and copy paper only reactors

		Anaerobic Consortium (L)	Synthetic Leachate (L)	DI Water ^a (L)	DBNPA ^b (g)	Streptomycin (g)	Copy Paper ^c (dry g)	Carpet (dry g)	Clothing (dry g)
Carpet	Live 1	1	1	1	n/a ^d	n/a	663.3	693.2	n/a
	2	1	1	1.1	n/a	n/a	544.7	580.6	n/a
	Abiotic								
	1	1	1	0.6	10	0.34	529.3	565.5	n/a
	2	1	1	0.9	10	0.34	481.5	519.0	n/a
Clothing	Live 1	1	1	1.2	n/a	n/a	508.1	n/a	566.8
	2	1	1	1.3	n/a	n/a	591.6	n/a	618.3
	Abiotic								
	1	1	1	1.7	10	0.34	597.2	n/a	662.7
	2	1	1	1.4	10	0.34	586.2	n/a	585.5
Copy	Live 1	1	1	0.6	n/a	n/a	959.3	n/a	n/a
Paper	2	1	1	0.6	n/a	n/a	956.5	n/a	n/a

a. Deionized Water

b. 2,2-dibromo-3-nitropropionamide

c. Volume of moisture in the sample was not presented as it was less than 0.1 L in all reactors

d. n/a = Not added

Table S2. Standards used during with LC/MS/MS analysis

Analyte	Standard Supplier (purity)	Internal Standard	Data Quality Level
PFBS	Wellington (>98%)	[¹⁸ O ₂]PFHxS	Qn ^a
PFPS	Wellington (residual)	[¹⁸ O ₂]PFHxS	Ql ^b
PFHxS	Wellington (>98%)	[¹⁸ O ₂]PFHxS	Qn
PFHpS	Wellington (residual)	[¹³ C ₂]PFOS	Ql
PFOS	Wellington (>98%)	[¹³ C ₂]PFOS	Qn
PFNS	Wellington (residual)	[¹³ C ₂]PFOS	Ql
PFDS	Wellington (>98%)	[¹³ C ₂]PFOS	Qn
4:2 FTSA	Wellington (>98%)	[¹³ C ₂] 6:2 FTSA	Sq ^c
6:2 FTSA	Wellington (>98%)	[¹³ C ₂] 6:2 FTSA	Qn
8:2 FTSA	Wellington (>98%)	[¹³ C ₂] 6:2 FTSA	Sq
PFBA	Wellington (>98%)	[¹³ C ₄]PFBA	Qn
PFPeA	Wellington (>98%)	[¹³ C ₃]PFPeA	Qn
PFHxA	Wellington (>98%)	[¹³ C ₂]PFHxA	Qn
PFHpA	Wellington (>98%)	[¹³ C ₄]PFOA	Qn
PFOA	Wellington (>98%)	[¹³ C ₄]PFOA	Qn
PFNA	Wellington (>98%)	[¹³ C ₅]PFNA	Qn
PFDA	Wellington (>98%)	[¹³ C ₂]PFDA	Qn
PFUnDA	Wellington (>98%)	[¹³ C ₂]PFUnDA	Qn
PFDoDA	Wellington (>98%)	[¹³ C ₂]PFDoDA	Qn
PFTriDA	Wellington (>98%)	[¹³ C ₂]PFDoDA	Sq
PFTeDA	Wellington (>98%)	[¹³ C ₂]PFDoDA	Ql
PFpDA	Wellington (residual)	[¹³ C ₂]PFDoDA	Sq
PFHxDA	Wellington (>98%)	[¹³ C ₂]PFDoDA	Ql
PFHpDA	Wellington (residual)	[¹³ C ₂]PFDoDA	Sq
PFOcDA	Wellington (>98%)	[¹³ C ₂]PFDoDA	Ql
4:2 FTCA	n/a ^d	[¹³ C ₂]FHEA	Sc ^e
6:2 FTCA	Wellington (>98%)	[¹³ C ₂]FHEA	Qn
8:2 FTCA	Wellington (>98%)	[¹³ C ₂]FOEA	Qn
10:2 FTCA	Wellington (>98%)	[¹³ C ₂]FDEA	Qn
3:3 FTCA	Wellington (>98%)	[¹³ C ₂]FHEA	Ql
5:3 FTCA	Wellington (>98%)	[¹³ C ₂]FHEA	Qn
7:3 FTCA	Wellington (>98%)	[¹³ C ₂]FOEA	Qn
9:3 FTCA	n/a	[¹³ C ₂]FDEA	Sc
4:2 FTUCA	n/a	[¹³ C ₂]FHUEA	Sc
6:2 FTUCA	Wellington (>98%)	[¹³ C ₂]FHUEA	Qn
8:2 FTUCA	Wellington (>98%)	[¹³ C ₂]FOEA	Qn
10:2 FTUCA	n/a	[¹³ C ₂]FDEA	Sc
FBSAA	n/a	[¹³ C ₂]PFHxA	Sc
FPeSAA	n/a	[¹³ C ₂]PFHxA	Sc
FHxSAA	n/a	[² H ₃]MeFOSAA	Sc
FHpSAA	n/a	[² H ₃]MeFOSAA	Sc
FOSAA	Wellington (>98%)	[² H ₃]MeFOSAA	Qn
MeFBSAA	3M (n/a)	[¹³ C ₂]PFHxA	Sq
MeFPeSAA	n/a	[¹³ C ₂]PFHxA	Sc
MeFHxSAA	n/a	[² H ₃]MeFOSAA	Sc
MeFHpSAA	n/a	[² H ₃]MeFOSAA	Sc
MeFOSAA	Wellington (>98%)	[² H ₃]MeFOSAA	Qn
EtFBSAA	n/a	[¹³ C ₂]PFHxA	Sc
EtFPeSAA	n/a	[¹³ C ₂]PFHxA	Sc

EtFHxSAA	n/a	[² H ₃]EtFOSAA	Sc
EtFHpSAA	n/a	[² H ₃]EtFOSAA	Sc
EtFOSAA	Wellington (>98%)	[² H ₃]EtFOSAA	Qn
4/4 PFPIA	n/a	[¹³ C ₄]6:2DiPAP	Sc
4/6 PFPIA	Wellington (residual)	[¹³ C ₄]6:2DiPAP	Ql
6/6 PFPIA	Wellington (>98%)	[¹³ C ₄]6:2DiPAP	Qn
6/8 PFPIA	Wellington (>98%)	[¹³ C ₄]6:2DiPAP	Qn
8/8 PFPIA	Wellington (>98%)	[¹³ C ₄]6:2DiPAP	Qn
4/4 diPAP	n/a	[¹³ C ₄]6:2DiPAP	Sc
4/6 diPAP	n/a	[¹³ C ₄]6:2DiPAP	Sc
6/6 diPAP	Wellington (>98%)	[¹³ C ₄]6:2DiPAP	Qn
6/8 diPAP	Wellington (residual)	[¹³ C ₄]8:2DiPAP	Ql
8/8 diPAP	Wellington (>98%)	[¹³ C ₄]8:2DiPAP	Qn
8/10 diPAP	Wellington (residual)	[¹³ C ₄]8:2DiPAP	Ql
10/10 diPAP	Wellington (residual)	[¹³ C ₄]8:2DiPAP	Ql
6/6 FTMAP	US FDA (n/a)	[¹³ C ₄]8:2DiPAP	Ql
6/8 FTMAP	US FDA (n/a)	[¹³ C ₄]8:2DiPAP	Ql
8/8 FTMAP	US FDA (n/a)	[¹³ C ₄]8:2DiPAP	Ql
8/10 FTMAP	US FDA (n/a)	[¹³ C ₄]8:2DiPAP	Ql
10/10 FTMAP	US FDA (n/a)	[¹³ C ₄]8:2DiPAP	Ql
8/8 SAmPAP	US FDA (n/a)	[¹³ C ₄]8:2DiPAP	Ql

- a. Quantitative (Qn) PFASs has analytical standards and the measured accuracy fell within 90 – 110% and precision was ≤20% RSD.
- b. For qualitative (Ql) PFASs, only a commercial reference material was available.
- c. Semi-quantitative (Sq) PFASs has analytical standards, but the measured accuracy did not fall within 90-110% and/or the precision was ≥20% RSD.
- d. Not applicable (n/a) as no standard was available.
- e. For screen (Sc) PFASs, no reference material was available.

Table S3. Initial concentration ranges of PFAS classes in anaerobic reactors (Day 0). See Table 1 for specific analytes included in each PFAS compound class. ^{a, b}

nmol/L		Σ PFCA _s (n=15) ^c	Σ FTCA _s (n=12)	Σ FTSA _s (n=3)	Σ DiPAP _s (n=7)	Σ PFSA _s (n=7)	Σ FASAA _s (n=15)	SAmPAP (n=1)	Σ PFPIA _s (n=5)	Σ PFAS _s (n=70)	
Copy Paper Only	1	<LOQ ^d	ND	<LOQ	ND	<LOQ	ND	ND	ND	<LOQ	
Day 0	Live	2	ND ^e	ND	<LOQ	ND	ND	ND	ND	<LOQ	
Carpet	Live	1	0.51	0.09	<LOQ	0.03	0.01	0.01	<LOQ	<LOQ	0.66
		2	0.82	0.07	0.01	0.05	<LOQ	0.02	<LOQ	<LOQ	0.97
Day 0	Abiotic	1	0.21	<LOQ	ND	0.01	0.01	ND	ND	ND	0.23
		2	0.51	0.01	<LOQ	<LOQ	0.11	0.01	ND	ND	0.65
Clothing	Live	1	0.13	<LOQ	0.02	0.02	0.02	0.01	<LOQ	ND	0.19
		2	2.28	0.56	1.95	0.01	0.03	<LOQ	ND	ND	4.84
Day 0	Abiotic	1	0.50	0.11	0.18	0.00	0.04	ND	ND	ND	0.83
		2	0.62	0.09	0.13	<LOQ	0.01	ND	ND	ND	0.84

a. Σ FTMAP_s (n = 5) were not presented because the measured concentration in all reactors was non-detect.

b.

c. Single samples were analyzed for each time point, but the accuracy of the method and whole-method precision were previously determined to be 81-120% and 5.5-33%, respectively. The number (n) of analytes included in each PFAS compound class

d. <LOQ: All signals for analytes in compound class were less than the limit of quantification

e. ND: All signals for analytes in compound class were non-detect

Table S4. Contribution of samples with and without analytical and/or internal standards at the final sampling point.

			Qn^a	Sq^b	Ql^c	Sc^d
Carpet	Live	1	98%	2%	<1%	<1%
		2	97%	2%	<1%	<1%
	Abiotic	1	98%	2%	<1%	<1%
		2	95%	5%	<1%	<1%
Clothing	Live	1	89%	2%	9%	<1%
		2	87%	13%	<1%	<1%
	Abiotic	1	73%	27%	<1%	<1%
		2	97%	3%	<1%	<1%

- a. Quantitative (Qn) PFASs has analytical standards and the measured accuracy fell within 90 – 110% and precision was $\leq 20\%$ RSD.
- b. Semi-quantitative (Sq) PFASs has analytical standards, but the measured accuracy did not fall within 90-110% and/or the precision was $\geq 20\%$ RSD.
- c. For qualitative (Ql) PFASs, only a commercial reference material was available.
- d. For screen (Sc) PFASs, no reference material was available.

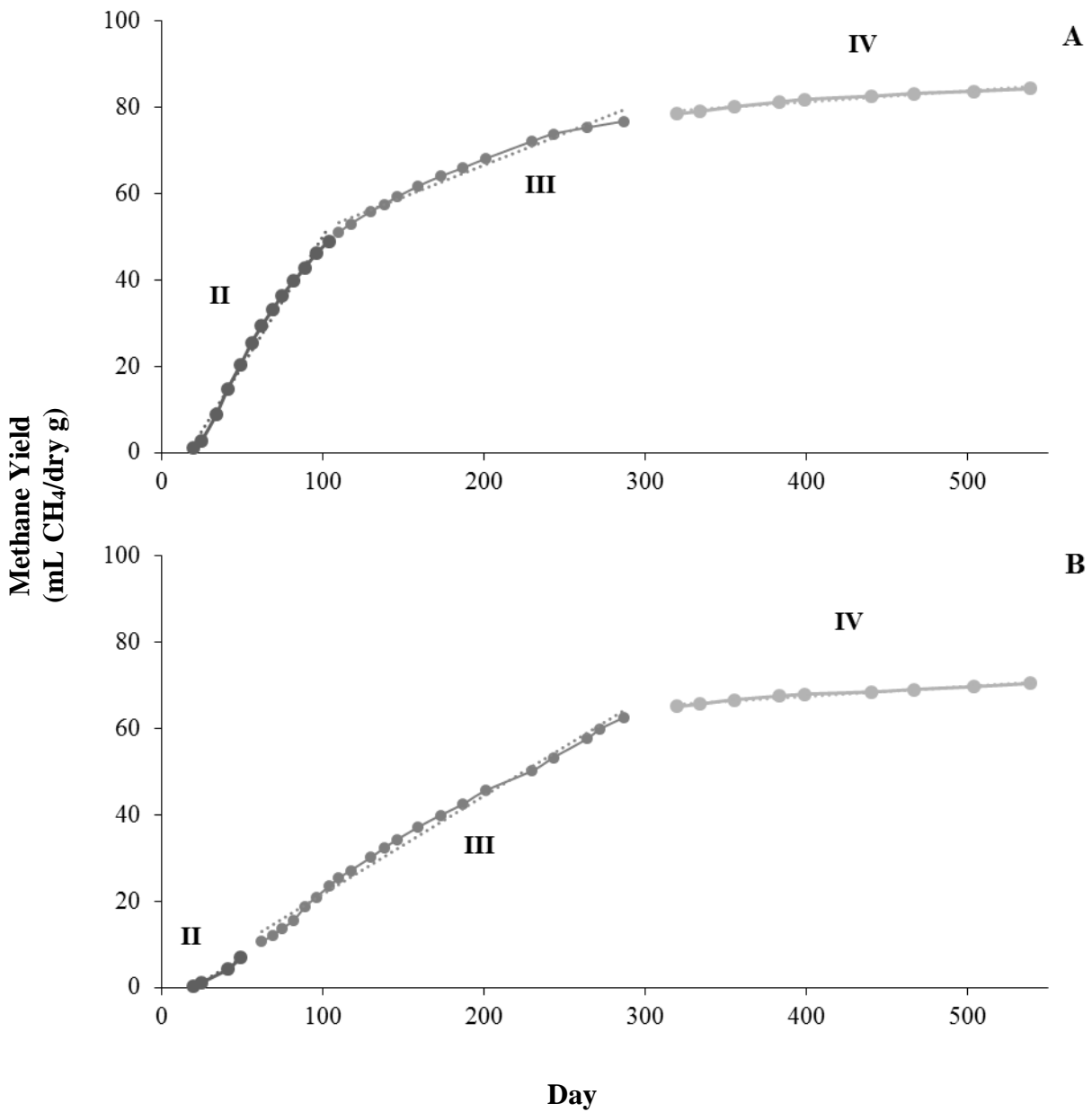


Figure S1. Methane production in carpet (A) live 1 and (B) live 2 during operation demonstrating four distinct phases: (I) lag phase, (II) exponential growth, (III) stationary, and (IV) stabilization phase.

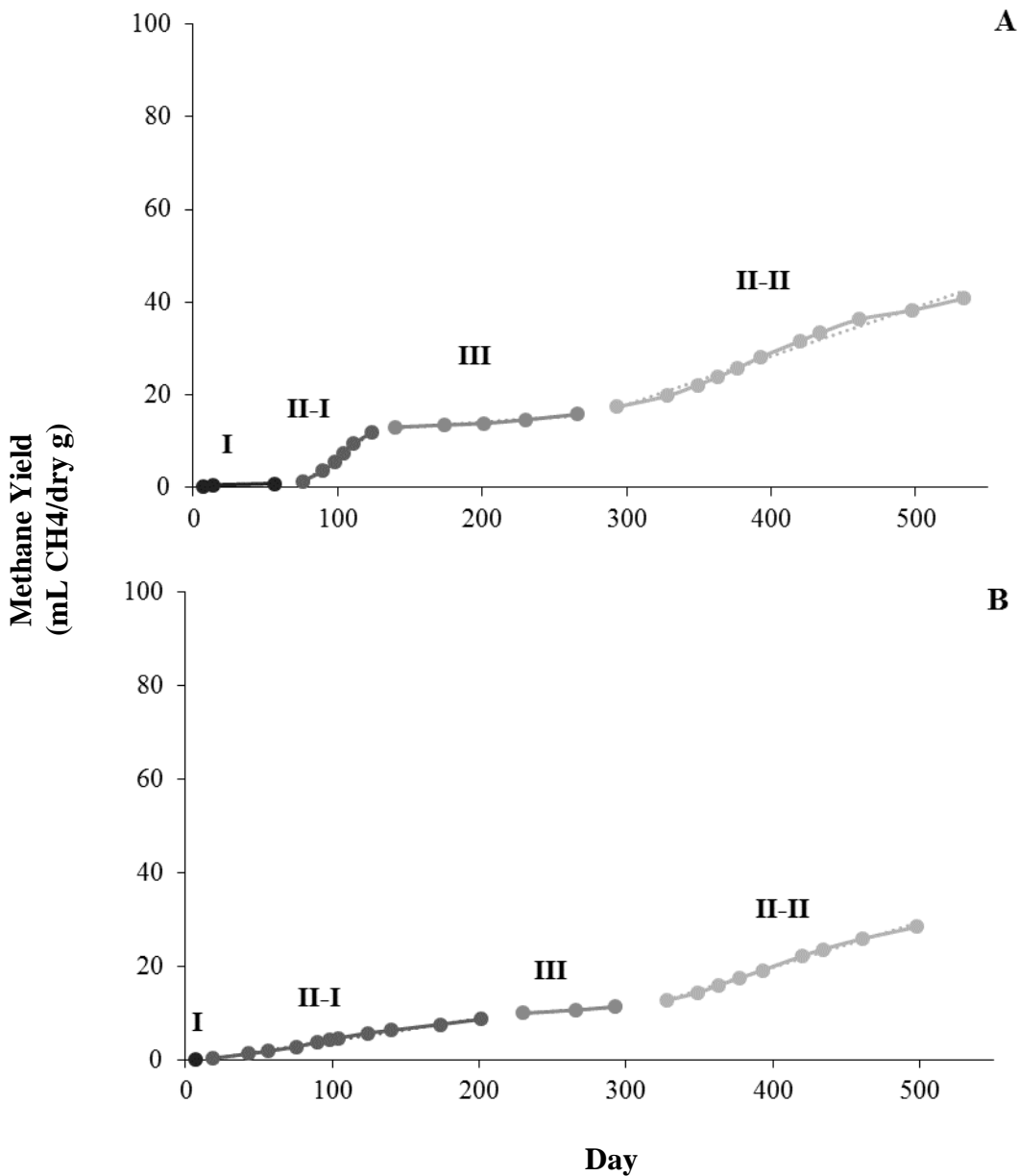


Figure S2. Methane production in clothing (A) live 1 and (B) live 2 during operation demonstrating four distinct phases: (I) lag phase, (II-I) first exponential growth, (III) stationary, and (II-II) second exponential growth phase.

