



The unique distribution pattern of PFAS in landfill organics

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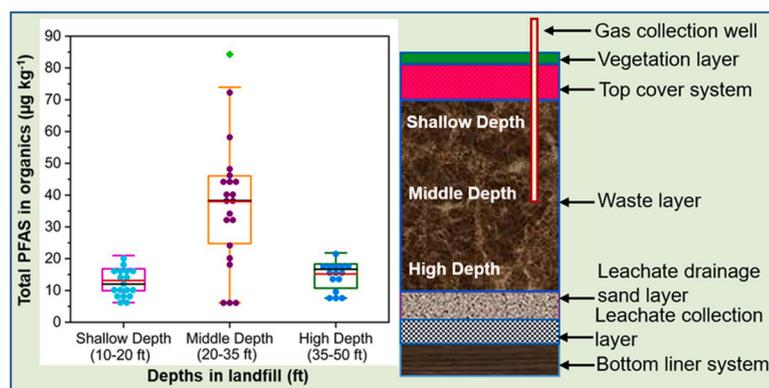
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HIGHLIGHTS

- PFAS concentrations were highest at mid-depths in the landfill.
- Dominant PFAS classes were per-fluorocarboxylic acids and fluorotelomer carboxylic acids.
- Short-chain PFCAs constituted a significant portion of total PFAS in landfill organics.
- Strong correlation between PFAS, total carbon, and dissolved organic matter observed.
- Study underscores the need for system-level analysis of PFAS fate in landfills.

GRAPHICAL ABSTRACT



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ABSTRACT

PFAS from degrading landfill waste partition into organic matter, leachate, and landfill gas. Driven by the limited understanding of PFAS distribution in landfill organics, we analyzed PFAS across various depths and seven spatially distinct locations within a municipal landfill. The measured PFAS concentrations in organics ranged from 6.71 to 73.06 µg kg⁻¹, a sum of twenty-nine PFAS from six classes. Perfluorocarboxylic acids (PFCAs) and fluorotelomer carboxylic acids (FTCAs) were the dominant classes, constituting 25–82 % and 8–40 % of total PFAS at different depths. PFBA was the most dominant PFCA with a concentration range of 0.90–37.91 µg kg⁻¹, while 5:3 FTCA was the most prevalent FTCA with a concentration of 0.26–17.99 µg kg⁻¹. A clear vertical distribution of PFAS was observed, with significantly greater PFAS concentrations at the middle depths (20–35 ft), compared to the shallow (10–20 ft) and high depths (35–50 ft). A strong positive correlation ($r > 0.50$) was

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noted between total PFAS, total carbon, and dissolved organic matter in landfill organics. Multivariate statistical analysis inferred common sources and transformations of PFAS within the landfill. This study underscores the importance of a system-level analysis of PFAS fate in landfills, considering waste variability, chemical properties, release mechanisms, and PFAS transformations.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have been extensively and indiscriminately used in everyday items and carelessly disposed of in municipal solid waste (MSW) landfills [1,2]. Studies reported PFAS in carpet and clothing [3,4], food packaging [5,6], industrial waste [7,8], and agricultural waste [9], and these wastes predominantly end up in landfills. In addition, MSW landfills receive wastewater sludge (i.e., biosolid) and compost (i.e., as landfill daily cover) that contain PFAS [10–12]. Waste in a typical landfill undergoes four decomposition phases: i) aerobic phase, ii) anaerobic acid phase, iii) initial methanogenic phase, and iv) stable methanogenic phase [13]. Biological and physicochemical parameters within landfills, such as temperature, pH, organic content, moisture levels, oxygen availability, and pressure, vary according to decomposition phases and landfill types [14,15]. During degradation, PFAS containing MSW releases PFAS into organics, leachate, and landfill gas [16–18]. Additionally, released PFAS precursors, such as fluorotelomer sulfonates and sulfonamides, transform into other PFAS (e.g., perfluoroalkyl acids) through different transformation pathways [3,8,19]. For instance, anaerobic biotransformation of 6:2 fluorotelomer alcohols (6:2 FTOH) and N-ethyl perfluorooctane sulfonamido ethanol (EtFOSE) into perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorobutane sulfonic acid (PFBS), and perfluorohexanoic acid (PFHxA) within a simulated landfill has been observed [20].

According to the latest U.S. EPA data, of the 146.1 million tons of landfilled MSW in 2018, more than 50 % was organic waste, dominantly constituted by food (24.1 %), paper and paperboard (11.8 %), wood (8.3 %), and yard trimmings (7.2 %) [21]. Once PFAS are released from PFAS-containing waste in landfills, they partition into organics, landfill gas, and landfill leachate [22]. For example, out of the 7.20 metric tons of total annual PFAS loading to US landfills, roughly 84 % stays within the landfill, while 5 % is released through landfill gas, and 11 % is discharged via leachate [23]. The partitioning of PFAS in landfills depends on many factors including the chemical characteristics of PFAS, the interaction of PFAS with organics, vapor pressure of PFAS that dictates partitioning in gas, solubility in landfill leachate, and the physicochemical (i.e., temperature, pH, moisture, and oxygen) and biological environments in landfills [22,24–28]. Although limited, some studies have focused on PFAS in landfill leachate and landfill gas. For instance, PFAS have been detected in leachate, providing evidence that PFAS are mobile under field conditions [29–33]. Studies reported PFBA (0.04–3.80 $\mu\text{g L}^{-1}$), PFPeA (0.06–6.90 $\mu\text{g L}^{-1}$), PFHxA (0.06–3.80 $\mu\text{g L}^{-1}$), PFHpA (0.08–6.0 $\mu\text{g L}^{-1}$), and PFOA (0.02–5.10 $\mu\text{g L}^{-1}$) in landfill leachate, with the total concentration of PFAS as high as 69 $\mu\text{g L}^{-1}$ [29–34]. In addition, previous studies reported that total semi-volatile fluorotelomer alcohols (FTOHs) ranged from 0.83 $\mu\text{g m}^{-3}$ to 4.90 $\mu\text{g m}^{-3}$ in landfill gas [63] and total PFAS ranged from 1.20 $\mu\text{g L}^{-1}$ to 22 $\mu\text{g L}^{-1}$ in gas condensate [34]. Despite landfill organics capturing the majority of PFAS, there is a surprising shortage of data regarding the occurrence and distribution of PFAS within landfill organics. Several studies have delved into the fate and transport of PFAS in soil, affected by factors including the land use patterns (e.g., biosolid application), yet none have specifically addressed PFAS in landfill organics [35–38]. Consequently, lacking data on PFAS in landfill organics would result in an incomplete understanding of their concentrations, distribution, and fate within landfills.

