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Evaluation of per- and polyfluoroalkyl substances (PFAS) in leachate, gas condensate, stormwater and groundwater at landfills

Yutao Chen^a, Hekai Zhang^a, Yalan Liu^b, John A. Bowden^{b,c}, Thabet M. Tolaymat^d, Timothy G. Townsend^b, Helena M. Solo-Gabriele^{a,*}

^aDepartment of Civil, Architectural, and Environmental Engineering, College of Engineering, University of Miami, Coral Gables, Florida 33146, United States

^bDepartment of Environmental Engineering Sciences, College of Engineering, University of Florida, Gainesville, FL 32611, United States

^cCenter for Environmental and Human Toxicology & Department of Physiological Sciences, College of Veterinary Medicine, University of Florida, Gainesville, FL 32610, United States

^dCenter for Environmental Solutions and Emergency Response, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268, United States

Abstract

Per- and polyfluoroalkyl substances (PFAS), found in many consumer products, are commonly disposed of in landfills at the end of their service lives. To identify landfill liquids that should be prioritized for treatment, this study aimed to evaluate PFAS levels in different aqueous samples from landfills and identify relationships between PFAS and landfill characteristics. Twenty-six PFAS including 11 perfluoroalkyl carboxylic acids (PFCAs), 7 perfluoroalkyl sulfonates (PFSAs), and 8 perfluoroalkyl acid precursors (PFAA-precursors) were measured in municipal solid waste (MSW) leachate, construction and demolition debris (CDD) leachate, municipal solid waste incineration (MSWI) ash leachate, gas condensate, stormwater, and groundwater from landfills. Based on the median, results show that PFAS levels in MSW leachate were the highest (10,000 ng L⁻¹), CDD leachate were intermediate (6200 ng L⁻¹), and MSWI ash leachate were the lowest (1300 ng L⁻¹) among the leachates evaluated. PFAS levels in gas condensate (7000 ng L⁻¹) were

*Corresponding author. 1251 Memorial Drive, McArthur Engineering Building, Room 512, Coral Gables, FL, 33146, USA. hmsolo@miami.edu (H.M. Solo-Gabriele).

Credit author statement

Yutao Chen: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Hekai Zhang:** Investigation, Writing – review & editing. **Yalan Liu:** Investigation, Writing – review & editing. **John A. Bowden:** Methodology, Writing – review & editing. **Thabet Tolaymat:** Methodology, Validation, Resources, Writing – review & editing. **Timothy G. Townsend:** Conceptualization, Methodology, Investigation, Writing-Reviewing and Editing, Funding acquisition. **Helena M. Solo-Gabriele:** Conceptualization, Methodology, Investigation, Writing-Reviewing and Editing, Funding acquisition, Supervision, Project administration.

Declaration of competing interest

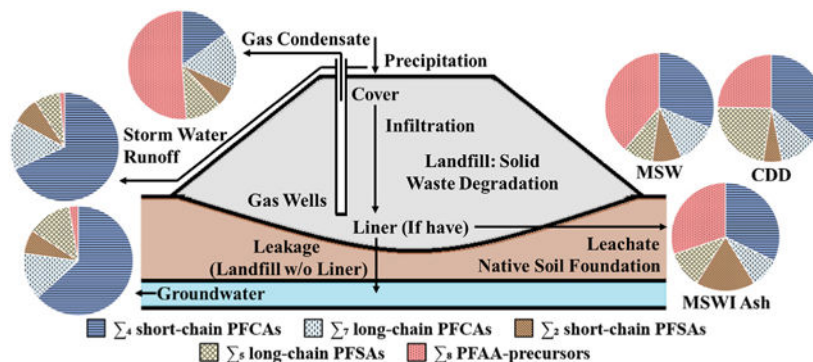
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.137903>.

similar to MSW leachate. PFAS in stormwater and groundwater were low (medians were less than 500 ng L⁻¹). Dominant subgroups included PFCAs and PFAA-precursors in all leachates. PFASs were also found in CDD leachate, PFAA-precursors in gas condensate, and PFCAs in stormwater and groundwater. Landfill characteristics significantly correlated with \sum_{26} PFAS included waste proportions (percentage of MSWI ash in landfill, $|r_s| = 0.22$), operational status (active or not, $|r_s| = 0.27$) and rainfall (30-d cumulative rainfall, $|r_s| = 0.39$). The results from this study can be used to prioritize which landfills and which reservoir of liquids (and corresponding subgroup of PFAS) to target for PFAS management.