In contrast to the carpet reactors (Figure S1), these reactors were not monitored through the stabilization phase.

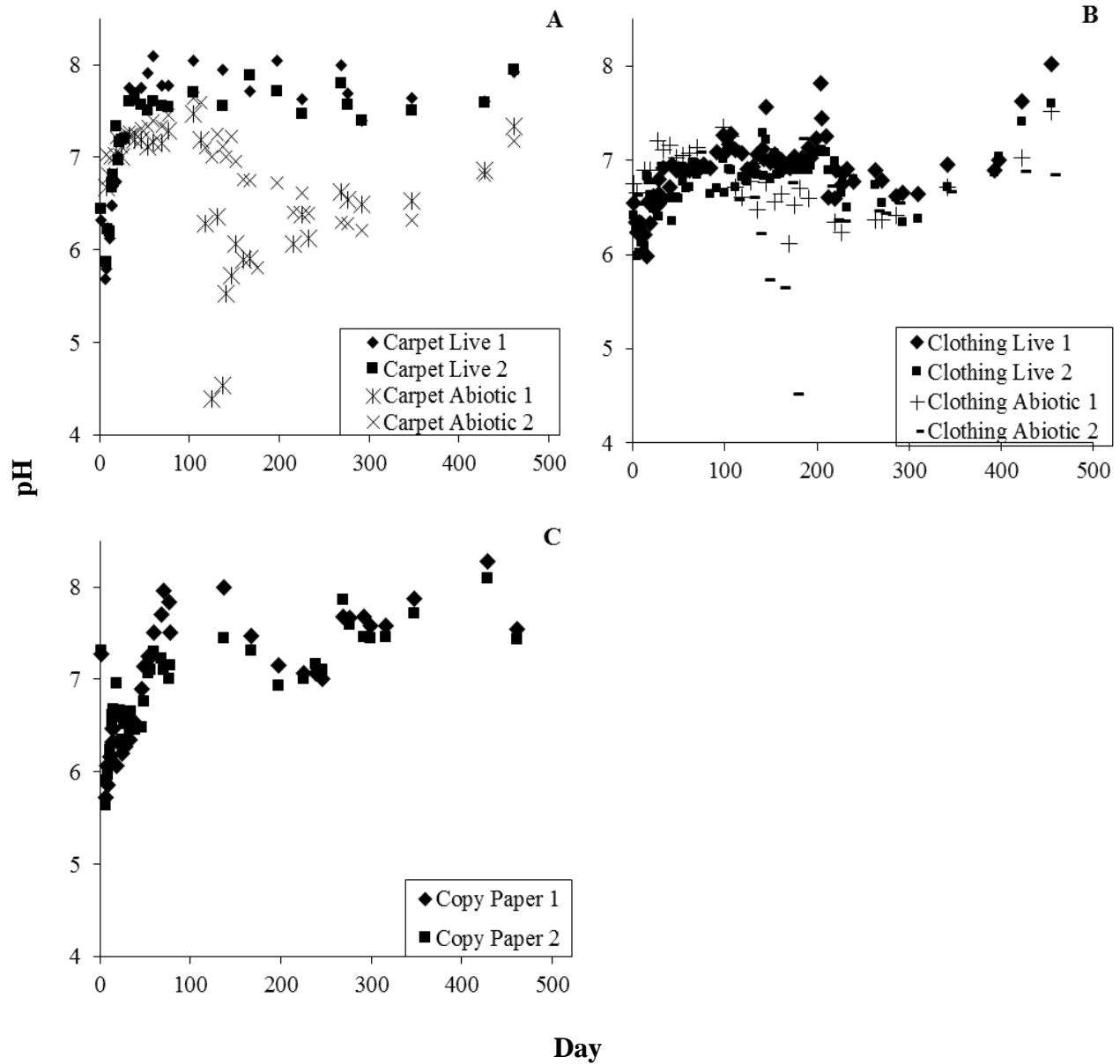


Figure S3. Reactor pH during anaerobic decomposition for (A) carpet, (B) clothing, and (C) copy paper reactors

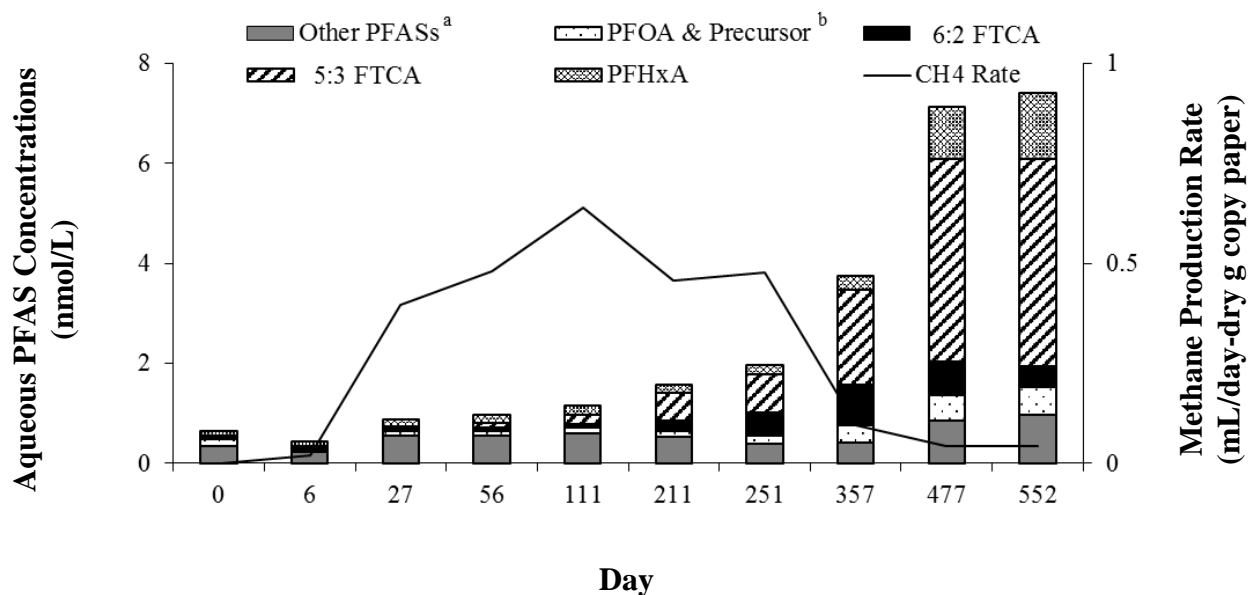


Figure S4. PFAS leaching from carpet live 1 presented as total concentrations at each sampling point.

Methane (CH₄) measurement from the previous sampling point was presented if a measurement was not made on the same day as PFAS samples. Note the non-linear x-axis. Other PFASs include the sum of concentrations for all other measured compounds (n = 59). PFOA & Precursors includes the sum of concentrations for PFOA, 8:2 FTCA, 8:2 FTUCA, 7:3 FTCA, 8:2 diPAPs, and 8:2 FTSA

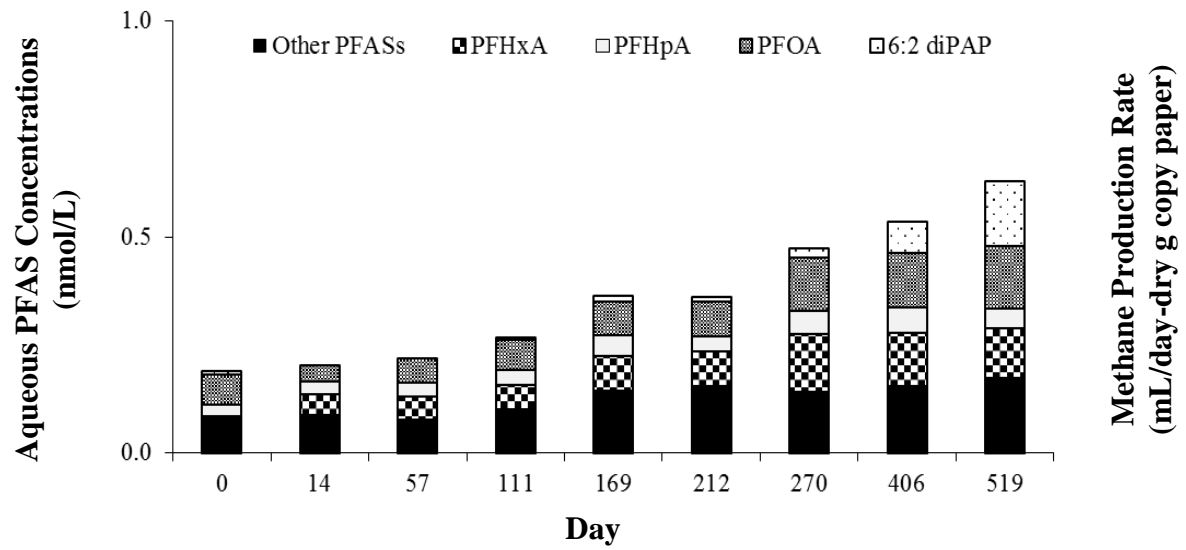


Figure S5. PFAS leaching from clothing live 1 presented as the total concentration at each sampling point.

Note non-linear x-axis. Other PFASs includes the sum concentrations for all other measured compounds ($n = 66$).

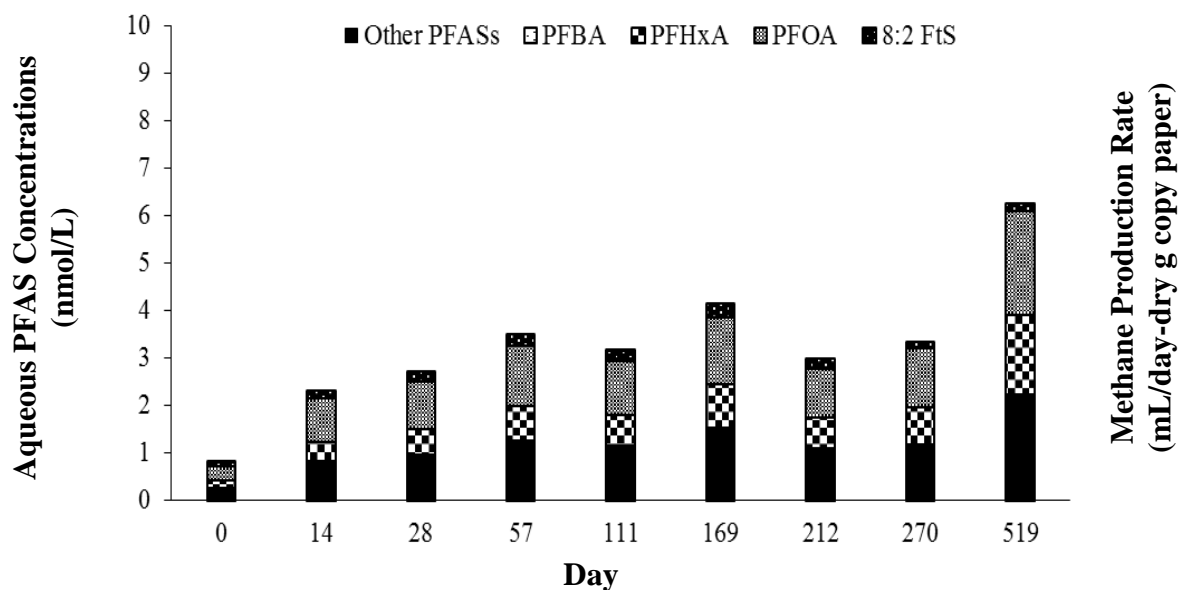


Figure S6. PFAS leaching from clothing abiotic 2 presented as the total concentration at each sampling point.

Note non-linear x-axis. Other PFASs includes the sum concentrations for all other measured compounds (n = 66).

Appendix B – Supporting information for Release of Per- and Polyfluoroalkyl substances to
U.S. Municipal Landfill Leachate

Equation S1. Maximum Likelihood Calculation. Releases of group 2 PFASs were evaluated using the following estimate for the population mean:

$$\hat{\mu} = \bar{x}' - (\bar{x}' - X_o) * \lambda (g,h)$$

Gibbons and
Coleman
(2001)

$\hat{\mu}$ = Population Mean

\bar{x}' = Measured Mean

X_o = **LOQ/2**

$\lambda(g,h)$ = Table value - given g and h

g = Measured Variance/ $(\bar{x}' - X_o)^2$

h = Proportion of ND

Table S1. Acronyms and structures of PFAS compound classes.

Adapted from Lang et al. (2016).

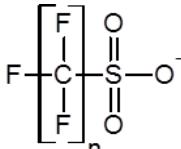
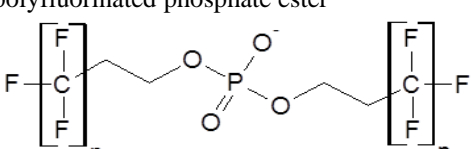
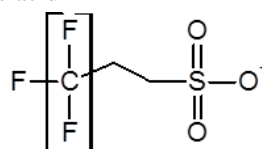
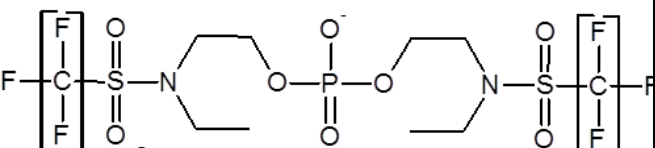
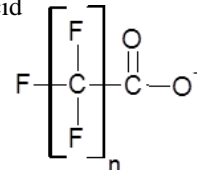
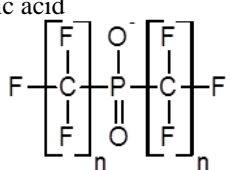
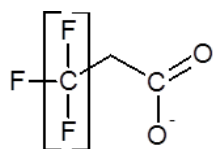
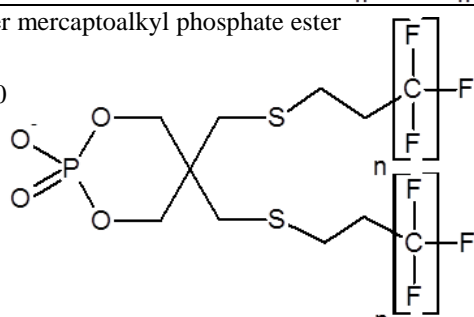
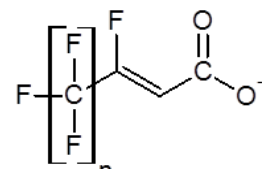
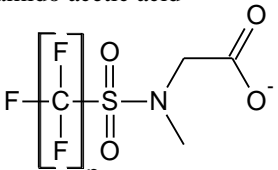
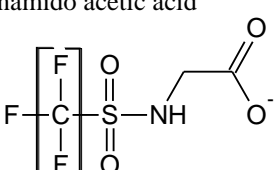
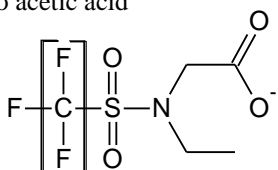
<p>Perfluoroalkyl sulfonic acid PFSA n = 4-10</p> 	<p>Di-substituted polyfluorinated phosphate ester DiPAP n = 4, 6, 8, 10</p> 
<p>Fluorotelomer sulfonic acid n:2 FTSA n = 4, 6, 8</p> 	<p>Bis(N-ethyl perfluoroalkylsulfonamidoethane) phosphate DiSamPAP n = 8</p> 
<p>Perfluoroalkyl carboxylic acid PFCAs n = 3-17</p> 	<p>Disubstituted perfluoroalkyl phosphinic acid PFPIA n = 4, 6, 8</p> 
<p>Fluorotelomer carboxylic acid n:2 FTCA n = 4, 6, 8, 10</p> 	<p>Fluorotelomer mercaptoalkyl phosphate ester FTMAP n = 4, 6, 8, 10</p> 
<p>Fluorotelomer unsaturated carboxylic acid n:2 FTUCAs n = 4, 6, 8, 10</p> 	<p>N-methyl fluoroalkyl sulfonamido acetic acid MeFASAA n = 4-8</p> 
<p>Fluoroalkyl sulfonamido acetic acid FASAA n = 4-8</p> 	<p>N-ethyl fluoroalkyl sulfonamido acetic acid EtFASAA n = 4-8</p> 

Table S2. Leachate generation rate for landfills located in arid and temperate climates

Leachate Generation		
(L/ha-day)		
Arid	Landfill 1	51
	2	0
	3	57
Temperate	Landfill 1	6360
	2	150
	3	1425
	4	46

Table S3. California landfill data for mass of waste contained per landfill surface area provided from Scott Walker

Site	Footprint (ha)	WIP (kg)	Tg/ha
1	6.9	1.8E+08	26.4
2	12.6	3.3E+08	26.6
3	11.7	6.7E+08	57.0
4	10.1	7.1E+08	70.0
5	36.0	8.7E+08	24.2
6	14.6	8.8E+08	60.6
7	16.6	9.5E+08	57.1
8	16.2	1.1E+09	65.8
9	12.8	1.2E+09	91.6
10	3.2	1.2E+09	361.9
11	16.1	1.2E+09	73.5
12	16.6	1.4E+09	82.6
13	32.4	1.4E+09	43.1
14	17.8	1.4E+09	79.9
15	15.4	1.5E+09	94.6
16	16.2	1.6E+09	97.7
17	42.9	1.7E+09	40.0
18	37.3	1.8E+09	48.8
19	10.1	1.8E+09	179.6
20	37.3	1.9E+09	50.3
21	36.9	1.9E+09	51.1
22	17.4	1.9E+09	111.0
23	37.3	2.1E+09	56.1
24	29.6	2.3E+09	76.8
25	42.5	2.3E+09	53.5
26	32.0	2.3E+09	73.5
27	51.0	2.4E+09	46.2
28	25.5	2.4E+09	94.1
29	25.1	2.4E+09	96.4
30	21.5	2.5E+09	116.6
31	27.9	2.5E+09	90.7
32	30.0	2.7E+09	89.0
33	49.8	2.7E+09	54.8
34	72.1	2.9E+09	40.9
35	47.8	3.0E+09	62.1
36	21.5	3.1E+09	145.6
Site	Footprint (ha)	WIP (kg)	Tg/ha
37	59.1	3.2E+09	54.2