Given these challenges, we analyzed refuse samples from multiple depths and locations in an MSW landfill, marking the first exploration

into the occurrence and distribution of PFAS within landfill organics. We employed the draft EPA Method 1633 [39] targeting 40 different PFAS from seven classes in landfill organics. To comprehensively elucidate the fate and distribution of PFAS in landfill organics, we studied their chemical properties (i.e., chain length, precursor compounds, water solubility, and volatility), the depth of organic samples within the landfill, total and dissolved organic carbon, dissolved organic matter (DOM), and moisture content of the organics. DOM characterization was performed to elucidate the effect of DOM fractions on PFAS distribution in the landfill.

2. Materials and methods

2.1. Site description and sample collection

Landfill refuse was collected from a Colorado landfill in December 2021. The waste was collected from different depths and locations during the construction of gas wells (GW) in the landfill. Refuse sample was collected from seven gas wells (GWs 1–7) at depths ranging from 10 to 50 ft. The sampling depths were categorized into shallow depth (10–20 ft), middle depth (20–35 ft), and high depth (35–50 ft). From each depth, 3–5 kg refuse sample was collected. The refuse samples were comprised of plastics, wood, metal, cardboard, and a mixture of organics. The waste fractions were separated and stored at 4 °C in LC-MS-grade methanol-cleaned plastic zip-lock bags before analysis. A total of 57 organic samples, including triplicates at different depths across seven gas-wells were analyzed. The details of the gas well coordinates, boring depths, and waste collection depths are provided in Table S1.

2.2. PFAS extraction and analysis of landfill organics

Homogenized organic samples were sieved twice through a 1.5 mm pore-sized LC-MS grade methanol-washed aluminum sieve. Ten-gram of sample from each organic sample was taken in triplicates in pre-cleaned 50 mL polypropylene tubes. A mixture of mass-labeled PFAS extracted internal standard (MPFAC-HIF-ES, Wellington Laboratories, Guelph, ON, Canada) containing 24 compounds was diluted 40-fold and a 100 μL aliquot of this dilution was added to the sample and mixed (Table S2). After that, 10 mL LC-MS grade methanol (Fisher Scientific, USA) was added in each sample tube for extraction on a shaker (Thermo Scientific, MA, USA) at 200 rpm for 24 h, followed by room temperature centrifugation at 10,000 rpm for 2 h. After centrifugation, methanol was poured into pre-cleaned 10 mL polypropylene tubes and concentrated to 1 mL with a nitrogen blowdown evaporator. We also prepared procedural blank samples to assess background PFAS contamination during extraction (Text S1). The targeted analytes, extracted internal standards, and non-extracted internal standards were similar to the EPA draft method 1633, version 4 (Table S3).

Forty PFAS (demonstrated in the EPA draft method 1633, version 4 [39]) were targeted from seven PFAS classes. These include eleven perfluorocarboxylic acids (PFCAs), eight perfluorosulfonic acids (PFASAs), three fluorotelomer carboxylic acids (FTCAs), three fluorotelomer sulfonic acids (FTSs), seven perfluoroalkane sulfonyl fluorides (PASFs), five perfluoro ether carboxylic acids (PFECAs), and three perfluoro ether sulfonic acids (PFESAs) (Table S4). The PFAS were quantified using an ultra-performance liquid chromatograph (UPLC) coupled to a Triple Quadrupole mass spectrometer (Vanquish UPLC-Altis MS, Thermo Scientific, USA) in the negative electrospray ionization mode. UPLC separation was carried out using a Phenomenex Luna Omega C18

column (100 × 2.1 mm, 1.6 μm) following an already published protocol (Text S2, Table S5) [40,41]. The extraction recovery for the mass-labeled PFAS internal standards was 58–126 %, which fell within the EPA 1633 draft method's recommended limit [39]. PFAS concentrations were normalized by dividing it with the dry mass of landfill organics.

For the detailed characterization of organics, the 1.5 mm-sieved organics were extracted with ultrapure water following the ASTM D3987–12 protocol (Text S3) [42] and the DOM content of the extract was quantified as dissolved organic carbon (DOC) (Table S6). The UV 254 nm absorbance of the extracts were measured using a GENESYS 150 UV-Visible Spectrophotometer (Thermo Scientific, USA) and divided by the DOC value of each extract to calculate the specific UV absorbance (SUVA) (Text S4, Table S7) [43]. The three-dimensional excitation-emission matrix (EEM) spectroscopy was conducted for each extract using an FP-8350 Spectrofluorometer (Jasco Inc., Japan). The three-dimensional spectral data were collected for emission wavelengths ranging from 250 to 550 nm and excitation wavelengths ranging from 200 to 500 nm (Text S4, Table S8). The three-dimensional data were viewed as two-dimensional contour plots to elucidate different organic fractions in landfill DOM (Figs. S1–S3, Table S8). Moreover, the excitation and emission absorbance data were used to calculate the fluorescence index (FI), biological index (BIX), and humification index (HIX), to explain the DOM characteristics (Text S4, Table S7, and S9) [24,44]. Additionally, we measured the moisture content of the organic samples (Table S6). Furthermore, the total carbon, biodegradable carbon, and non-biodegradable carbon concentrations of the organic samples were measured using a Shimadzu TOC solid sample analyzer following a specific sample preparation protocol (Text S5, Table S6).