Graphical Abstract



Keywords

PFAS; PFAA-Precursors; Landfill leachate; Gas condensate; Stormwater; Groundwater

1. Introduction

Landfills are one of the most significant environmental reservoirs of PFAS due to the disposal of PFAS-containing products (Chen et al., 2020; Favreau et al., 2017; Lang et al., 2016; Schaidler et al., 2017; Schultes et al., 2018; US EPA, 2018; Wang et al., 2017) at the end of their service lives. Studies have shown that PFAS can be released from these consumer products to result in high levels of PFAS in landfill leachates (Benskin et al., 2012; Chen et al., 2022; Hamid et al., 2018; Podder et al., 2021; Solo-Gabriele et al., 2020). These leachates have been shown to impact water quality at wastewater treatment plants (WWTP) (Masoner et al., 2020) and have a potential to impact natural water bodies. Given that PFAS have been detected in high concentrations in landfill leachates, we hypothesize that other liquid sources like gas condensate, stormwater, and groundwater, may also be impacted by high levels of PFAS originating from disposed consumer products at landfills.

To the best of our knowledge, there are no studies that have comprehensively compared all liquid sources (landfill leachates, gas condensate, stormwater, and groundwater) in and across landfills of differing characteristics. In addition, to the best of our knowledge, no studies have been published that evaluate differences among the types of gas condensates in landfills, the influence of stormwater detention systems, nor the correlations between lined

systems and groundwater PFAS levels. Significant gaps therefore exist in understanding the PFAS levels in different aqueous reservoirs in landfills.

In the growing body of literature related to PFAS in landfill leachates (Busch et al., 2010; Gallen et al., 2016; Liu et al., 2020, 2022), some studies focused on the performance of onsite treatment systems for their abilities to change the PFAS concentrations in the landfill leachate (Chen et al., 2022; Zhang et al., 2022). Also, some landfill characteristics evaluated include landfill size, age of waste, landfill operational status, climate, and geographic location (Gallen et al., 2016, 2017; Lang et al., 2017; Solo-Gabriele et al., 2020). For example, a study about the relationship between the detected PFAS and operational status of Australian landfills showed that some short-chain PFCAs in active landfills were significantly higher than that in inactive landfills (Gallen et al., 2016), but this difference was not significant in another study by the same group (Gallen et al., 2017). Studies that evaluate the impacts of PFAS on groundwater focus on contamination from aqueous film forming foams (Backe et al., 2013). Only one research group (Hepburn et al., 2019a, 2019b) evaluated impacts to groundwater from legacy landfills.

Given the paucity of comprehensive data focused on different liquid types in landfills, this study aimed to evaluate a wide cross-section of solid waste disposal facilities to identify PFAS levels in leachates (from municipal solid waste (MSW), construction and demolition debris (CDD), municipal solid waste incineration (MSWI) ash), gas condensates (from MSW and CDD gas wells, flare stations, and mixed sources), stormwater (including inlets and outlets from retention areas) and groundwater (from landfills with different leachate containment systems). Results from this study can be used to prioritize which landfills, liquid types within a landfill, and PFAS subgroups should be targeted to minimize off-site impacts. Given the range of landfills evaluated, we also had the opportunity to evaluate characteristics of the landfills that correlated with PFAS levels (e.g., waste proportion, age of waste, operational status of the landfill, and cumulative rainfall) based on statistical correlation analysis. These relationships were evaluated as a first step in understanding operational and environmental conditions which may also influence PFAS levels at landfills.

2. Materials and methods

2.1. Landfill aqueous samples type

In total, 281 aqueous landfill samples were collected from 39 landfills in 29 counties in Florida, US. The landfills sampled in this study mainly accepted MSW, CDD, and MSWI ash (incineration temperature of 820–1400 °C). The number of landfills evaluated by waste type and active status is provided in Supplemental Table S1. The number of samples broken down by waste type and aqueous sample type (leachate, gas condensate, stormwater, and groundwater) are provided in Supplemental Table S2. Details about sampling methods are provided in Supplemental Table S3.