38	47.8	3.2E+09	67.5
39	35.6	3.3E+09	91.6
40	87.1	3.4E+09	38.6
41	35.2	3.4E+09	95.7
42	32.6	3.4E+09	105.2
43	52.7	3.6E+09	69.1
44	63.6	3.8E+09	59.6
45	29.2	4.2E+09	143.5
46	50.6	4.2E+09	83.1
47	35.6	4.3E+09	120.5
48	46.6	4.3E+09	92.4
49	41.3	4.6E+09	112.0
50	46.2	4.8E+09	105.1
51	61.2	5.2E+09	85.8
52	37.3	5.5E+09	147.8
53	38.5	5.6E+09	147.2
54	25.1	5.9E+09	234.9
55	56.7	6.0E+09	105.9
56	84.6	6.0E+09	71.0
57	66.0	6.4E+09	97.9
58	20.3	6.6E+09	328.4
59	50.3	6.7E+09	133.5
60	127.6	7.6E+09	59.7
61	30.8	7.9E+09	258.6
62	96.8	8.0E+09	82.8
63	47.8	8.5E+09	178.4
64	90.1	9.1E+09	101.7
65	46.6	9.2E+09	197.3
66	45.5	1.0E+10	222.0
67	69.7	1.0E+10	146.1
68	37.3	1.0E+10	280.1
69	77.0	1.1E+10	140.0
70	64.8	1.1E+10	167.7
71	89.9	1.1E+10	124.2
72	69.9	1.2E+10	170.7
73	70.1	1.5E+10	216.7

Site	Footprint (ha)	WIP (kg)	Tg/ha
74	70.1	1.6E+10	222.0

75	55.9	1.6E+10	289.0
76	50.2	1.7E+10	345.1
77	67.2	1.7E+10	259.7
78	88.2	1.8E+10	199.3
79	101.3	1.8E+10	178.0
80	77.0	2.0E+10	260.0
81	168.5	2.1E+10	126.3
82	70.9	2.2E+10	304.9
83	111.0	2.3E+10	210.0
84	137.3	2.3E+10	171.4
85	93.2	2.4E+10	258.6
86	104.1	2.4E+10	234.1
87	89.5	2.5E+10	283.0
88	178.2	2.6E+10	147.9
89	192.8	2.9E+10	151.5
90	69.3	3.1E+10	442.5
91	101.7	3.9E+10	382.9
92	95.2	4.0E+10	421.8
93	149.9	4.2E+10	278.0
94	170.1	4.7E+10	278.1
95	243.0	1.1E+11	464.4

Table S4. Evaluation of group 1 PFAS mean concentrations substituted different values for samples where the concentration was less than the limit of quantification (<LOQ).
 There were no concentrations that were <LOQ for the group 1 PFASs not presented here.

ng/L	Substituted Value		
	LOQ	LOQ/2	0
PFNA	44.2	44.1	44.1
PFDA	43.6	43.5	43.5
6:2 FTCA	591.4	591.2	591.0
8:2 FTCA	114.4	114.2	114.0
5:3 FTCA	2161.2	2161.0	2160.8
PFBS	150.6	150.5	150.4
PFPS	18.4	18.4	18.3
6:2 FTSA	179.7	179.7	179.6
8:2 FTSA	34.5	34.3	34.2
MeFBSAA	371.7	371.4	371.2
MeFOSAA	138.7	138.7	138.7
EtFOSAA	115.3	115.2	115.1

Table S5. Group 1 PFAS concentrations in landfills closed before 1982. For Landfill C, only concentrations before on-site landfill leachate treatment were presented.

nmol/L	Landfill C		Landfill D	
	1	2	1	2
PFBA	0.07	0.14	0.35	0.64
PFPeA	0.06	0.06	0.14	0.21
PFHxA	0.08	0.08	0.30	0.39
PFHpA	0.05	0.05	0.11	0.14
PFOA	0.17	0.10	0.38	0.34
PFNA	<LOQ	<LOQ	<LOQ	<LOQ
PFDA	<LOQ	ND	ND	ND
6:2 FTCA	ND	ND	ND	ND
8:2 FTCA	ND	ND	ND	ND
5:3 FTCA	ND	0.01	0.09	0.03
7:3 FTCA	ND	0.01	0.02	0.00
PFBS	0.01	0.01	0.01	0.01
PFHxS	0.04	0.03	0.02	0.04
PFOS	0.11	0.09	0.05	0.05
6:2 FTSA	<LOQ	ND	<LOQ	ND
8:2 FTSA	ND	ND	ND	ND
MeFBSAA	0.01	0.01	0.02	0.02
MeFOSAA	ND	ND	ND	ND
EtFOSAA	<LOQ	ND	ND	0.02
Total	0.62	0.60	1.52	1.88

Table S6. Mean group 1 PFAS concentrations for landfills presented by waste age. Only group 1 PFASs that were demonstrated as quantitative and semi-quantitative in Allred et al. (2014) were included for analysis.

µg/L	<10 yrs. ^a (n = 32)	>10 yrs. ^b (n = 23)	P – value
PFBA	1.2 (1.3)	1.1 (1.0)	0.76
PFPeA	1.2 (1.1)	0.8 (0.8)	0.19
PFHxA	2.6 (2.6)	1.7 (1.9)	0.21
PFHpA	0.9 (0.9)	0.5 (0.4)	0.04
PFOA	1.5 (1.5)	0.8 (0.9)	0.06
PFNA	0.08 (0.08)	0.03 (0.05)	<0.01
PFDA	0.08 (0.1)	0.03 (0.05)	0.01
6:2 FTCA	1.2 (0.9)	0.5 (0.6)	<0.01
8:2 FTCA	0.2 (0.2)	0.1 (0.2)	0.02
5:3 FTCA	6.7 (6.8)	2.5 (3.8)	<0.01
7:3 FTCA	1.1 (1.4)	0.2 (0.4)	<0.01
PFBS	0.6 (1.1)	0.1 (0.3)	0.02
PFHxS	0.4 (0.4)	0.3 (0.2)	0.21
PFOS	0.2 (0.2)	0.1 (0.1)	0.08
6:2 FTSA	0.2 (0.2)	0.2 (0.4)	0.73
8:2 FTSA	0.08 (0.15)	0.03 (0.05)	0.14
MeFBSAA	0.8 (0.7)	0.3 (0.4)	<0.01
MeFOSAA	0.3 (0.3)	0.1 (0.2)	0.08
EtFOSAA	0.1 (0.2)	0.1 (0.2)	0.76
Total	19.2 (17.6)	9.6 (9.1)	0.01

- a. Landfill G (n = 2 mean for each sampling event), H (n = 2), J (n = 2), K (n = 2 mean for each sampling event), N (n = 2 single sampling point doubled), R (n = 2 mean for each sampling event), Q (n = 2), U (n = 2), and S (n = 2) included for the <10 yr waste age mean
- b. Landfill B (n = 2), E (n = 2), F (n = 2 mean for each sampling event), I (n = 2), L (n = 2), M (n = 2), R (n = 4), T (n = 2 mean for each sampling event), and U (n = 2 means for two sampling events) included for the >10 yr. waste age mean

Table S7. Mean group 1 PFAS concentrations ($\mu\text{g/L}$) for landfills presented by climate. Only group 1 PFASs that were demonstrated as quantitative and semi-quantitative in Allred et al. (2014) were included for analysis.

$\mu\text{g/L}$	Wet^a (n = 25)	Temperate^b (n = 12)	Arid^c (n = 6)	P – value
PFBA	1.0 (1.0)	1.1 (1.0)	0.7 (0.6)	0.70
PFPeA	0.8 (0.8)	1.1 (0.9)	0.4 (0.5)	0.61
PFHxA	1.5 (1.5)	2.1 (2.6)	1.3 (1.0)	0.52
PFHpA	0.6 (0.5)	0.6 (0.4)	0.5 (0.6)	0.92
PFOA	0.9 (1.0)	0.7 (0.6)	0.5 (0.6)	0.53
PFNA	0.05 (0.05)	0.02 (0.01)	0.03 (0.04)	0.12
PFDA	0.05 (0.09)	<0.01	<0.01	0.12
6:2 FTCA	0.6 (0.5)	0.6 (0.6)	1.1 (1.7)	0.33
8:2 FTCA	0.1 (0.1)	0.1 (0.1)	0.1 (0.2)	0.80
5:3 FTCA	2.1 (3.0)	4.1 (5.0)	5.2 (7.6)	0.19
7:3 FTCA	0.4 (0.6)	0.2 (0.2)	0.3 (0.5)	0.51
PFBS	0.2 (0.4)	0.03 (0.02)	0.1 (0.2)	0.33
PFHxS	0.3 (0.2)	0.3 (0.3)	0.2 (0.3)	0.41
PFOS	0.09 (0.1)	0.07 (0.1)	0.07 (0.1)	0.73
6:2 FTSA	0.2 (0.4)	0.06 (0.06)	0.1 (0.09)	0.42
8:2 FTSA	0.03 (0.06)	0.03 (0.06)	0.03 (0.05)	0.99
MeFBSAA	0.4 (0.4)	0.3 (0.3)	0.3 (0.4)	0.58
MeFOSAA	0.2 (0.2)	0.07 (0.2)	0.01 (0.02)	0.22
EtFOSAA	0.1 (0.2)	0.1 (0.3)	0.01 (0.02)	0.42
Total	9.4 (9.5)	11.2 (8.2)	11.0 (14.0)	0.85

- Landfills B (n = 2), H (n = 2), I (n = 2), J (n = 2), N (n = 1), P (n = 4), Q (n = 2), U (n = 2 means for two sampling events), R (n = 2 means for two sampling events), and S (n = 2) included for wet climate mean
- Landfills E (n = 2), F (n = 4), G (n = 2 means for two sampling events), and T (n = 4) included in the mean for temperate climate
- Landfills L (n = 2), M (n = 2), and K (n = 2 means for two sampling events) included in the mean for arid climate

Table S8. Distribution parameters and Kolmogorov-Smirnov/Lillefors test of normality results for each Monte Carlo input variable. Lognormal distributions were used for every variable except the arid leachate production, where an exponential distribution was used.

		Mean ln(x)	StDev ln(x)	N	D_n^a	D_{critical}^a ($\alpha = 0.05$)
Waste per area (Gg/ha)		4.8	0.7	114	0.042	0.083
Leachate Production (L/ha-d)	Wet	8.0	1.3	43	0.130	0.134
	Temperate	6.2	2.2	4	0.21	0.38
	Arid^c (λ; ha-d/L)	0.028	N/A	3	N/A	N/A
Total PFAS Concentration (ng/L)	Wet <10 yrs	9.4	1.1	15	0.14	0.22
	Wet >10 yrs	8.7	0.76	25	0.14	0.17
	Temperate <10 yrs	8.5	0.91	8	0.22	0.29
	Temperate >10 yrs	9.0	1.0	10	0.13	0.26
	Arid <10 yrs	10	0.59	10	0.11	0.26
	Arid >10 yrs	7.5	0.48	4	0.20	0.38

- a. D_n is the Kolmogorov-Smirnov test statistic and is equal to the maximum absolute error between the cumulative distribution function (CDF) of the lognormal distribution and the empirical CDF ($S(x_k) = k/N$; k - sample number). Lognormal and empirical CDFs for each variable where $N \geq 10$ are shown in Figure S8.
- b. Critical values for the Kolmogorov-Smirnov/Lillefors test of normality for N and $\alpha = 0.05$ as reported by Abdi and Molin (2007).
- c. An exponential distribution was used for the arid leachate generation because it was a better fit based on the limited data ($\lambda = 1/\mu$). The Kolmogorov-Smirnov/Lillefors test was not performed because it requires at least 4 data points.

Figure S1: Estimates for annual waste disposal in U.S. landfills. Calculated values use the Powell et al. (2015) values decreased by the rates presented in the EPA waste report.

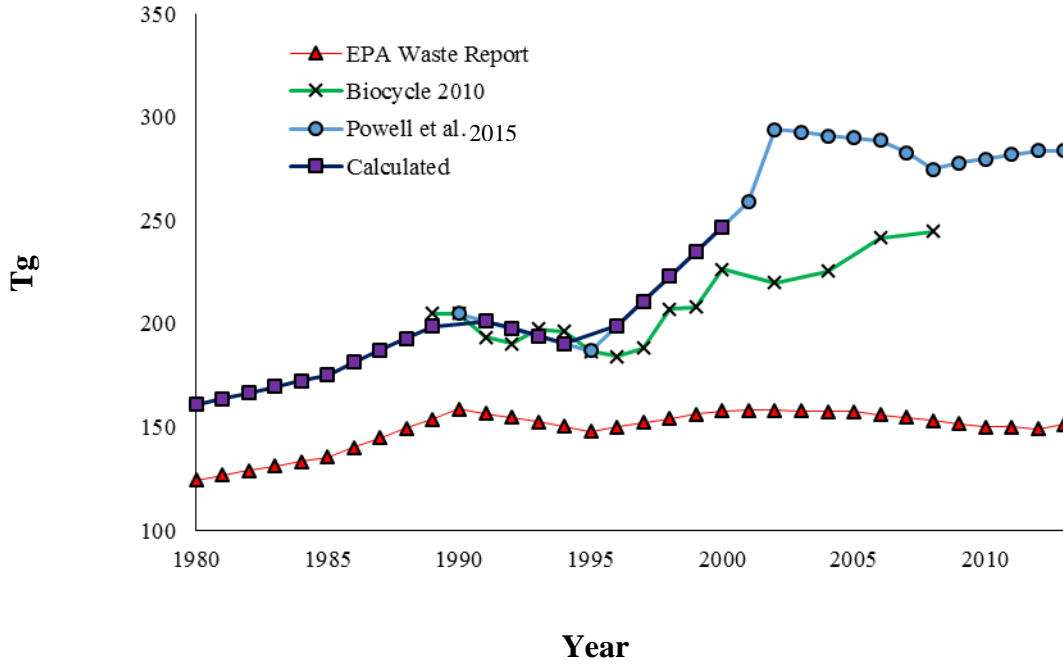


Figure S2: Distribution of volume of leachate generated per landfill surface area in wet climates

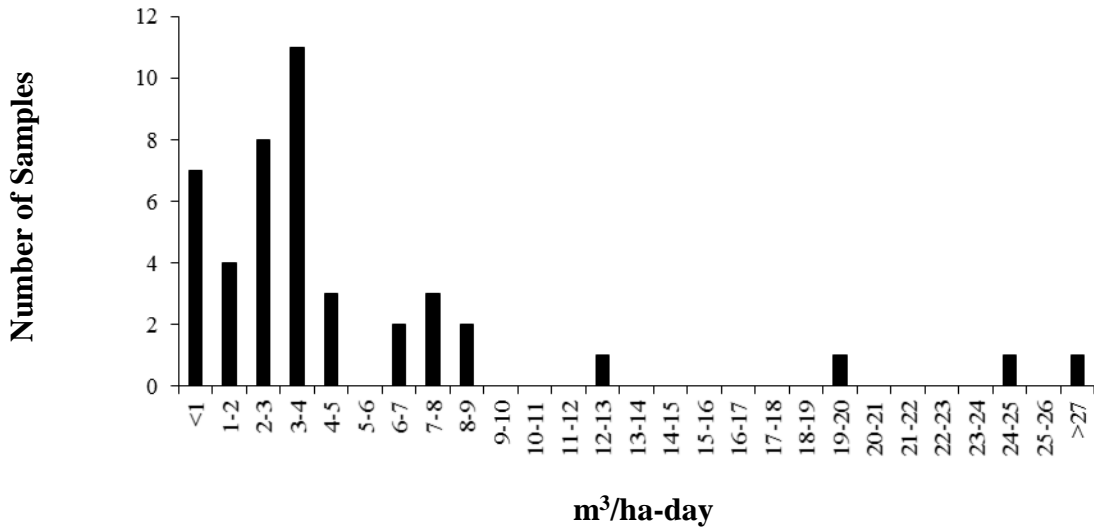


Figure S3: Distribution of mass of waste contained per landfill surface area. Data obtained from state reports (n = 18)^{NY} and data obtained from a consulting engineering (n = 95 – Table S3), including both public and privately owned landfills.