2.3. Statistical analysis

Statistical analysis and plotting were conducted using JMP Pro (version 17.2) and OriginPro (version 2023b, 10.05) software. Kruskal-Wallis one-way ANOVA analysis was conducted on the concentration of PFAS classes and total PFAS in landfill organics at different depths. A normality test (i.e., Shapiro-Wilk, Kurtosis, and Skewness) of the PFAS concentrations in landfill organics was performed to check the distribution (Table S10). PFAS concentration values in organics at different depths were log-transformed (Log-PFAS) to apply multivariate statistical analysis as the PFAS in organics were not normally distributed. Simple linear regression analysis was performed on PFAS classes to elucidate the correlation with moisture content, non-biodegradable carbon, total carbon, DOM, SUVA₂₅₄, and three-dimensional excitation-emission matrix indices of landfill DOM. Additionally, multiple linear regression analysis was performed to elucidate the impact of depth, moisture, and carbon content of landfill organics on PFAS distribution in the landfill. Furthermore, multivariate analyses such as Principal component analysis (PCA), Hierarchical cluster analysis (HCA), and Pearson correlation analysis were performed to test for the co-occurrence of different PFAS in the landfill. Regression analyses were considered significant at a significance level of $\alpha = 0.05$, and correlation analyses were considered significant when the correlation coefficient (r) exceeded 0.5 [45,46]. Details on statistical analyses are provided in Text S6. After an extensive literature search, we critically summarized the vapor pressure, Log-K_{oc}, and water solubility values of the commonly reported PFAS to aid in discussing our findings (Figs. S4–S6).

3. Results and discussion

3.1. PFAAs and FTCAs dominate the total PFAS in landfill organics

Total PFAS concentration in landfill organics ranged from 6.71–73.06 μg kg⁻¹ (Fig. S7). Twenty-nine analytes, out of the forty targeted PFAS, from six PFAS classes (except PFESAs) were detected in landfill organics. No significant difference was observed in the

concentrations of the total PFAS and different PFAS classes at same depths when compared among seven gas wells (Table S11). The total PFAS in landfill organics is comparable to the total PFAS reported in other PFAS-contaminated solid mediums including biosolids (2–182 μg kg⁻¹) [12,47], municipal organic compost (8.6–70.8 μg kg⁻¹) [9], and yard waste compost (16–20 μg kg⁻¹) [48]. Notably, 25–82 % of the total PFAS were contributed by PFCAs, 8–40 % by FTCAs, and 2–29 % by PFSAs across the gas wells (Fig. S7). In landfill organics, short-chain PFCAs (C ≤ 7), such as perfluorobutanoic acid (PFBA: 0.90–37.91 μg kg⁻¹), perfluoropentanoic acid (PFPeA: 0.11–2.31 μg kg⁻¹), perfluorohexanoic acid (PFHxA: 0.13–2.95 μg kg⁻¹), and perfluoroheptanoic acid (PFHpA: 0.03–1.29 μg kg⁻¹) were dominant (Fig. 1). Short-chain PFCAs constituted 29.2–72.4 % of total PFAS in landfill organics (Fig. 1 and Fig. S7). Despite the phasing out of PFOA in the USA from 2002, we detected 0.07–3.65 μg kg⁻¹ PFOA in landfill organics (Fig. 1). Of the sulfonate PFAS, perfluorobutane sulfonic acid (PFBS) concentration ranged from 0.08–0.41 μg kg⁻¹, linear perfluorohexane sulfonic acid (L. PFHxS) from 0.03–0.86 μg kg⁻¹, branched perfluorohexane sulfonic acid (B. PFHxS) from 0.01–0.77 μg kg⁻¹, and PFOS from 0.11–5.20 μg kg⁻¹ in landfill organics (Fig. 1).

High concentrations of PFAA precursors, including FTCAs and FTSs, were detected in landfill organics (Fig. 1). The dominant FTCA in organics was 5:3 FTCA: 0.26–17.99 μg kg⁻¹ and the dominant FTS was 6:2 FTS: 0.05–4.88 μg kg⁻¹. Precursor PFAS, such as FTCAs and FTSs, can transform into both short and long-chain PFAAs, including PFOS and PFOA, in anaerobic conditions commonly found in landfills [49–51]. Thus, a fraction of the detected PFAAs in landfill organics could have transformed from the precursors. Accordingly, a study reported that leachate from aged waste contained lower concentrations of precursor PFAS such as FTCA and FOSAA compared to young waste, suggesting the transformation of these precursors [30]. Our finding on dominant PFAS classes in landfill organics is similar to studies on dominant PFAS classes in leachate. For instance, of the annual release of 563 to 638 kg PFAS to WWTPs from US landfills, PFCAs accounted for the majority (291 kg yr⁻¹), closely followed by FTCAs (285 kg yr⁻¹), with lower releases of PFSAs and their precursors (84 kg yr⁻¹) [52]. The abundance of PFCAs and FTCAs in landfills can be attributed to their extensive application in non-stick cookware, water-resistant coatings, textiles, and carpets, resulting in their release in landfill organics [8].

3.2. Accumulation of PFAS at mid-depths in the landfill

The total PFAS concentration in landfill organics varied significantly with depth, peaking at the middle depth (20–35 ft) with 28.10–73.06 μg kg⁻¹, compared to 7.24–16.92 μg kg⁻¹ at shallow (10–20 ft) and 6.71–19.55 μg kg⁻¹ at high (35–50 ft) depths (Fig. 2, Table S12). The median total PFAS at middle depth was 36.97 μg kg⁻¹, about 2.5 times greater than at shallow and high depths (Fig. 2). Individual PFAS classes (PFCAs, PFSAs, FTCAs, PASFs) followed the similar distribution pattern (Fig. 2, Tables S13–S16). For instance, the median concentration of PFCAs was 21.83 μg kg⁻¹ at middle depth, compared to 7.22 μg kg⁻¹ at shallow and 5.03 μg kg⁻¹ at high depths (Fig. 2). Lower PFAS concentrations at high depths might result from complete PFAS release and transport via leachate, consistent with findings that older waste leachate has lower PFAS levels [10]. In addition to moisture-driven descent, degradation of PFAS can reduce their levels in aged waste situated at greater depths. The lower PFAS concentration at shallow depths is likely due to minimal release from less decomposed waste. In contrast, elevated PFAS levels at mid-depths suggest sufficient waste degradation for PFAS release, without significant downward moisture movement.