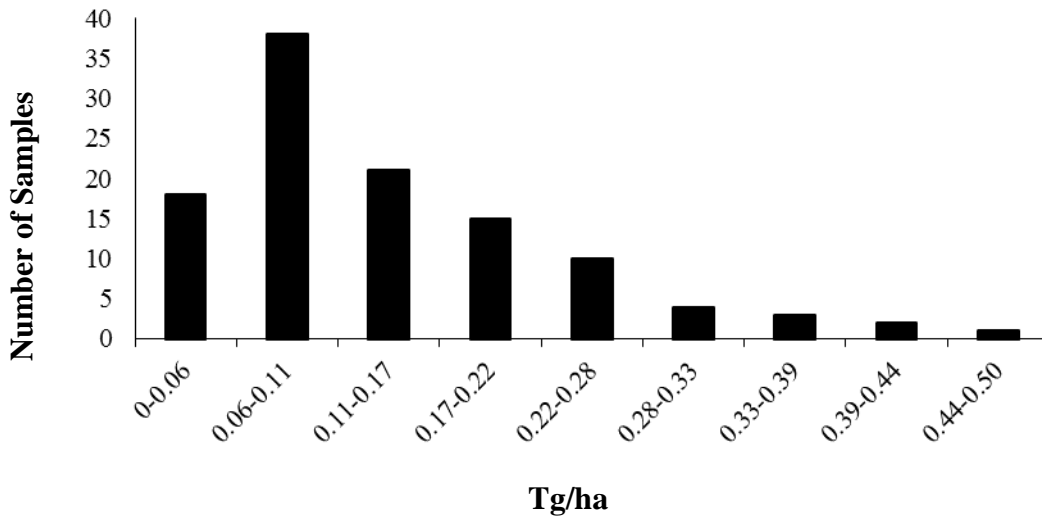
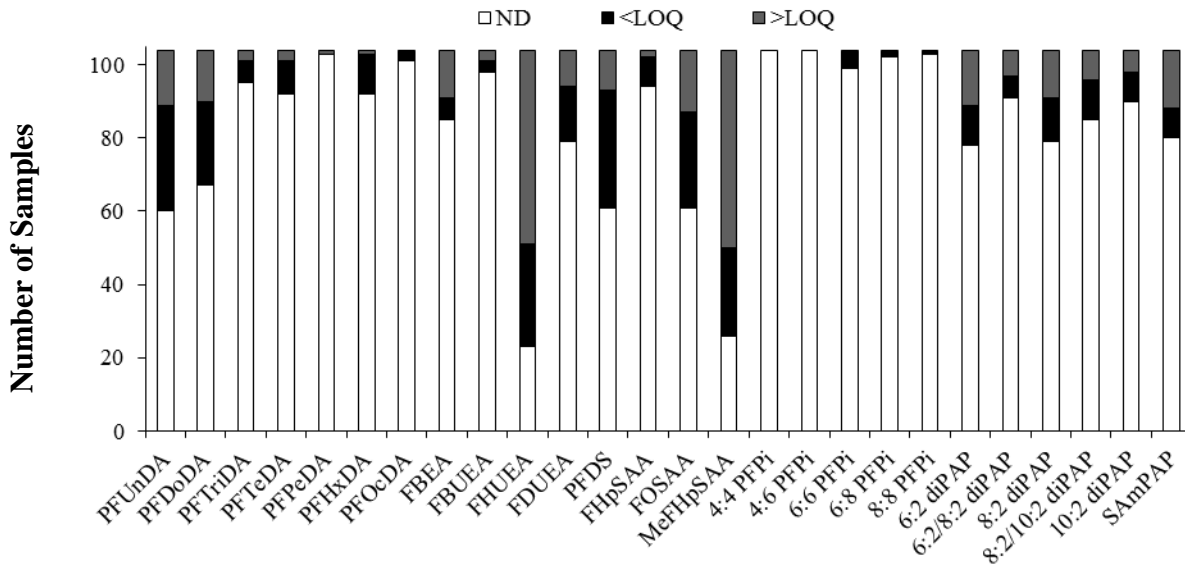


Figure S4. The number samples^a for group 3 compounds^b that was greater than the limit of quantification (>LOQ), less than the limit of quantification (<LOQ) and non-detect (ND)



- a. Total number of samples equals 104
- b. Group 3 per- and polyfluoroalkyl substance (PFAS) compounds are listed in Table 2 (n = 35)

Figure S5. Leachate flows for landfill U

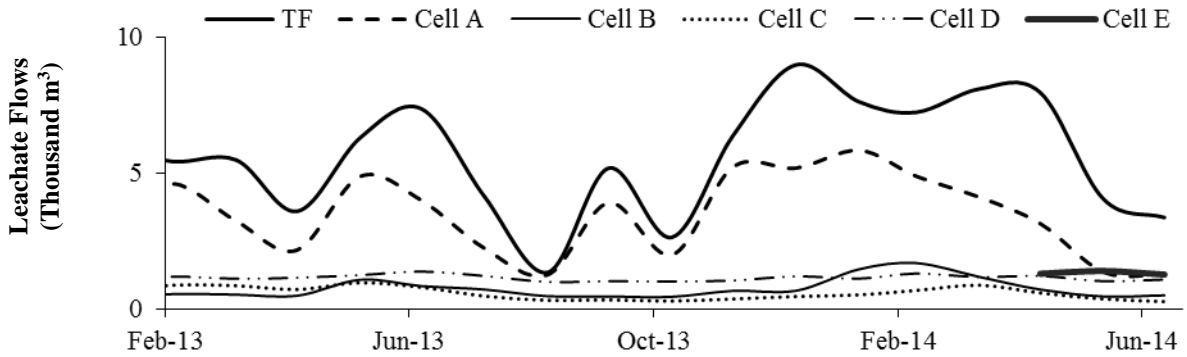


Figure S6: Annual waste disposal in landfills in each climate. Data points filled with black represent data from EPA Greenhouse Gas Report, with other data extrapolated to obtain a data point for each year.

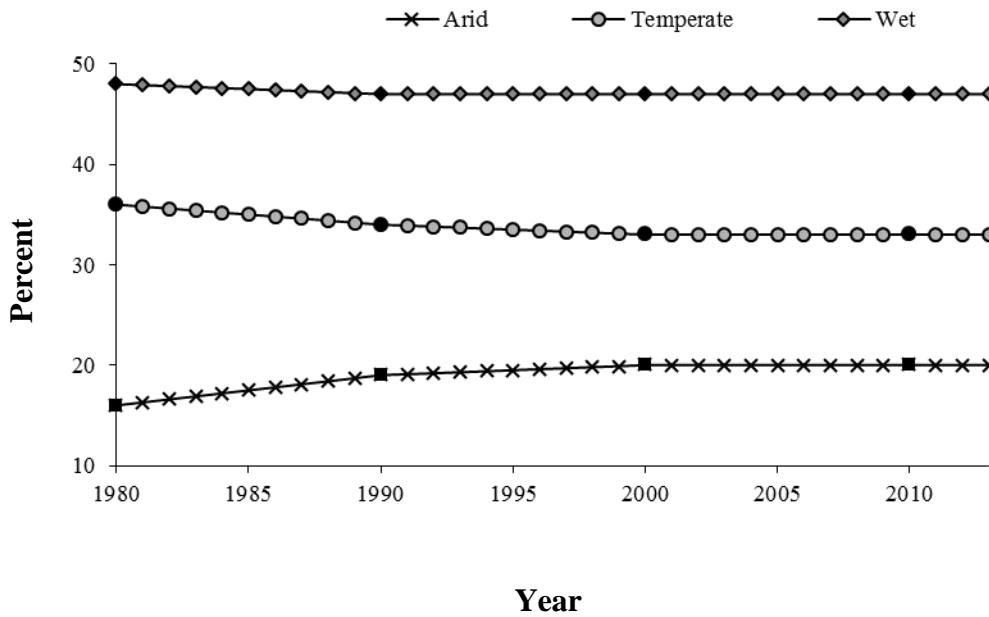


Figure S7: Correlated PFAS concentrations for US landfill samples included in the inventory model excluding samples collected from evaporation ponds and old waste.

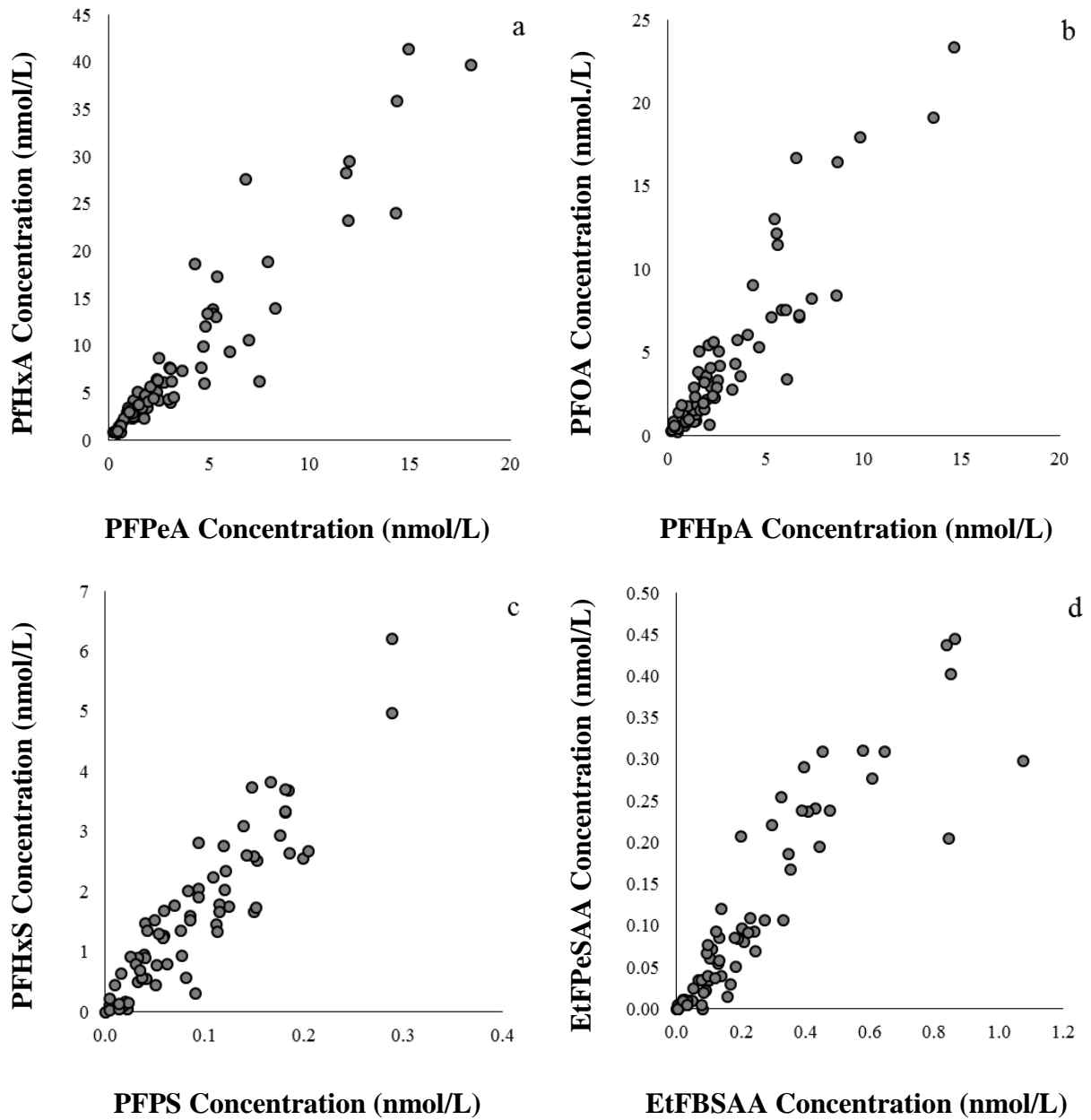
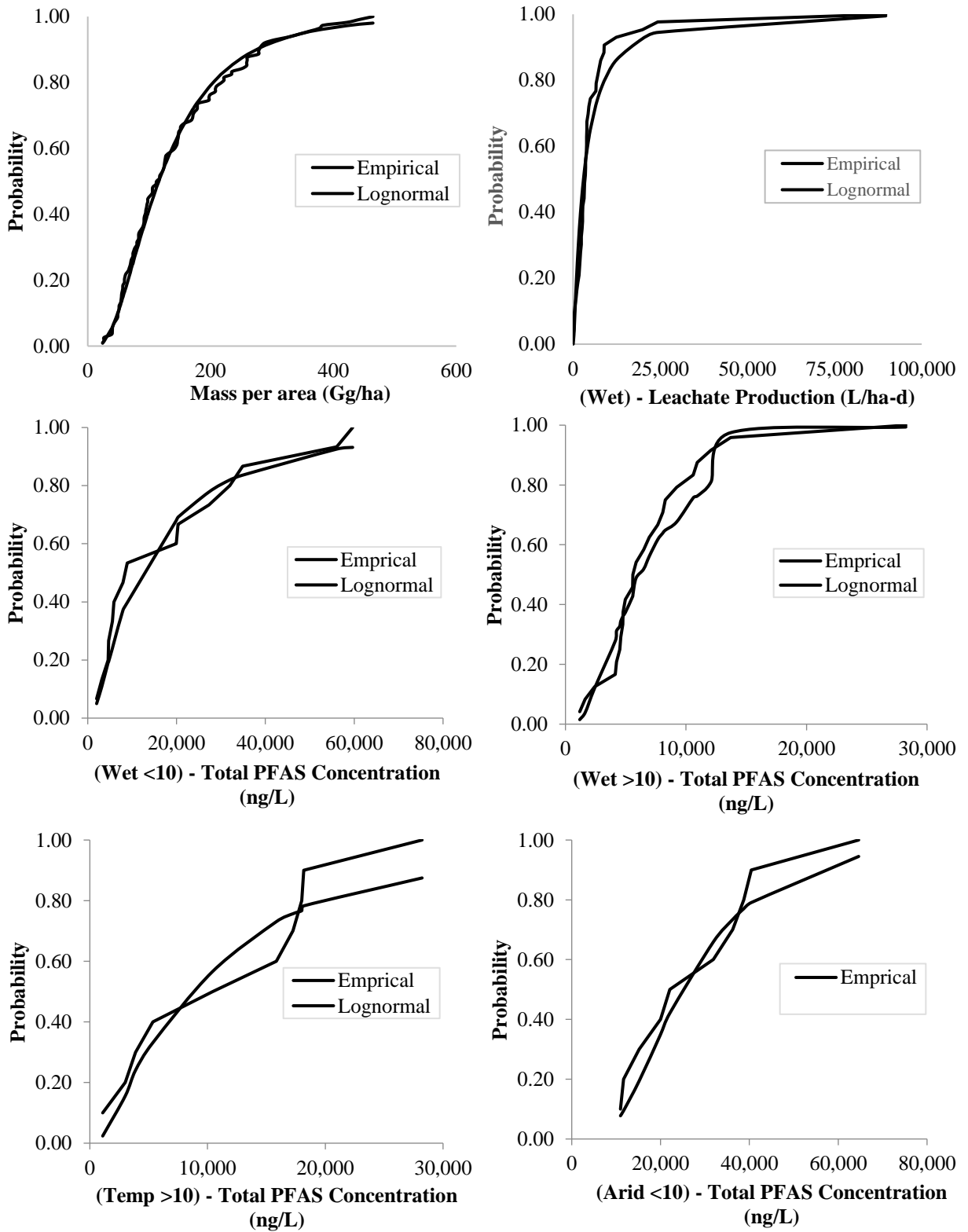


Figure S8. Empirical and lognormal CDFs for each Monte Carlo input variable where $N \geq 10$.



Appendix C – Supporting information for Variations in Per- and Polyfluoroalkyl (PFAS)

Release from Municipal Solid Waste (MSW) in Anaerobic Model Landfill Reactors

Table S1. Reactor masses and volumes

			Synthetic	DI				
			Culture	Leachate	Water	DBNPA ^a	Streptomycin	MSW
			(L)	(L)	(L)	(g)	(g)	(dry g)
November	Live	1	1	1	0.7	0	0	1294.5
		2	1	1	1.1	0	0	1315.8
	Abiotic	1	1	1	0.7	12.5	0	1432.7
		2	1	1	0.7	12.5	0	1271.6
May	Live	1	1	1	1.6	0	0	1389.5
		2	1	1	1.2	0	0	1422.0
	Abiotic	1	1	1	1.8	10.0	0.34	1466.4
		2	1	1	1.8	10.0	0.34	1192.3
August	Live	1	1	1	1	0	0	989.9
		2	1	1	0.6	0	0	964.7
	Abiotic	1	1	1	0.8	12.5	0.459	968.7
		2	1	1	0.8	12.5	0.459	1015.9

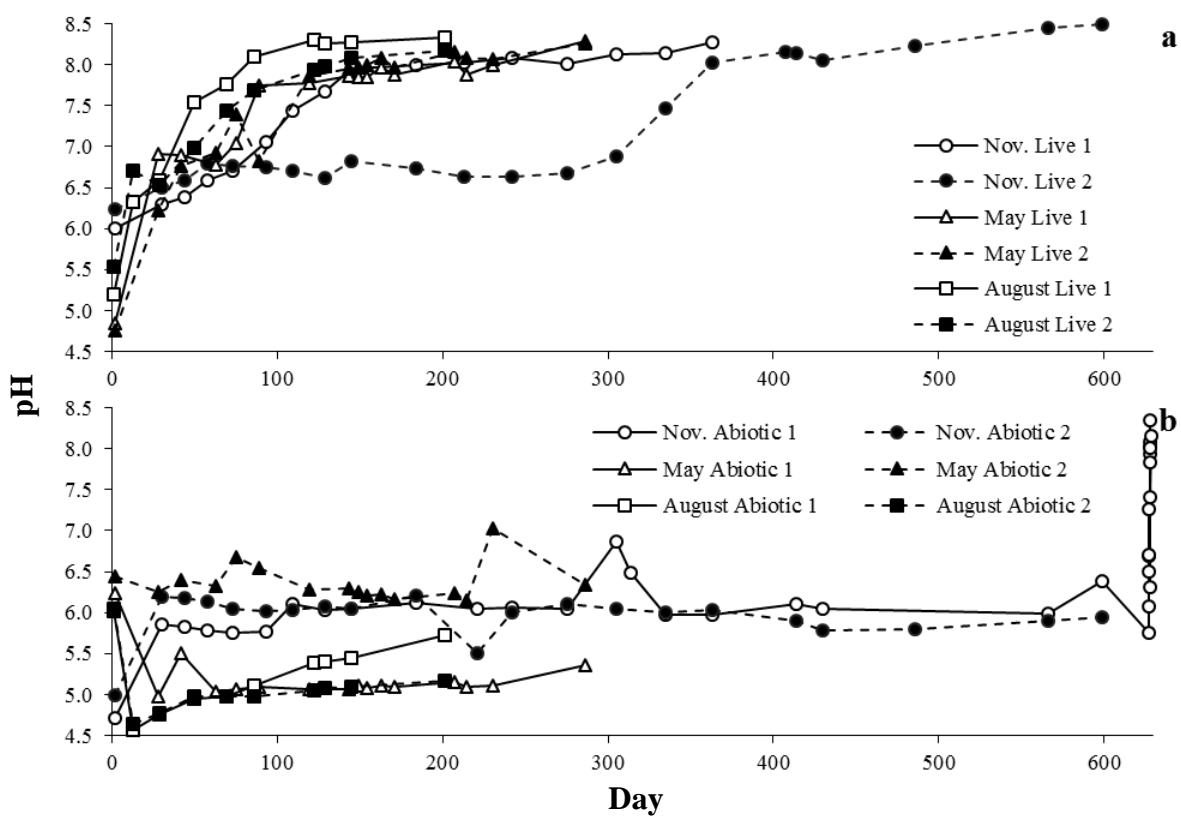


Figure S1. Leachate pH during operation of (a) live and (b) abiotic MSW reactors.

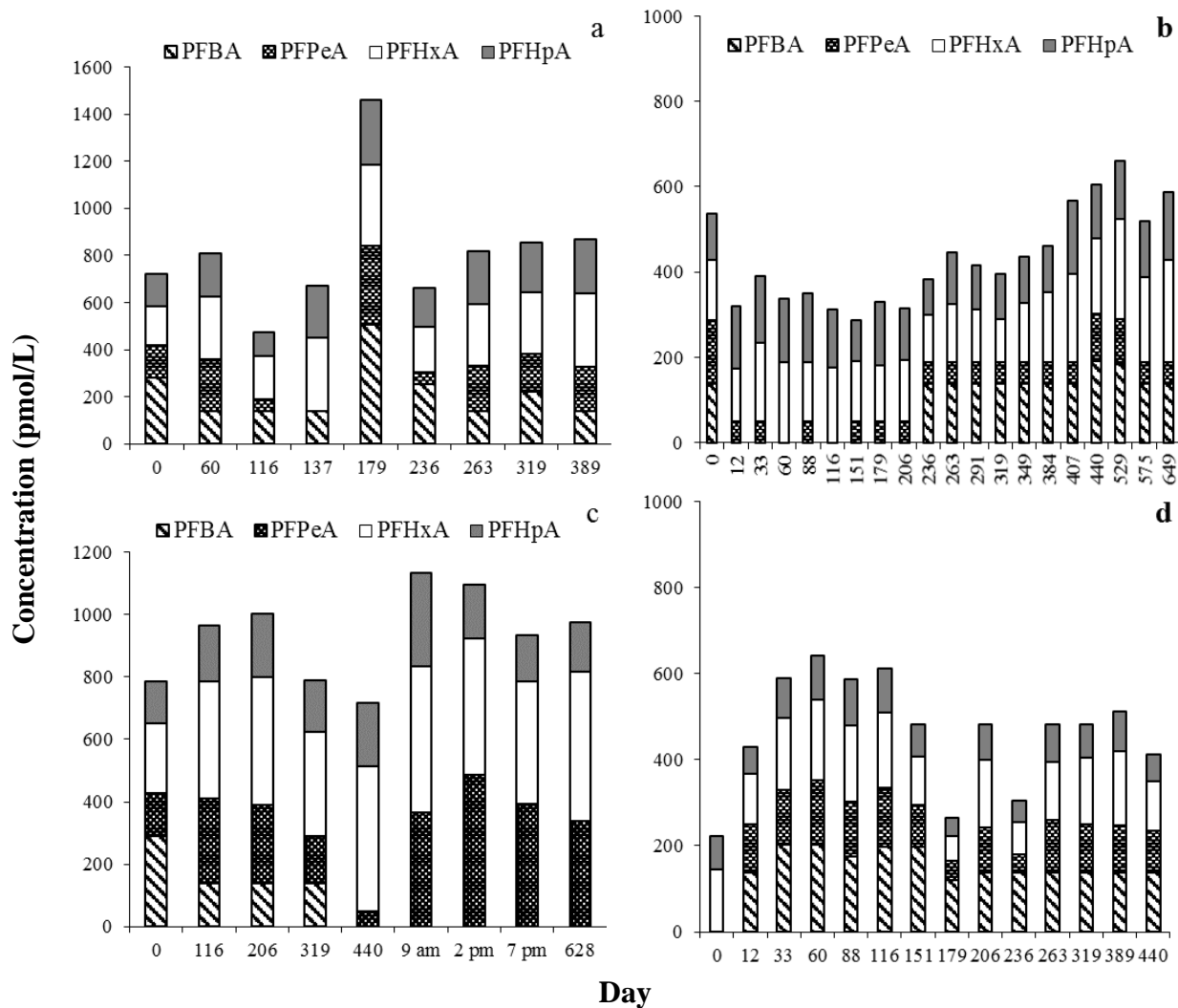


Figure S2. Concentrations of short chain PFCAs in November (a) live 1, (b) live 2 (c) abiotic 1 and (d) abiotic 2 during operation.

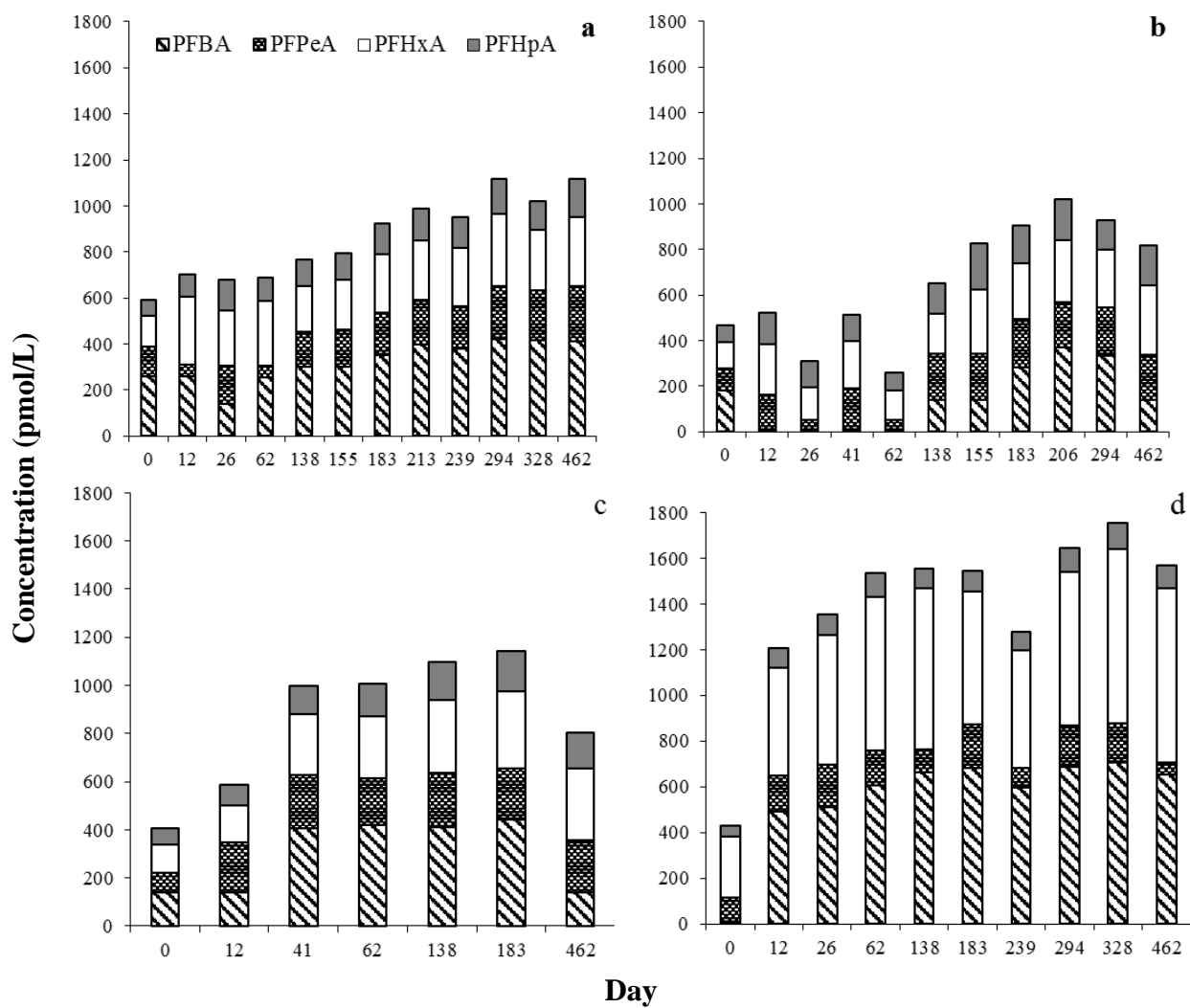


Figure S3. Concentrations of short chain PFCAs in May (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

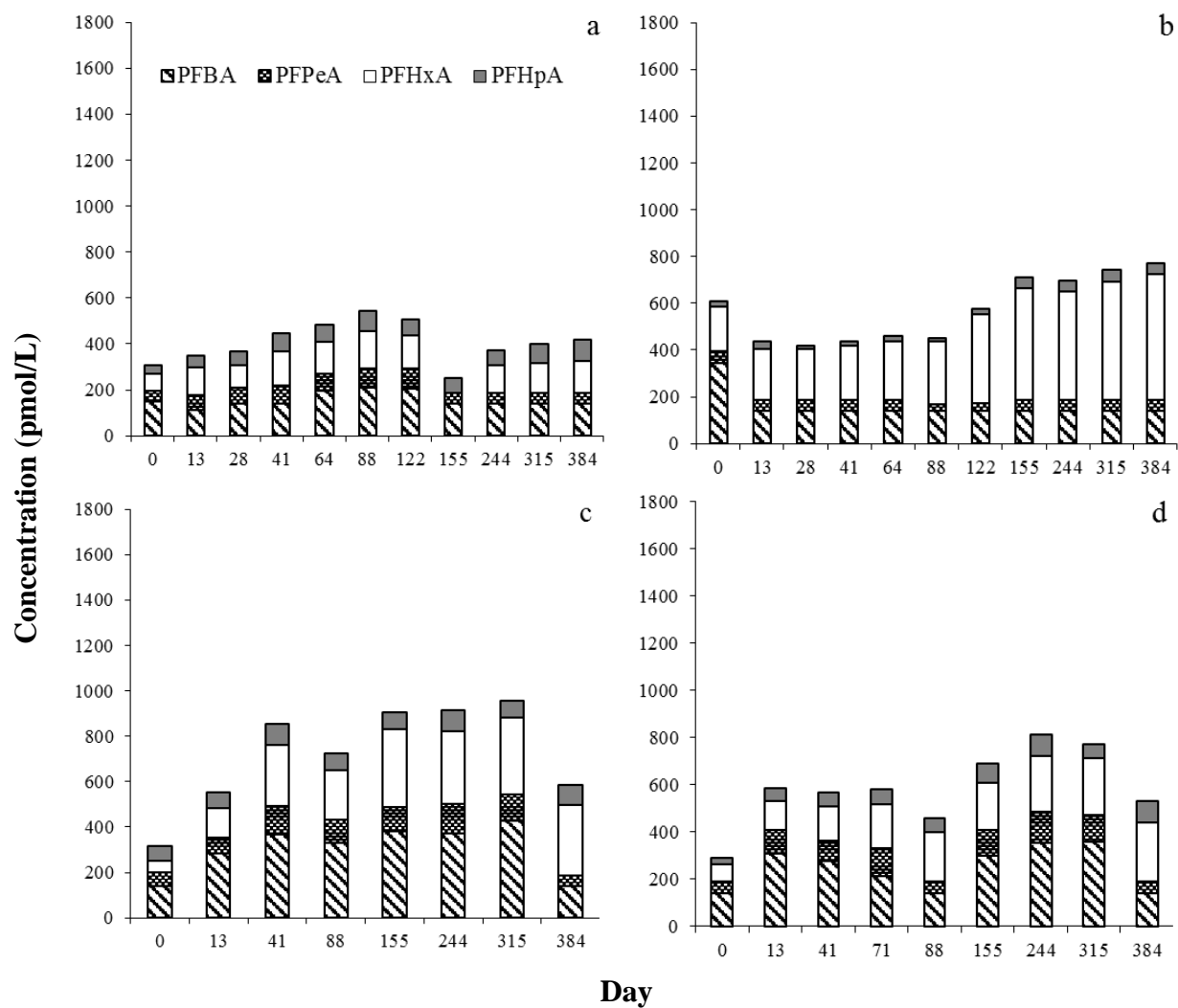


Figure S4. Concentrations of short chain PFCAs in August (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

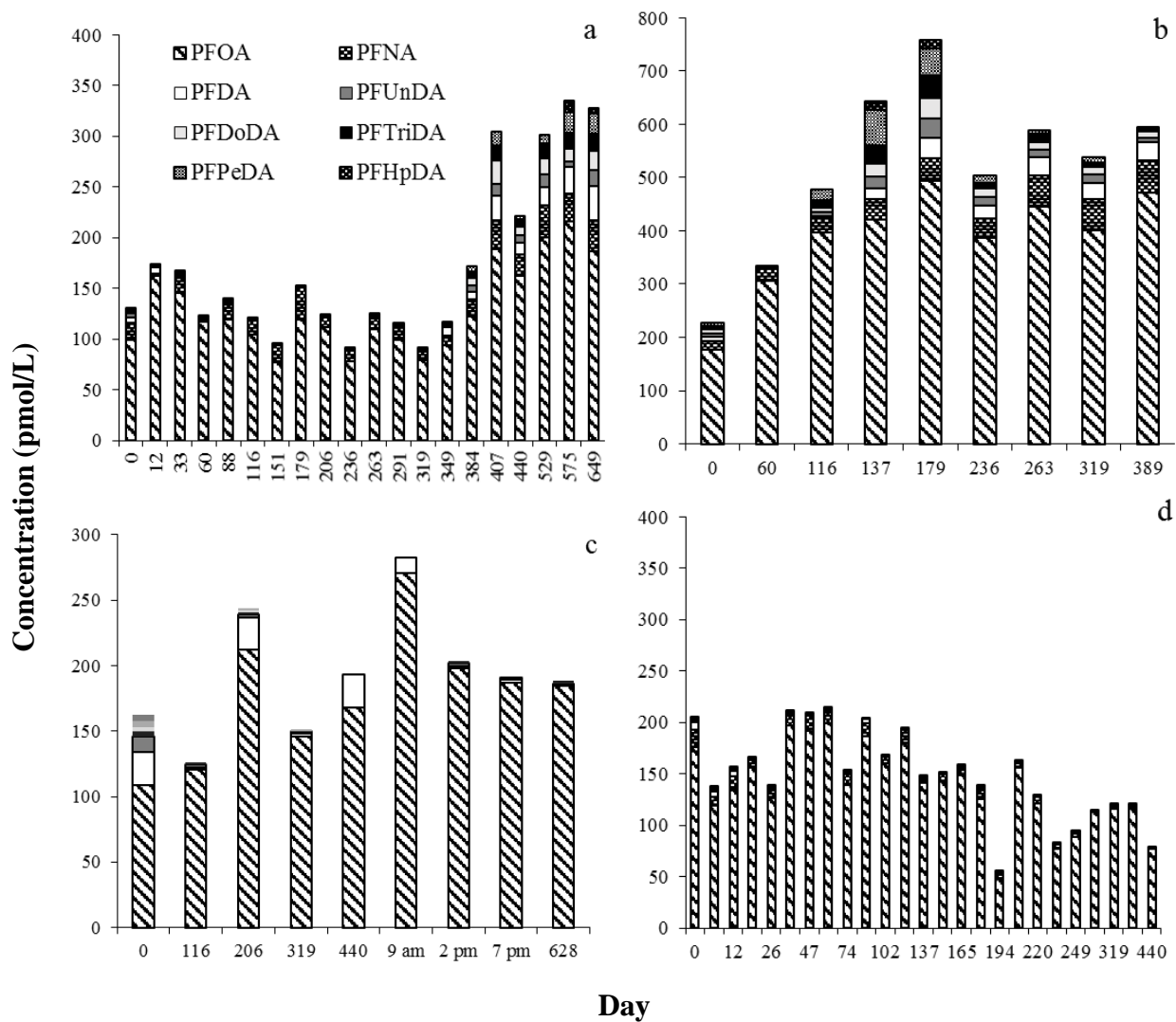


Figure S5. Concentrations of long chain PFCAs in November (a) live 1, (b) live 2 (c) abiotic 1 and (d) abiotic 2 during operation.

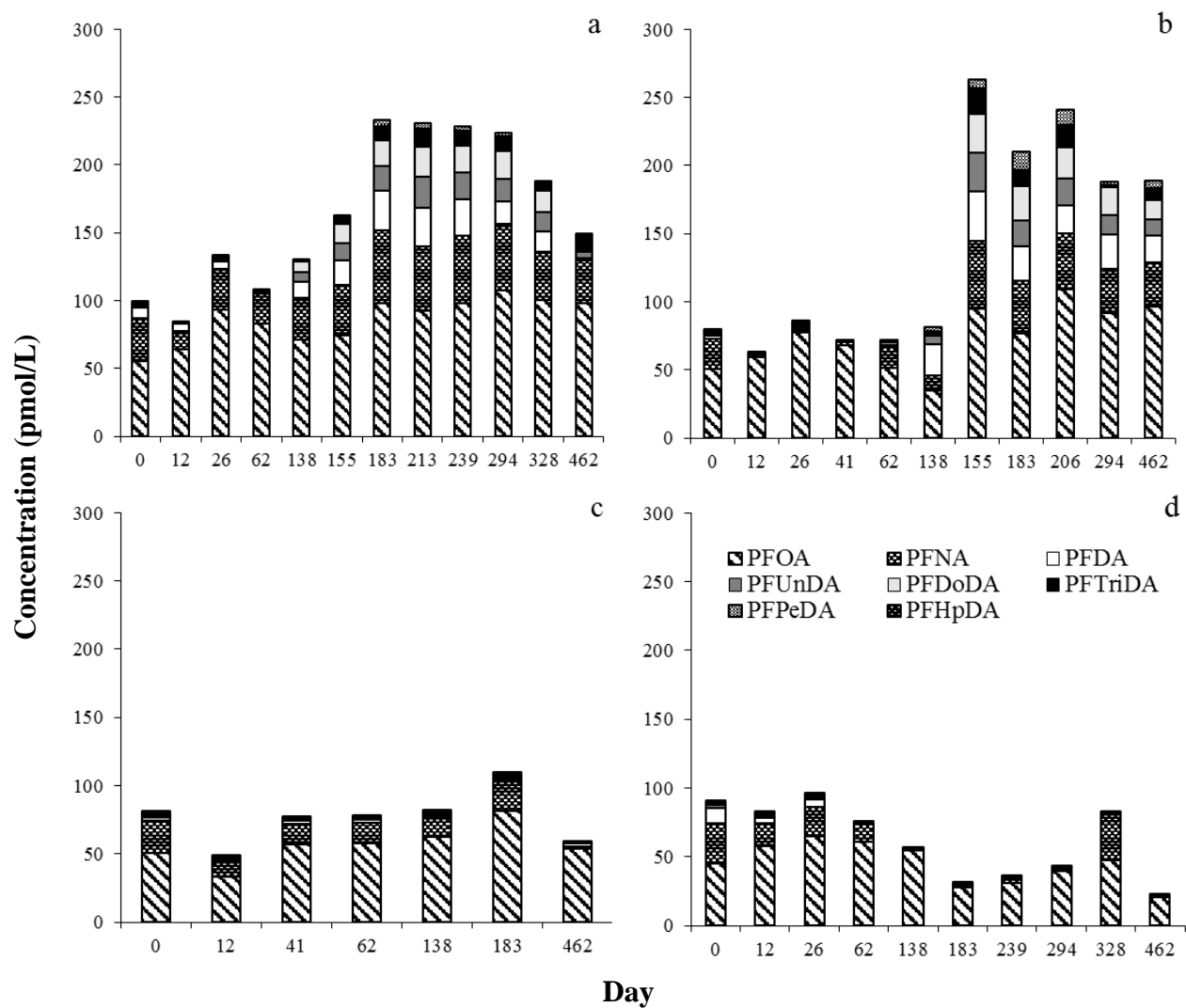


Figure S6. Concentrations of long chain PFCAs in May (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