The relative distribution analysis confirmed that PFCAs and FTCAs are the most dominant PFAS at varying depths in the landfill (Fig. 3, Figs. S8–S9). The dominant short-chain PFCA, PFBA contributed 78–92 % of the total PFCA at middle depth with a concentration of 12.0–37.91 μg kg⁻¹ (Figs. S10, S11). The dominant FTCA, 5:3 FTCA

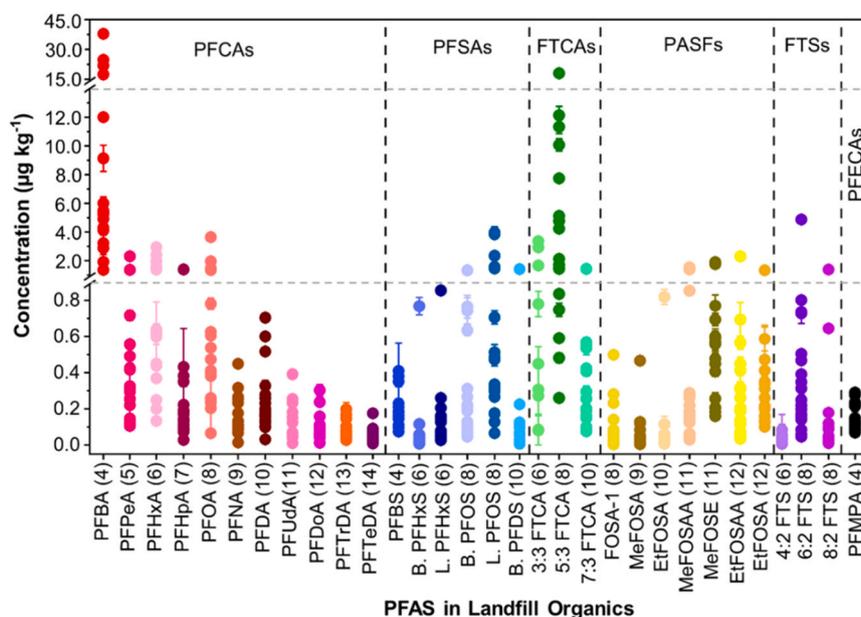


Fig. 1. Concentrations of twenty-nine PFAS in landfill organics collected during boring for gas well (GWs 1–7) construction. Twenty-nine PFAS spanned from six PFAS classes- perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSA), fluorotelomer carboxylic acids (FTCAs), perfluoroalkane sulfonyl fluorides (PASFs), fluorotelomer sulfonic acids (FTSs), and perfluoro ether carboxylic acids (PFECA)- were measured in organics. Only perfluoro-3-methoxy propanoic acid (PFMPA) was detected in the PFECA class. The mean and standard error for each compound were calculated from three measurements. The dotted horizontal lines denote the breaks on the Y-axis. Extended forms of the PFAS are available in Table S4.

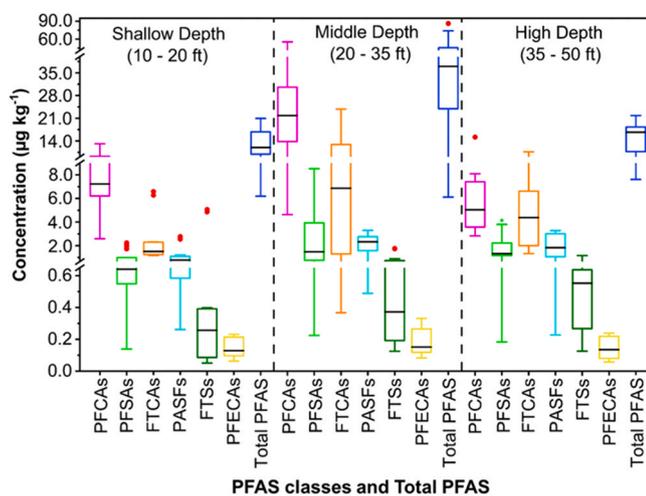


Fig. 2. Concentrations of six PFAS classes and total PFAS in organics at varying depths are represented as box-whisker plots. Six PFAS classes include perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSA), fluorotelomer carboxylic acids (FTCAs), perfluoroalkane sulfonyl fluorides (PASFs), fluorotelomer sulfonic acids (FTSs), and perfluoro ether carboxylic acids (PFECA). Shallow, middle, and high depths represent young, semi-aged, and aged waste, respectively. The box in each box-whisker plot represents the interquartile range and median, and the whisker extends to the lowest and highest values within 1.5 times the interquartile range from the quartiles.

contributed 19–98 % of the total FTCA at middle depth with a concentration of 1.50–17.99 $\mu\text{g kg}^{-1}$ (Figs. S10, S12). Linear PFOS was the dominant PFSA, contributing 19–80 % of total PFSA at varying depths (Figs. S10, S13). Precursor PFAS, PASFs constituted 2–11 %, 3–15 %, and 3–20 % at shallow, middle, and high depths in the landfill (Figs. S10, S14). The distribution of FTSs and PFECA remained similar at varying depths due to their low concentrations (Figs. S15 and Tables S17–S18). Unlike soil, landfill materials have greater porosity and release PFAS from within, resulting in unique PFAS distributions in

landfill. Previous studies reported that total PFAS concentrations decrease with soil depth, with long-chain PFAS ($\geq C7$) showing more hydrophobic interactions and short-chain PFAS ($\leq C6$) experiencing stronger electrostatic interactions [53–55]. The downward movement of short-chain PFAS is driven by their high water-solubility, while sulfonate PFAS, being more hydrophobic than carboxylates, demonstrate greater adsorption at shallow depths [56,57].

The volatility of PFAS can also impact the vertical distribution of PFAS in landfills. Our literature review demonstrated that short-chain PFCAs have greater vapor pressure than their long-chain counterparts (Fig. S4). Fluorotelomer sulfonates and sulfonamides are semi-volatile attributed to their molecular size and robust intermolecular forces, which constrain the process of evaporation [58,59]. Volatile PFAS can move within landfills with landfill gas and gas condensate, which can impact PFAS distribution in organics. Previous studies reported the presence of volatile 8:2 FTOH (3000 ng m^{-3}) and 10:2 FTOH (4900 ng m^{-3}) in landfill gas and gas condensate [22,60]. Although the volatility of PFAS can impact its distribution within a landfill, it is unlikely that volatile PFAS directly ends up in the atmosphere through the top liner system. For instance, a previous study reported 2500–26,000 $\text{pg m}^{-3} \sum \text{FTOH}$ in ambient landfill air of an active landfill compared to 70–100 $\text{pg m}^{-3} \sum \text{FTOH}$ in the ambient air of a closed landfill [28,61,62].

3.3. PFAS distribution as a function of carbon and DOM content

The concentrations of total PFAS, total precursor PFAS, total terminal PFAAs, PFSA, and FTCAs in landfill organics at the shallow, middle, and high depths were strongly positively correlated with the total carbon content (Fig. 4, Fig. S16 and Tables S19–S20). Along with total carbon, non-biodegradable carbon demonstrated a strong positive correlation with the total PFAS at varying depths (Fig. 4, Fig. S17 and Table S21). Additionally, FTCAs ($r = 0.48$), total precursor PFAS ($r = 0.46$), and total terminal PFAAs ($r = 0.43$) were positively correlated with the non-biodegradable carbon at varying depths (Fig. 4, Fig. S17 and Tables S21–S22). Interestingly, there was no significant positive correlation between biodegradable carbon content and either

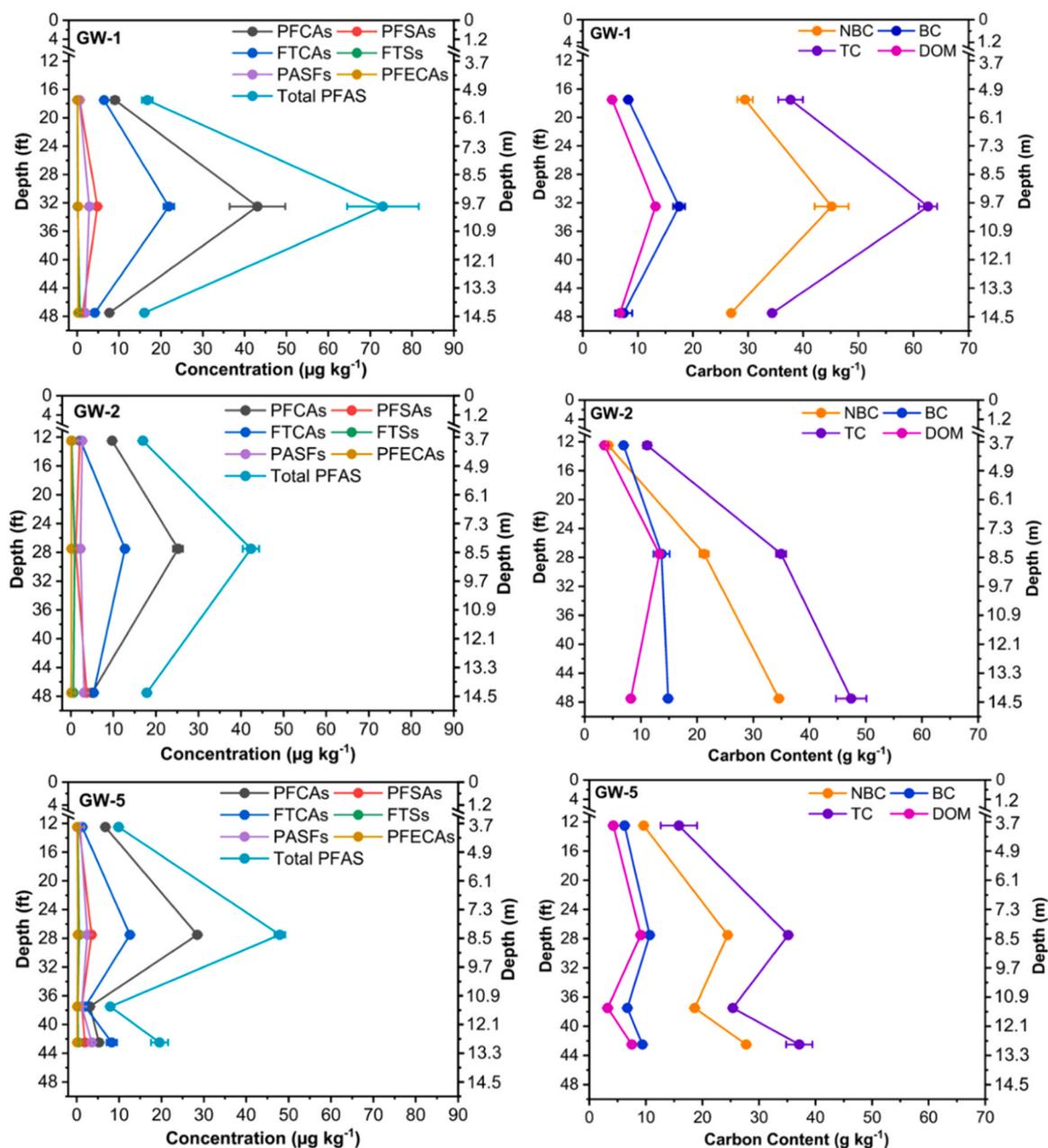


Fig. 3. Concentrations of different PFAS classes, total PFAS, total carbon (TC), dissolved organic matter (DOM), biodegradable carbon (BC), and non-biodegradable carbon (NBC), in landfill organics at different depths in gas wells (GWs) 1, 2, and 5. Similar information on GWs 3, 4, and 6 is available in Fig. S9. Six PFAS classes were perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), fluorotelomer carboxylic acids (FTCAs), perfluoroalkane sulfonyl fluorides (PASFs), fluorotelomer sulfonic acids (FTSs), and perfluoro ether carboxylic acids (PFECAs). The right Y-axis presents the gas well depths in meters (m). The mean and standard error of each parameter were calculated from three measurements. Extended forms of PFAS are available in Table S4.

total PFAS or various PFAS classes (Fig. 4 and Tables S23-S24). However, a strong positive correlation was observed between biodegradable carbon and total PFAS precursors ($r = 0.47$), as well as with FTCAs ($r = 0.42$) (Fig. 4). This suggests that the precursors in the biodegradable waste fraction have not yet transformed, which may take place as the waste degrades. Multiple linear regression analysis between Log-PFAS concentrations, total carbon, and non-biodegradable carbon demonstrated a significant impact of both on the distribution of PFAAs, FTCAs, and PASFs (Table S25). In contrast, these factors showed no impact on the distribution of FTSs and PFECAs, possibly because of no observable distribution patterns of these PFAS classes with depth (Table S25).