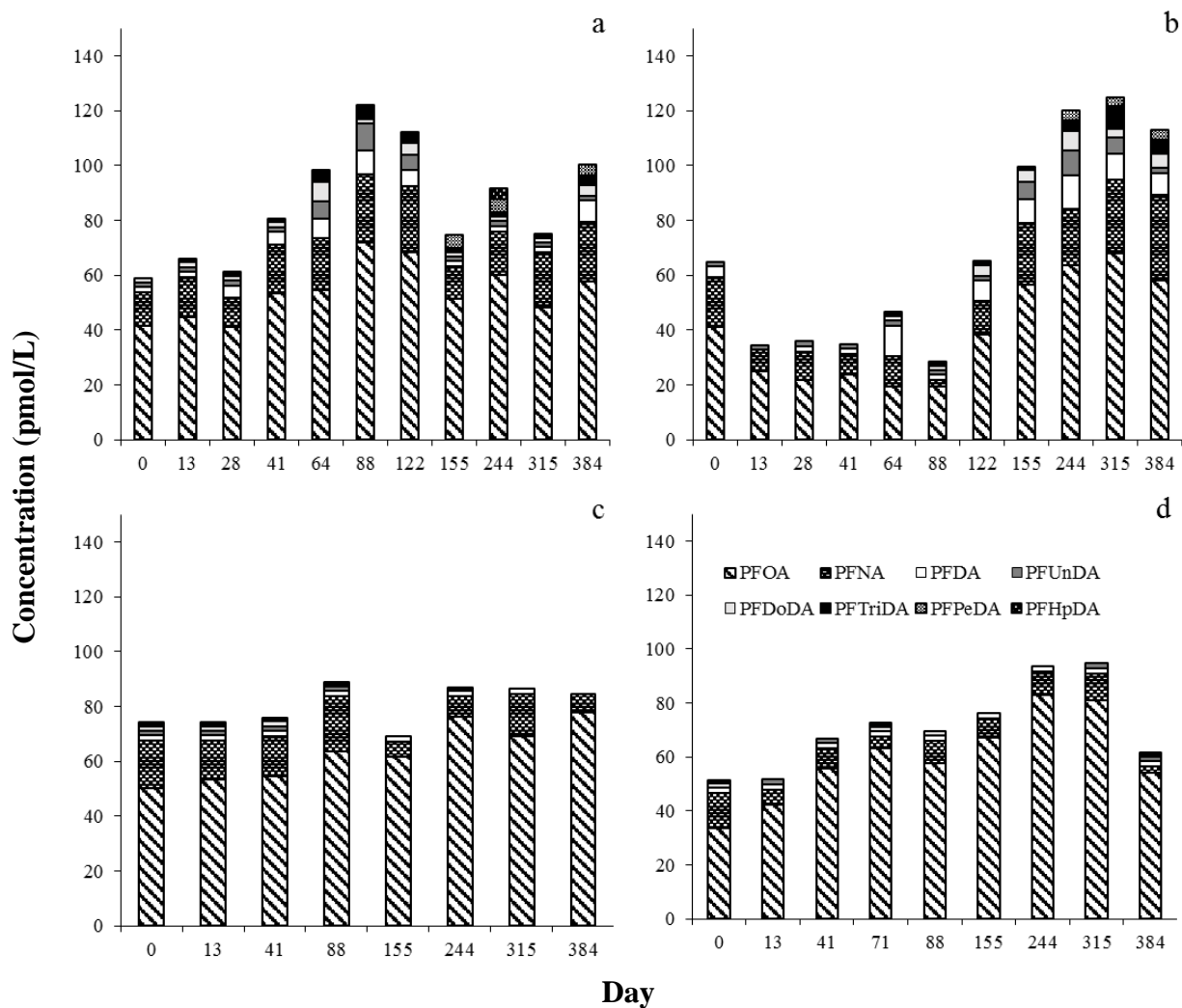


Figure S7. Concentrations of long chain PFCAs in August (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

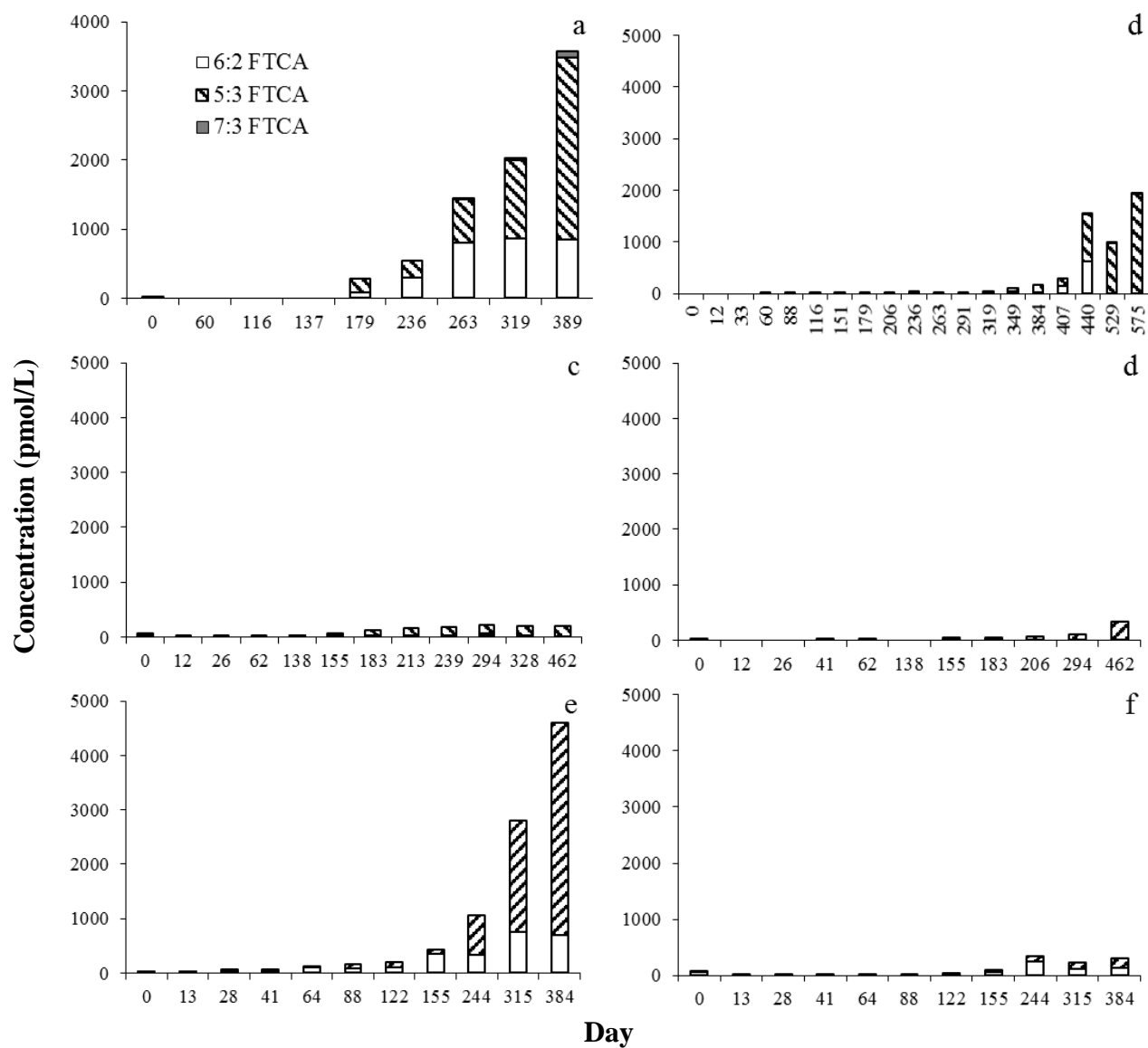


Figure S8. Concentrations of FTCAs in November (a) live 1 and (b) live 2, May (c) live 1 and (d) live 2, and August (e) live 1 and (f) live 2 during operation. Abiotic reactors were not shown as FTCA concentrations remained below 200 pmol/L during operation.

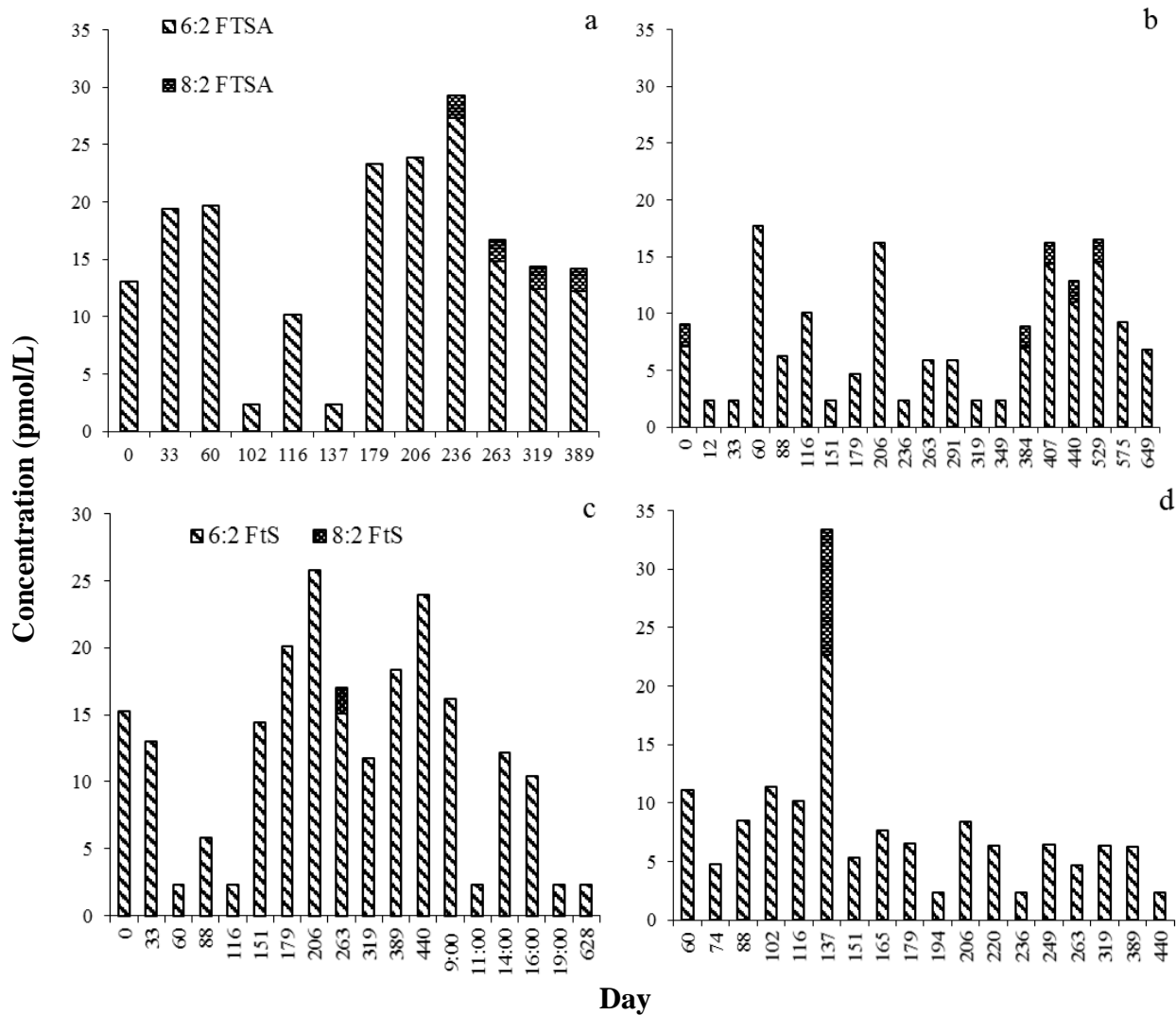


Figure S9. Concentrations of FTSA in November (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

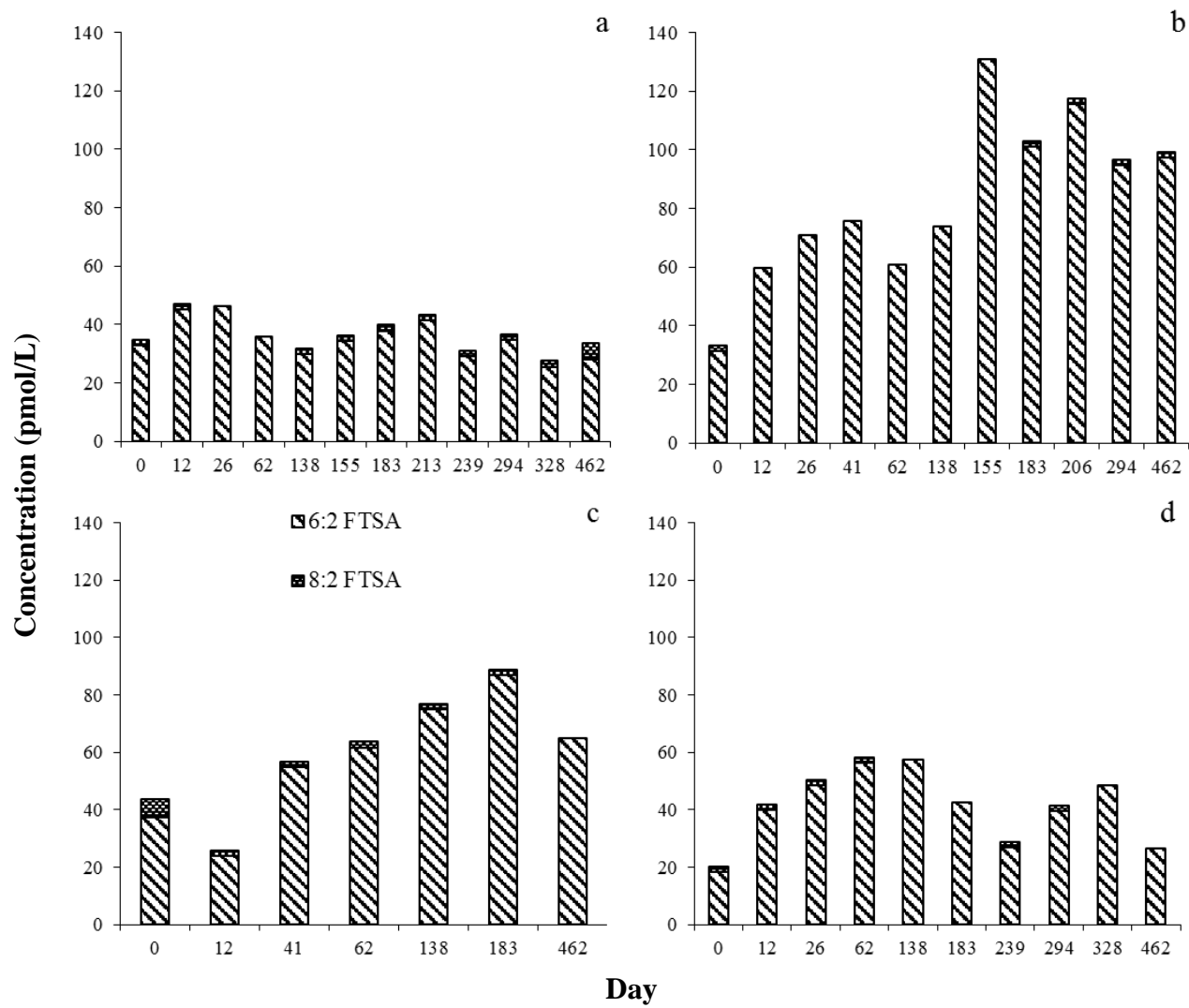


Figure S10. Concentrations of FTSA in May (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

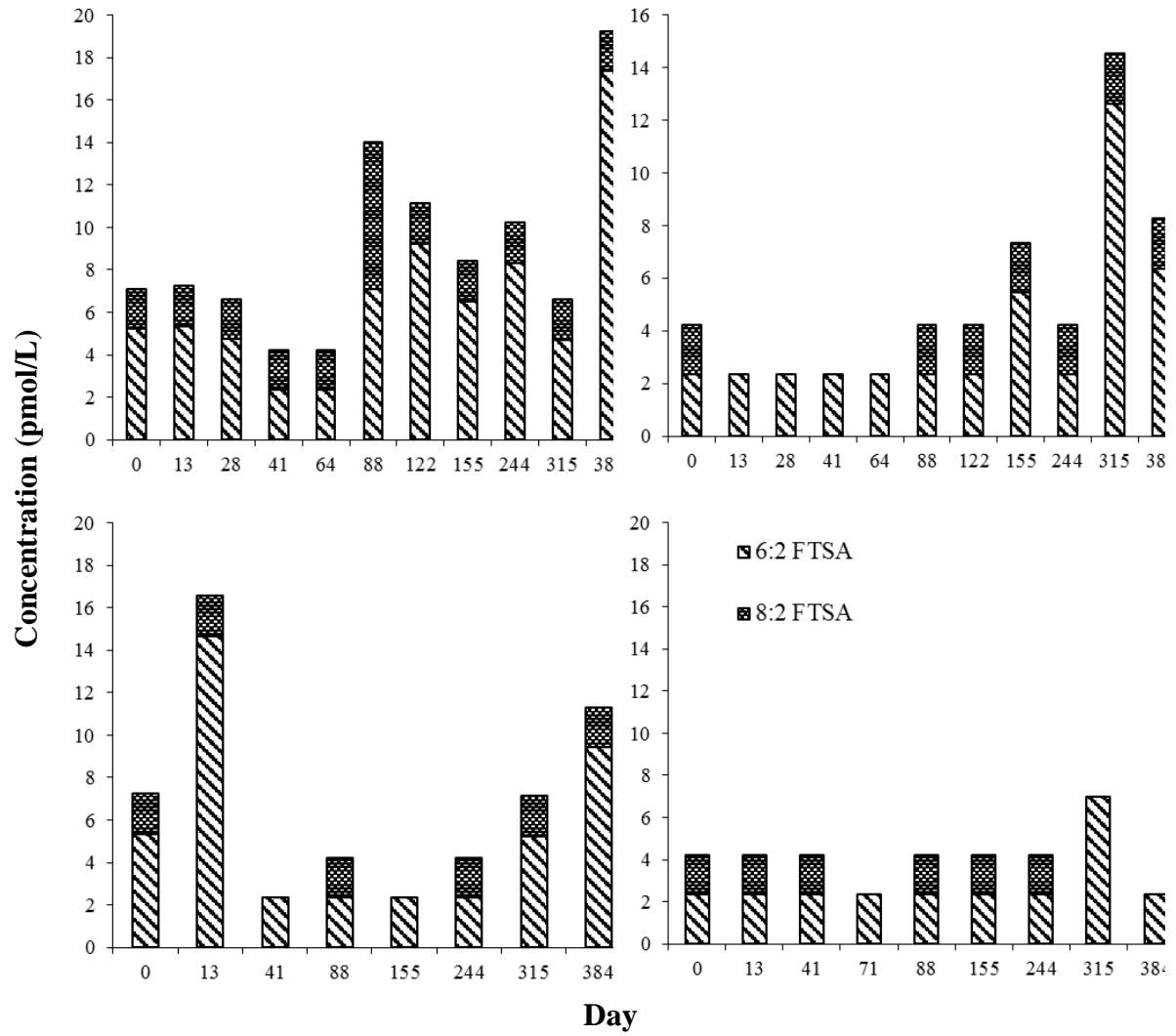


Figure S11. Concentrations of FTSAs in August (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