The total PFAS, total precursor PFAS, total terminal PFAAs, and the DOM content of the organics at different depths were significantly

correlated (Fig. 4, Fig. S16 and Tables S26-S27). Besides total PFAS, DOM demonstrated a strong positive correlation with PFCAs and FTCAs (Fig. 4 and Table S26). Landfill organics contained significantly greater DOM at mid-depth (5.8–13.3 g kg⁻¹), compared to shallow (3.6–5.3 g kg⁻¹) and high depth (3.2–8.2 g kg⁻¹) (Fig. 3, and Table S28). The elevated concentrations of PFOA (0.21–3.65 µg kg⁻¹) and PFOS (0.22–5.20 µg kg⁻¹) at the middle depths, coupled with high DOM levels, demonstrate the strong influence of DOM on these long-chain PFAS distributions (Fig. 3 and Figs. S18-S24). The concentration of these long-chain PFAS significantly decreased with the reduction in DOM at high depths (Figs. S18-S24). Long-chain PFAS exhibit high sorption coefficient (Log- K_{OC}), indicating a greater affinity for adsorption onto organic matter compared to short-chain PFAS (Fig. S5). Organic matter in solid media (e.g., soil, biosolids) strongly influences

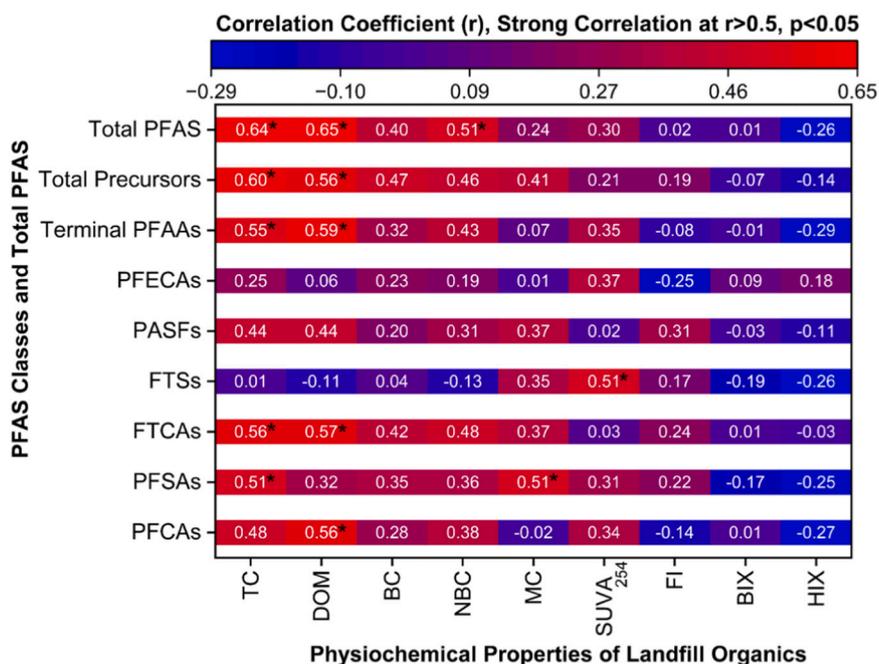


Fig. 4. Pearson correlation between the physiochemical properties of landfill organics and six PFAS classes, total PFAS, total precursor PFAS, and total terminal PFAAs, across distinct depths in the gas wells (GWs 1–7). The analysis employed simple linear regression, with significant correlations indicated by a red rectangle and the ‘*’ symbol at $\alpha = 0.05$. Nine physiochemical parameters, total carbon (TC), dissolved organic matter (DOM), biodegradable carbon (BC), non-biodegradable carbon (NBC), moisture content (MC), specific ultraviolet absorbance at 254 nm (SUVA₂₅₄), fluorescence index (FI), biological index (BIX), and humification index (HIX) were considered, for the linear regression analysis. Correlation coefficients (r) exceeding 0.5 were deemed significant. Extended forms of all PFAS classes are available in Table S4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PFAS distribution [56,63]. Soils with higher organic matter content can effectively adsorb PFAS, reducing their mobility, especially for long-chain PFAS, which are more hydrophobic. DOM can attract or repel PFAS depending on their charges [64]. When negatively charged DOM repels similarly charged anionic PFAS, cations can bridge the gap, linking PFAS and DOM [65]. This complex formation significantly affects the behavior and movement of shorter-chain, more hydrophilic PFAS. The high concentrations of short-chain PFAS observed at mid-depth in this study could be driven by cation-induced complexation with DOM and subsequent movement with DOM. In the complex landfill environment, the interactions between PFAS and DOM can also be influenced by the pH of the organics [56]. The pH of landfill organics ranged from 7.35 to 8.12 (Table S6), indicating alkaline conditions that promote DOM leaching and reduce its sorption capacity [66]. Consequently, the leaching of anionic PFAS from landfill organics can be enhanced under these alkaline conditions.

DOM in landfill organics mainly consists of protein-like substances, with higher fluorescence intensity than humic and fulvic-like substances (Figs. S1-S3 and Table S8). Protein-like substance intensity was higher at middle (800–4600 au) and high depths (800–5250 au) compared to shallow depths (800–3800 au), indicating more aromatic regions at these depths (Figs. S1-S3 and Table S8) [44]. Proteinophilic PFAS, like PFAAs, are more likely to bind with proteins than other DOM fractions (e.g., humic and fulvic components) [67,68]. Furthermore, the high humification index (HIX > 0.8), fluorescence index (FI > 1.8), and SUVA₂₅₄ values (> 2 L mg⁻¹ m⁻¹) of landfill DOM at various depths suggest that a major portion of landfill organics are hydrophobic and contains aromatic substances (Fig. S25, Tables S7 and S9) [24]. Besides, landfill organics were rich in biological components at different depths (biological index, BIX > 0.7) (Fig. S25, Tables S7 and S9) [69]. These indices showed no distinct pattern or significant differences with depth (Tables S29-S32). Consequently, total PFAS, total precursors, total terminal PFAAs, and PFAS classes did not significantly correlate with these indices (Fig. 4, Tables S33-S40). This suggests that individual characteristics of landfill DOM may not significantly impact PFAS distribution;

rather, it is the combined characteristics of landfill DOM under varying environmental conditions that likely influence PFAS distribution. For instance, a study reported that at pH < 5, electrostatic attraction and hydrogen bonding significantly influence the sorption of PFASs on humic substances, while at pH 5–8, aliphaticity-induced hydrophobic interactions control their adsorption [70].

3.4. PFAS distribution as a function of moisture content

The multiple linear regression analysis exploring the relationship between Log-PFAS, depth, and moisture content in landfill organics showed that depth and moisture together had a negligible impact on PFAS distribution (Table S25). This might be due to the differing patterns of PFAS and moisture distribution at various depths. Significant variations were observed in the moisture content of landfill organics at different depths (Table S41), with percentages ranging from 9.2–14.9 % at shallow depths, 11.8–20.8 % at middle depths, and 19.3–23.1 % at greater depths (Table S6). However, simple linear regression analysis of Log-PFAS across different classes, total PFAS, total precursors, total terminal PFAAs with moisture content indicated no significant correlations (Fig. 4, Fig. S17, and Tables S42-S43). Although moisture typically influences the fate and distribution of water-soluble PFAS (Fig. S6), this study’s landfill organics did not exhibit such a relationship. The complexity of PFAS release mechanisms from waste, diversity in waste age and composition, intricate moisture pathways within landfills, and the timing, intensity, and amount of precipitation likely contributed to this finding. Moisture begins percolating at the onset of waste degradation, whereas PFAS release is delayed. A previous study reported that the release of PFAS from carpets and clothing in a bioreactor landfill was high during the stable methanogenic phase spanning from 111 to 251 days [71]. Therefore, PFAS movement is significantly influenced by additional environmental moisture, like rainfall, seeping into the landfill. This is because the initial moisture in the waste dissipates prior to the release of PFAS from the waste materials. By analyzing PFAS concentrations in leachate from different cells of a landfill, a study

concluded that climate (i.e., rainfall) as opposed to internal processes within the landfill was responsible for variations in leachate PFAS concentrations [52].

The transport of PFAS is also influenced by their structural variations, such as isomers. Research indicates that linear PFAS isomers tend to adhere to organic medium, whereas branched isomers are more likely to undergo movement [72]. This difference is attributed to the greater polarity of branched isomers compared to their linear counterparts [72]. Although we measured both linear and branched PFHxS and PFOS in landfill organics, the effect of isomerism on the downward migration in landfill organics was not significant (Figs. S10, S18-S24).

3.5. Correlation analysis for PFAS source identification

Multivariate statistical analyses (i.e., Principal component analysis, Pearson correlation analysis, Hierarchical cluster analysis) of the analyzed PFAS infer common origins and transformation of precursor PFAS in the landfill. The first component (PC-1) of the PCA explained 54.23 % of the variability in the analyzed PFAS and the second component (PC-2) explained 16.22 % of the variability (Table S44 and

Fig. 5A). Particularly, the positive loadings of long-chain (i.e., PFOA, PFNA, and PFOS) and short-chain PFAS (i.e., PFPeA, PFHpA, and PFHxS) demonstrated a strong correlation in PC-1 (Table S45 and Fig. 5A). Similarly, Pearson correlation analysis demonstrated a significant correlation among short-chain PFAS (i.e., PFPeA, PFHxA, and PFHpA), indicating a common origin (Fig. 5B). Additionally, PFAA precursors (i.e., 8:2 FTS, MeFOSA, FOSA-1, and EtFOSA) were significantly correlated with the above-mentioned long and short-chain PFAS (Fig. 5A). These short-chain and long-chain PFAAs could be generated from the transformation of PFAA precursors, as indicated by the strong correlation (Fig. 5B). Short-chain PFAS such as PFBA, PFPeA, and PFHxA are commonly found in water-resistant coatings, metal plating, and sewage sludge [85,86]. Sewage sludge has been reported to contain long-chain PFAAs, such as 23.2–298 ng g⁻¹ PFOA and 27.6–173 ng g⁻¹ PFOS, as well [73,74].

Fluorotelomer carboxylates such as 5:3 FTCA and 7:3 FTCA demonstrated a strong correlation in PCA, indicating a shared origin (Fig. 5A). FTCAs are predominantly used in textiles and carpets and released in landfill organics and leachate as the waste degrades. For instance, 5:3 FTCA was detected in the leachate of a landfill bioreactor treating carpets [16]. Both 5:3 FTCA and 7:3 FTCA have been detected frequently in WWTP sludge [75]. Hierarchical cluster analysis of the PFAS in organics identified four distinct PFAS groups (Fig. S26). HCA infers that long-chain PFAS such as PFNA, PFDA, PFDS, PFTrDA, and PFTEdA are correlated and might have originated from the same source such as textiles, carpets, surface coating, and paints [76]. Additionally, short-chain PFAS (i.e., PFBA, PFBS, PFMPA, and PFHxA) were correlated with the PFAA precursors such as 3:3 FTCA, 7:3 FTCA, and EtFOSA (Fig. S26). Previous studies observed a similar correlation among PFAA precursors and short and long-chain PFAS in the environment through HCA analysis [77,78]. Similar to our findings, previous studies highlighted strong correlations among different PFAS in the natural environments through multivariate analysis, indicating common origins [46, 79–81]. Although the correlation analysis provides valuable information on the origins of PFAS in landfills, to pinpoint the sources of PFAS in landfills, the incoming heterogeneous MSW needs to be individually scrutinized and the transformation of PFAS precursors needs to be studied in controlled lab settings.

4. Conclusion

The analysis of PFAS in landfill organics revealed a dominant presence of perfluorocarboxylic acids (PFCAs) and fluorotelomer carboxylic acids (FTCAs), reflecting their extensive use in consumer products and robust environmental persistence. A significant vertical stratification of PFAS concentrations was observed, with notably higher concentrations at middle depths compared to shallower and deeper layers. The vertical distribution of PFAS in landfills can affect their migration, with deeper layers dictating leachate PFAS levels and shallower layers releasing PFAS into the atmosphere, posing significant environmental risks to water, air, ecosystems. Strong correlations between PFAS concentrations and the carbon content of landfill organics underscore the crucial role of organic matter, including dissolved organic matter, in the adsorption and retention of PFAS. High DOM concentrations at specific depths were linked to increased PFAS levels, illustrating how organic matter characteristics drive PFAS distribution within landfills.