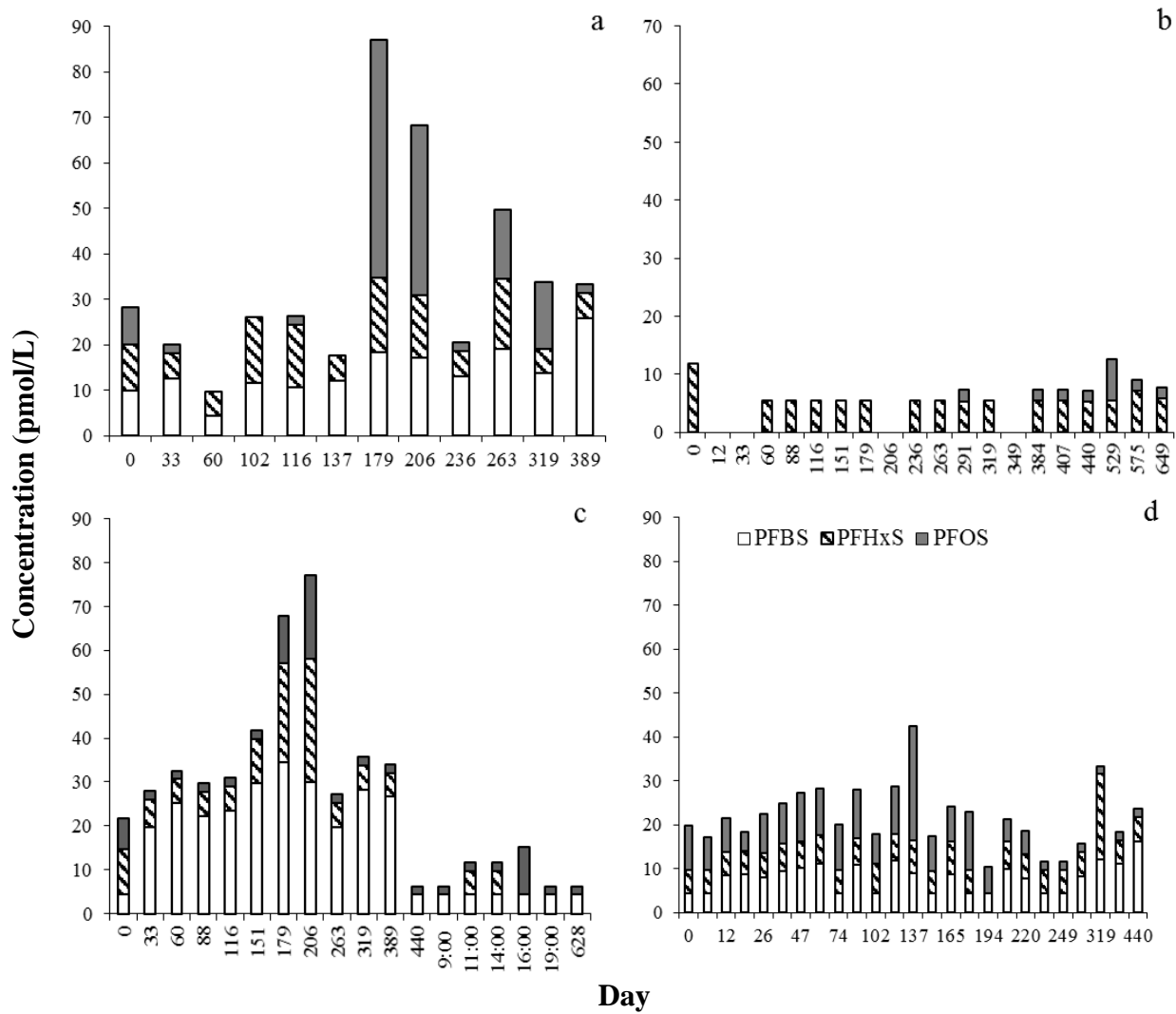


Figure S12. Concentrations of PFASs in November (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

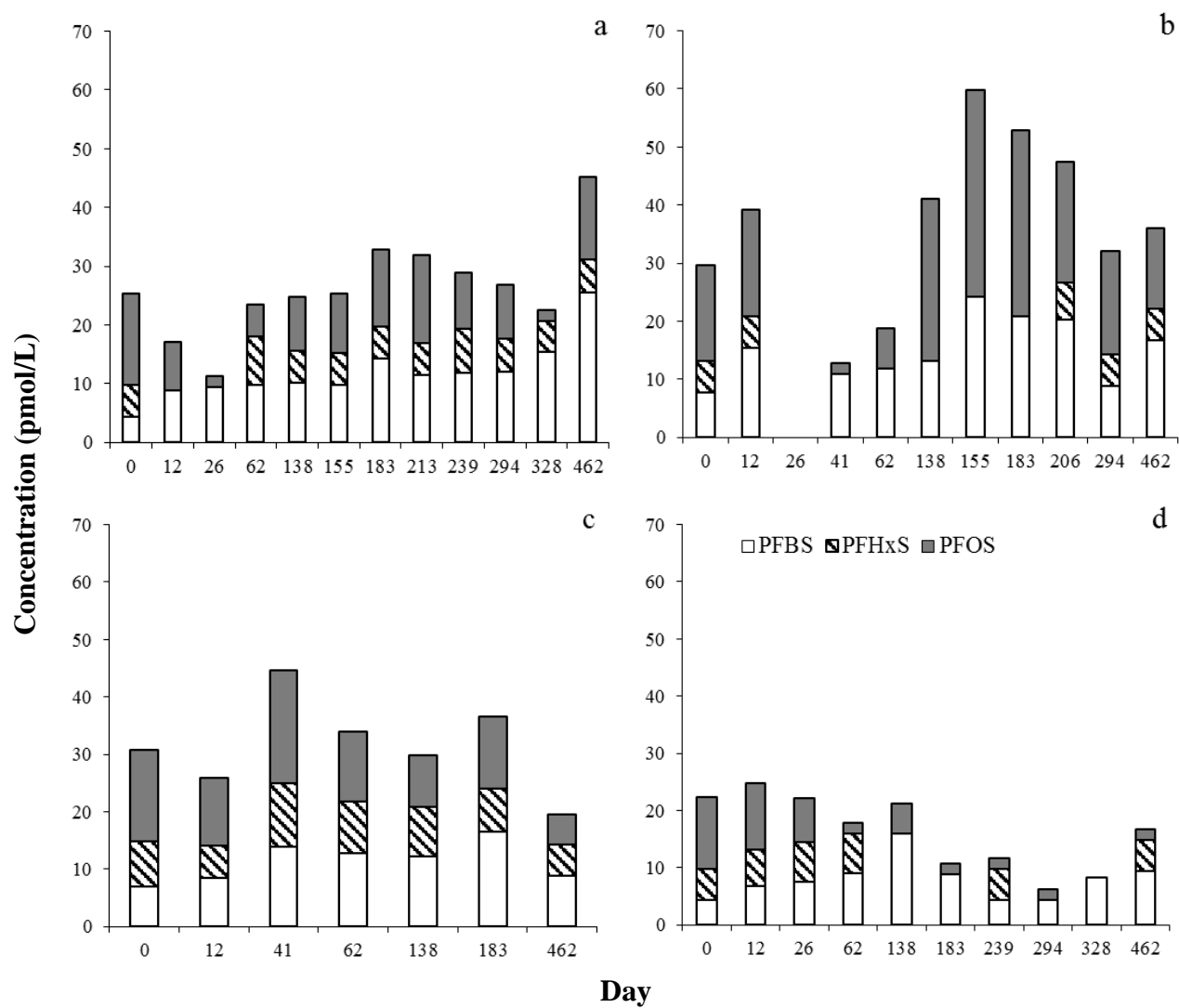


Figure S13. Concentrations of PFSA in May (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

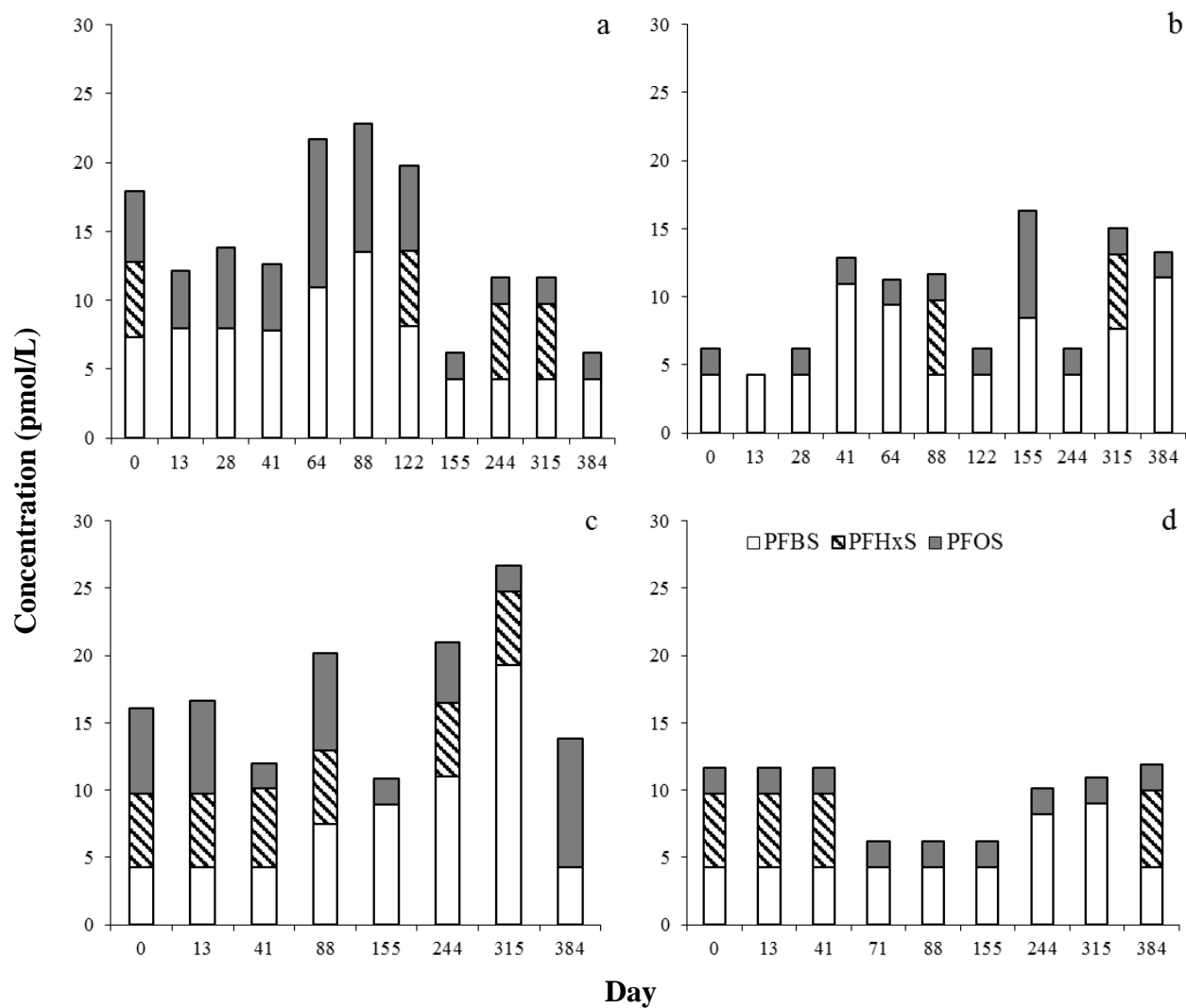


Figure S14. Concentrations of PFASs in August (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

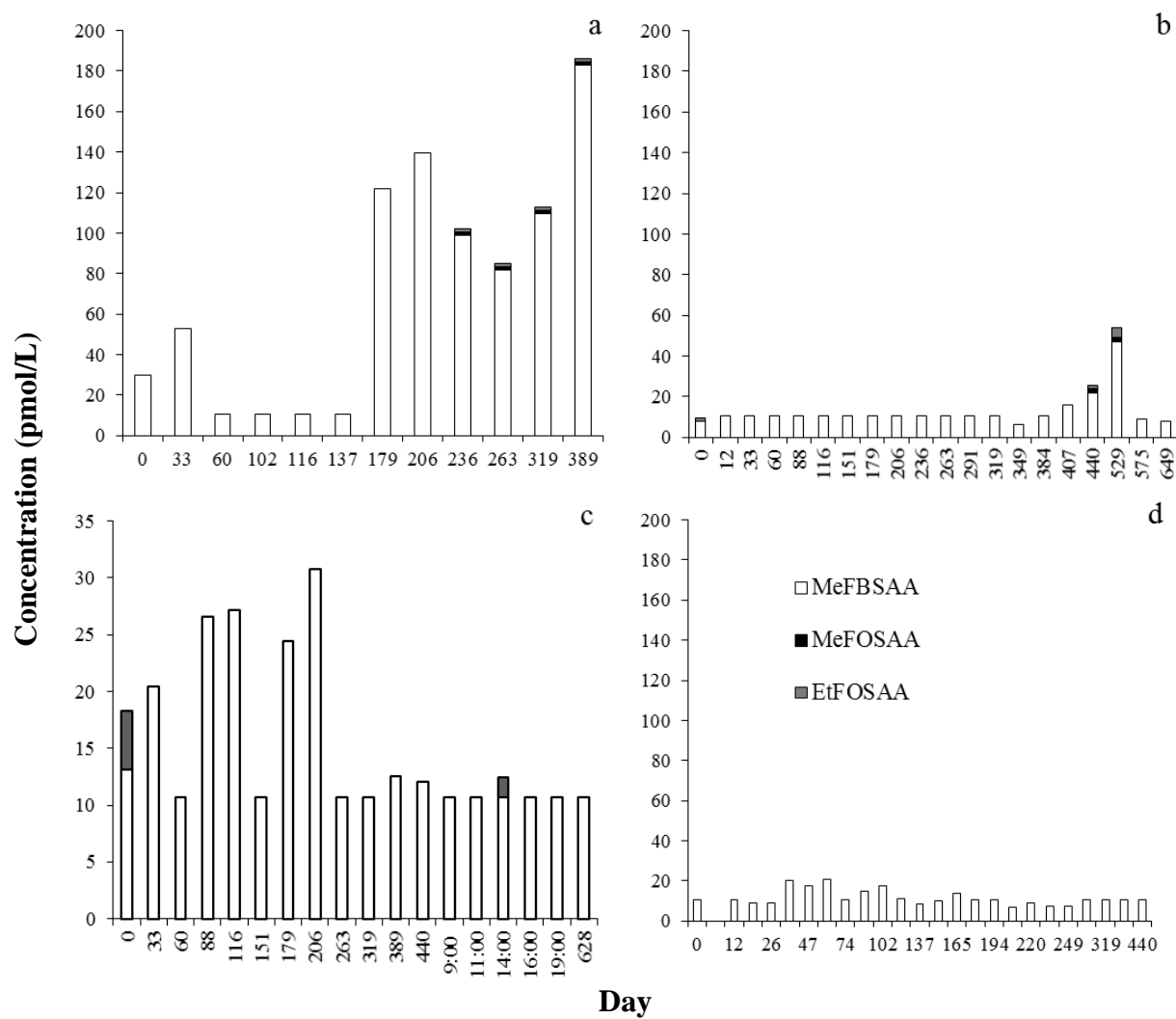


Figure S15. Concentrations of FASAs in November (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

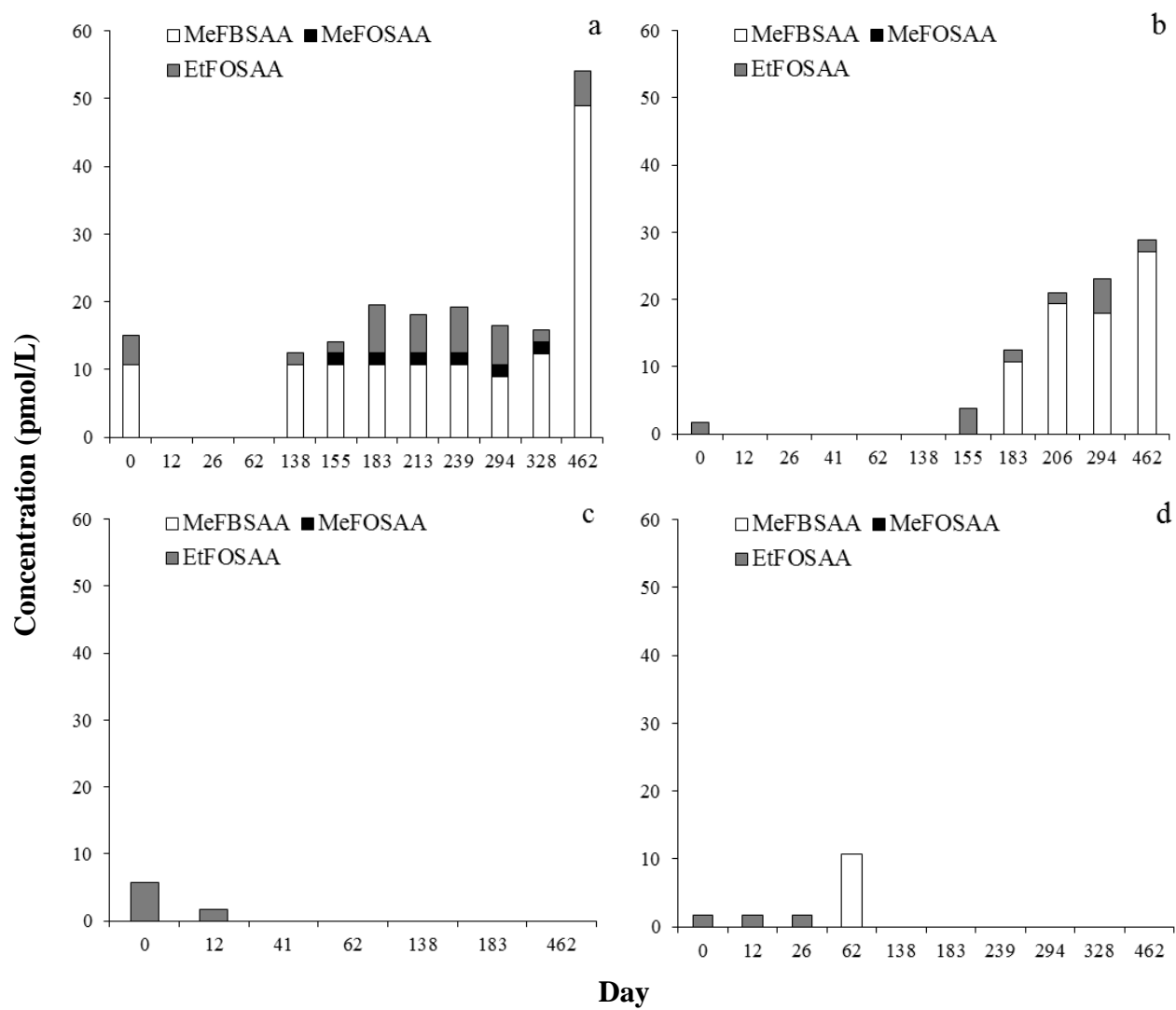


Figure S16. Concentrations of FASAA in May (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