Multivariate statistical analysis revealed common sources and transformation pathways for PFAS, highlighting the conversion of precursor compounds under landfill conditions. Understanding these pathways is crucial for evaluating the risks associated with PFAS in landfills and devising targeted mitigation strategies. The designation of PFOA and PFOS as hazardous substances by the U.S. EPA on April 19, 2024, underscores the need for extensive investigation into the potential transformation of precursor compounds to these potential terminal products. A system-level study is essential to elucidate these pathways, given the complex interplay of influencing factors.

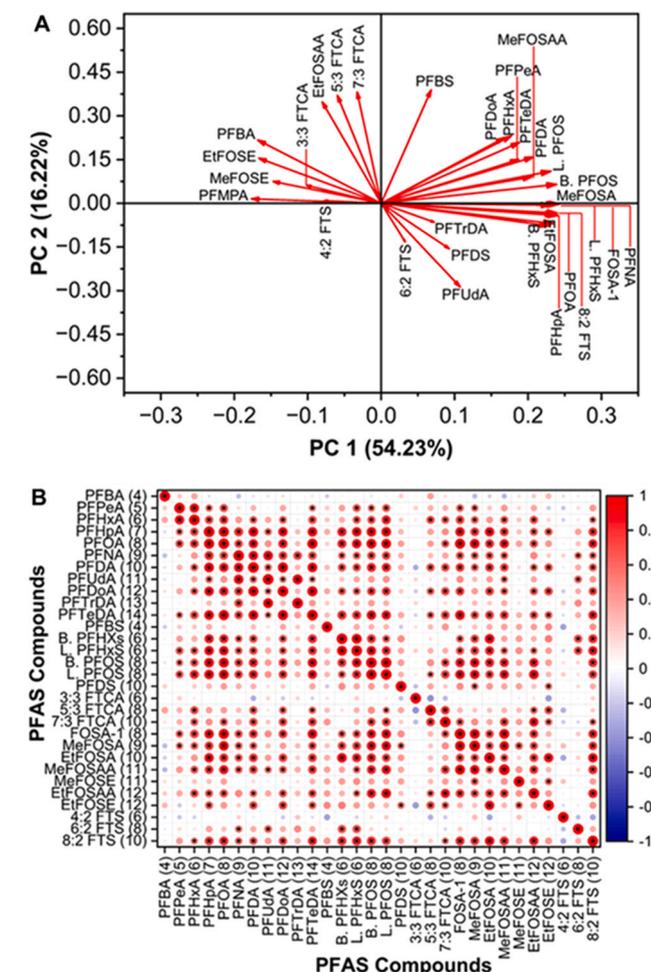


Fig. 5. A. Principal component analysis (PCA) loading plot on the Log transformed PFAS concentrations at different depths of the gas wells. PC-1 and PC-2 explain 70.45 % of the variability of the analyzed PFAS. B. Pearson correlation between the PFAS at different depths in the gas wells. The red circle with '*' denotes a significant correlation between the corresponding PFAS pairs. The red color in the right-side bar indicates the intensity of a strong correlation and the blue color denotes the intensity of a weak correlation among the PFAS. Extended forms of the PFAS are provided in Table S4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Comprehensive knowledge of PFAS vertical distribution in landfills is essential for designing or retrofitting sites to reduce PFAS migration in leachate. For example, recirculating leachate can decrease long-chain PFAS concentrations, reducing their environmental impact. This approach could transform landfills into 'PFAS sinks' rather than 'PFAS sources,' minimizing the environmental footprint of these substances. Additionally, strategic placement of PFAS-containing waste in the upper landfill layers, where degradation can be controlled once the final cover is in place, can further reduce PFAS leaching. This method will limit the likelihood of precipitation reaching the waste, thereby minimizing PFAS migration into the leachate.

Environmental implication

This study investigates the distribution and transformation of per- and polyfluoroalkyl substances (PFAS) in landfill organics. PFAS are considered hazardous materials due to their persistence, bio-accumulation potential, and toxicity, posing significant risks to human health and the environment. Our research reveals how PFAS migrate within landfill environments, predominantly accumulating at middle depths. By elucidating the vertical distribution and interactions of PFAS with organic matter, this work advances our understanding of PFAS fate in landfills and informs strategies for mitigating their environmental impact, thereby addressing a critical environmental contamination issue.

CRedit authorship contribution statement

Sujan Fernando: Writing – review & editing, Methodology. **Juby R. Varghese:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis. **Mohamed Ateia:** Writing – review & editing, Writing – original draft, Methodology. **Thabet Tolaymat:** Writing – review & editing, Writing – original draft, Conceptualization. **Syeed Md Iskander:** Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Biraj Saha:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Nirupam Aich:** Writing – review & editing, Writing – original draft, Visualization, Methodology. **John Briest:** Writing – review & editing, Methodology, Investigation, Conceptualization. **Jiale Xu:** Writing – review & editing, Visualization, Methodology. **Debasis Golui:** Writing – review & editing, Writing – original draft, Methodology. **Achintya Bezbaruah:** Writing – review & editing, Methodology.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supporting texts on carbon analysis of landfill organics, pH analysis, dissolved organic matter analysis, dissolved organic matter characterization, quality assurance, and quality control (QA/QC), UPLC-MS/MS analysis, and statistical analysis; supporting tables on moisture content, carbon content, dissolved organic matter, ultraviolet and fluorescence 3D excitation-emission matrix indices, mass-labelled PFAS internal standards, UPLC-MS/MS operating conditions, extended forms of PFAS, normality test, one-way ANOVA, linear and multiple linear regression analysis; supporting figures of water solubility, Log K_{OC} , and vapor pressure of PFAS, relative distribution PFAS, concentrations of the investigated PFAS at different depths, linear regression curve fitting, PFAS concentrations versus total carbon and non-biodegradable carbon, landfill DOM components, ultraviolet and fluorescence 3D excitation-emission matrix indices, and Hierarchical cluster analysis. Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2024.135678](https://doi.org/10.1016/j.jhazmat.2024.135678).

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