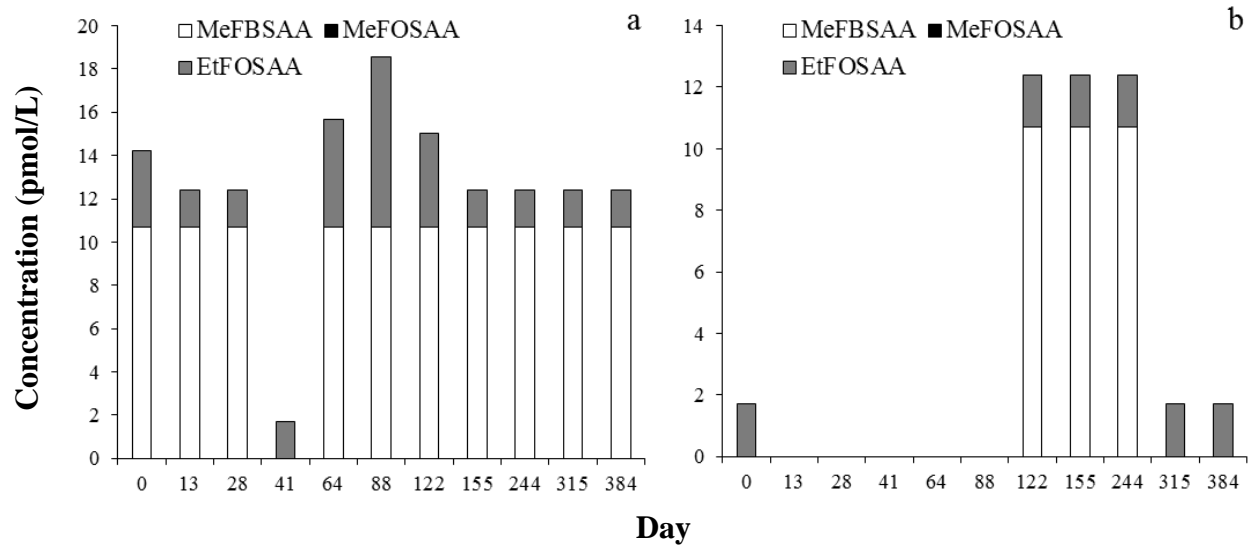


Figure S17. Concentrations of FASAA in August (a) live 1 and (b) live 2 during operation.

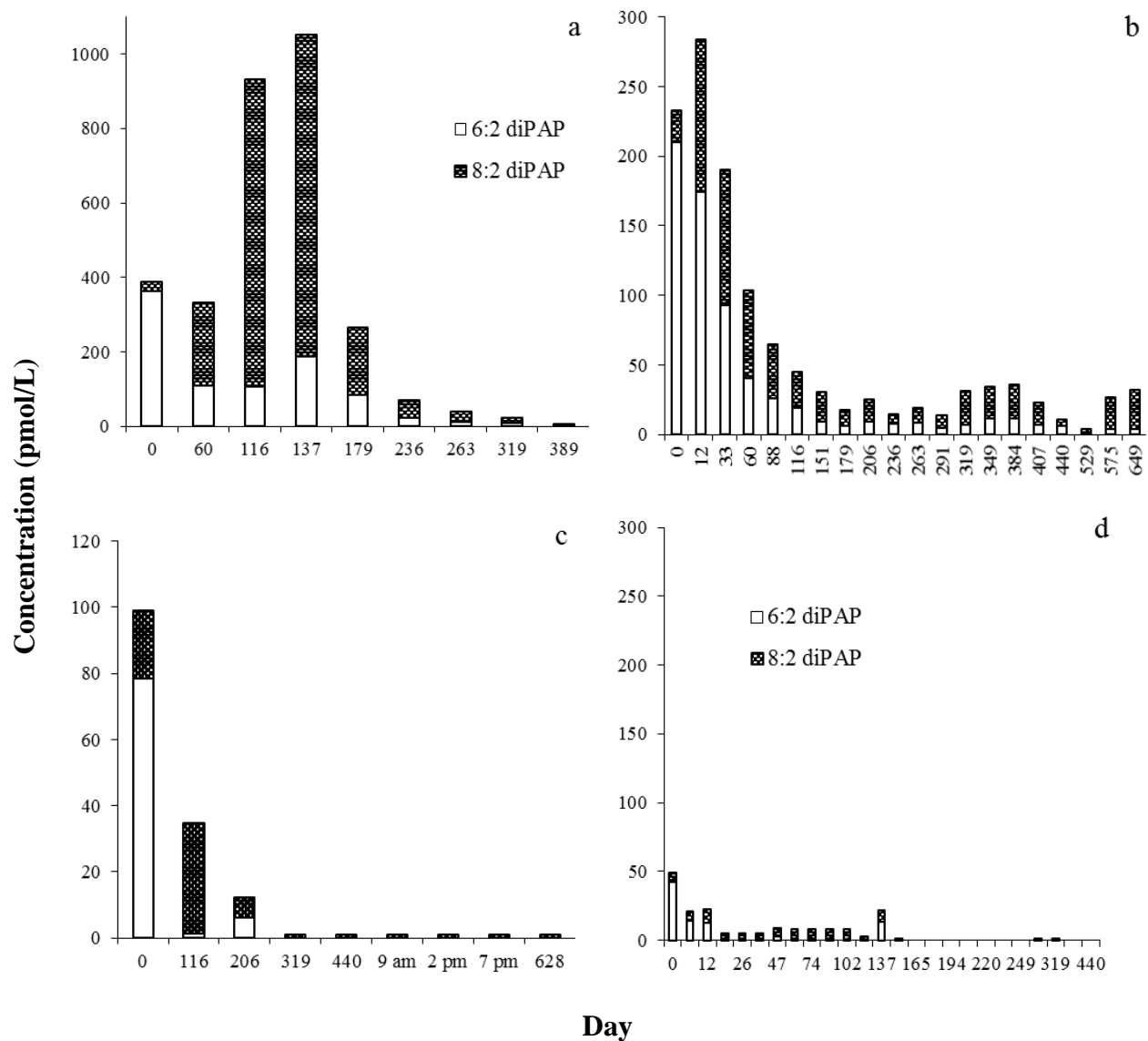


Figure S18. Concentrations of diPAPs in November (a) live 1, (b) live 2 (c) abiotic 1 and (d) abiotic 2 during operation.

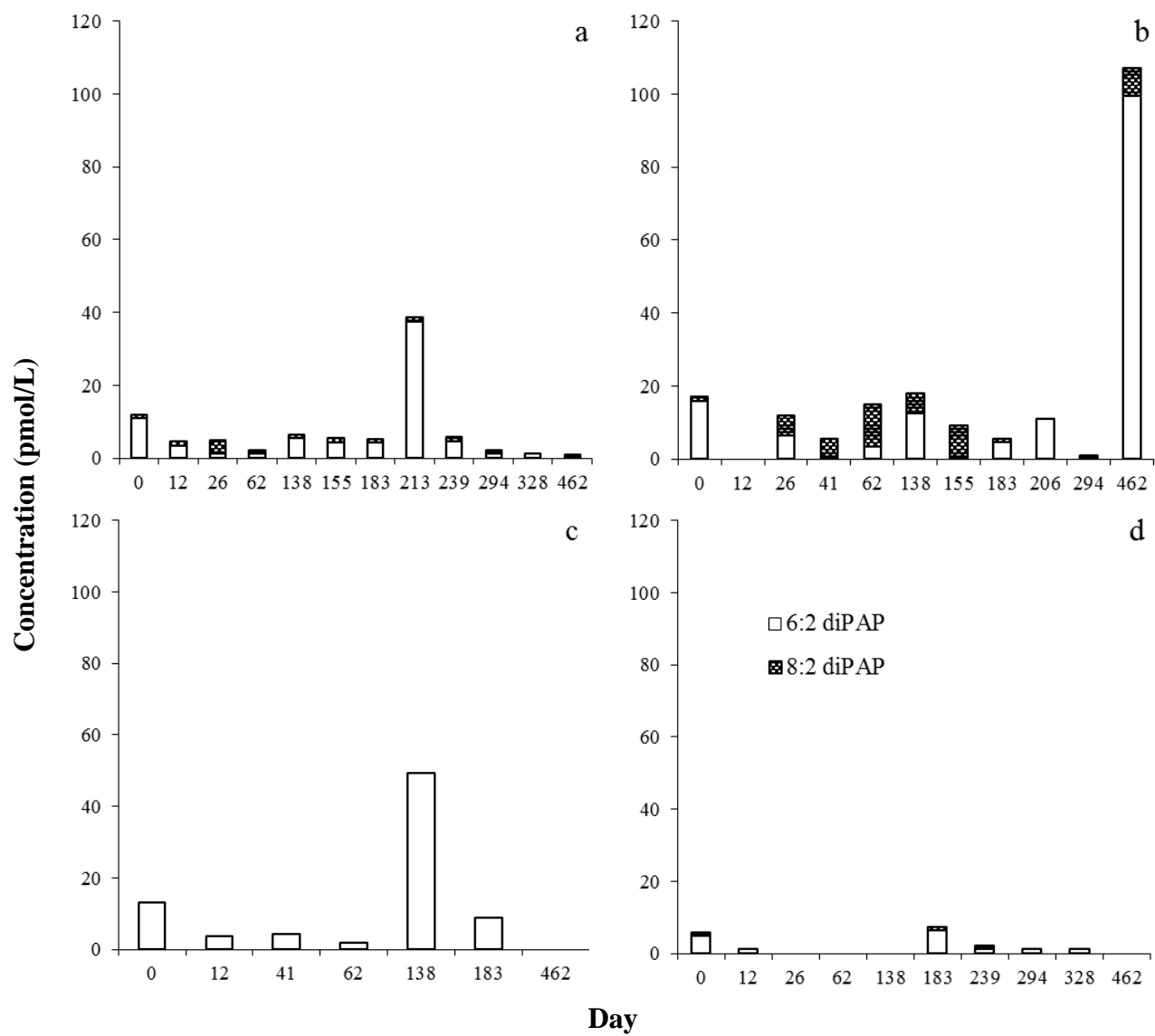


Figure S19. Concentrations of diPAPs in May (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

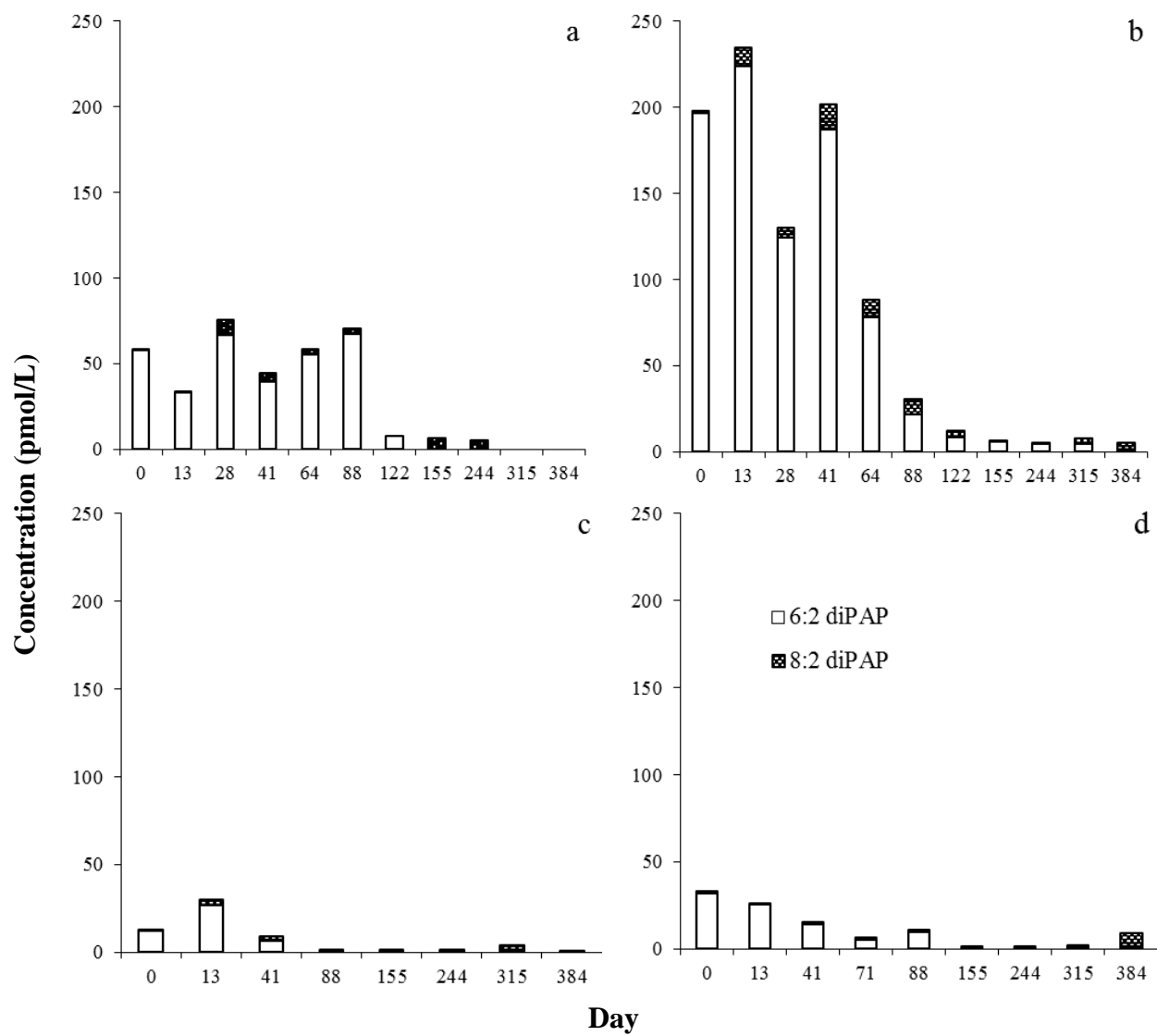


Figure S20. Concentrations of diPAPs in August (a) live 1, (b) live 2, (c) abiotic 1 and (d) abiotic 2 during operation.

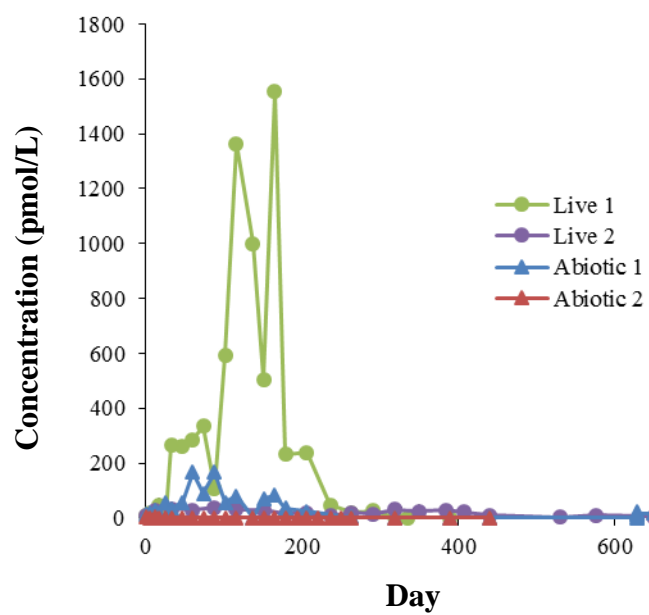


Figure S21. Concentrations of SAMPAPs in November reactors during operation.

Appendix D – Physical and biological release of poly- and perfluoroalkyl substances (PFASs) from municipal solid waste in anaerobic model landfill reactors.

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ABSTRACT

A wide variety of consumer products that are treated with poly- and perfluoroalkyl substances (PFASs) and related formulations are disposed in landfills. Landfill leachate has significant concentrations of PFASs and acts as secondary point sources to surface water. Here, we model how PFASs enter leachate using four lab-scale anaerobic bioreactors filled with municipal solid waste (MSW) and operated over 273 days. Duplicate reactors were monitored under live and abiotic conditions to evaluate influences attributable to biological activity. The biologically-active reactors simulated the methanogenic conditions that develop in all landfills, producing ~140 mL CH₄/dry g refuse. The average total PFAS leaching measured in live reactors (16.7 nmol/kg dry-refuse) was greater than the average for abiotic reactors (2.83 nmol/kg dry-refuse), indicating biological processes were primarily responsible for leaching. The low level leaching in the abiotic reactors was primarily due to PFCAs ≤C8 (2.48 nmol/kg dry-refuse). Concentrations of known biodegradation intermediates, including methylperfluorobutane sulfonamide acetic acid and the n:2 and n:3 fluorotelomer carboxylates, increased steadily in concentration after the onset of

methanogenesis, with the 5:3 fluorotelomer carboxylate becoming the single most concentrated PFAS observed in live reactors (9.53 nmol/kg dry-refuse).