Landfill leachate is one of the main landfill liquids evaluated in this study. It is designated by the primary type of solid waste (MSW, CDD, and MSWI ash) accepted by the facility or specific landfill cell. In total for leachates specifically, 120 samples were collected, including 78 MSW leachates, 13 CDD leachates, and 29 MSWI ash leachates, as identified by the

landfill operators (Table S2). Among the 78 MSW landfill leachates, nine were influenced by co-disposal with MSWI ash. These nine MSW leachates plus 29 MSWI ash leachates constitute a total of 38 samples influenced by MSWI ash, and these samples were used to evaluate the proportion of ash on PFAS levels in leachate. The 38 samples were further separated into 20 leachates from landfill cells with low MSWI ash proportion ($0\% < \text{ash} < 50\%$) and 18 leachates from landfill cells with high MSWI ash proportion (ash $\geq 50\%$).

In addition to the designation of accepted solid waste, other landfill characteristics, including waste age, landfill operational status, and rainfall, were also evaluated regarding PFAS levels in leachates. In this study, waste age was the year sampled minus the start year of the disposal area's acceptance of solid waste. Based on the estimated waste age, collected waste leachates (including MSW, CDD and MSWI ash leachate) were separated into 31 leachates corresponding to young waste (waste age ≤ 15 years), 54 leachates corresponding to moderate age waste ($15 \text{ years} < \text{waste age} \leq 30$ years) and 35 leachates corresponding to old waste (waste age > 30 years). For landfill operational status, 79 leachate samples corresponded to landfill cells still accepting solid waste at the time of sampling, and thus were listed as active. The remaining 41 landfill leachate samples came from landfill cells that were closed or in preparation to be closed and thus they were listed as inactive. In addition, cumulative rainfall was calculated for 14 d, 30 d and one year before the sampling dates. The rainfall data was downloaded from the National Oceanic and Atmospheric Administration's (NOAA) weather station closest to the sampling location (NOAA, 2022), in which estimated 14-d rainfall ranged from 0 to 190 mm, 30-d rainfall ranged from 18 to 211 mm, and annual rainfall ranged from 1.08 to 2.04 m for the 39 study landfills.

Among other types of collected aqueous landfill samples, gas condensate was defined as the liquid condensed when warm gas (around $50\text{ }^{\circ}\text{C}$) collected by gas wells in the landfill gas collection and control system was cooled by ambient air temperature (around $25\text{ }^{\circ}\text{C}$). In this study, 21 gas condensate samples, as defined by the landfill operators, were collected from MSW gas wells ($n = 7$), CDD gas wells ($n = 8$), flare stations ($n = 3$), or other mixed sources (like leachate management structures that receive both leachate and gas condensate, $n = 3$); thus, these samples had variable characteristics. In general, gas condensates collected from gas wells were likely influenced by some landfill leachate in comparison to gas condensates collected from flare stations which were generally away from the landfill base and not influenced by direct sources of leachate; gas condensates collected from mixed sources included pump stations and other drainage systems where leachate and gas condensate mix.

Stormwater is defined as surface water runoff from within the landfill property. Stormwater management systems in landfills are designed to avoid stormwater contact with solid waste and leachate. Therefore, stormwater is usually held within the landfill property and collected from the detention ponds usually located near the perimeter of the landfills. In total, 63 stormwater samples were collected in this study. When possible, stormwater samples were collected in pairs and separated into inlets ($n = 12$) and outlets ($n = 12$) of detention ponds. The remaining stormwater samples were not paired.

In terms of groundwater, 77 samples were collected from shallow groundwater monitoring wells, and they were separated based on the primary accepted solid waste. There were 49

samples below MSW disposal areas, 11 samples below CDD disposal areas, and 12 samples below MSWI ash disposal areas. There were also 5 groundwater samples collected below areas without disposed solid waste but within the landfill boundaries, such as under on-site wetlands and groundwater treatment systems. Thus, those samples were not included in this classification. In addition, 62 out of 77 groundwater samples were collected in pairs and further classified based on different leakage control systems (including landfill without leakage control systems, with synthetic lined systems and with slurry wall systems) and remaining groundwater samples were not paired. Some paired groundwater samples were separated into upgradient and downgradient, based on the direction of the groundwater flow, as documented in consultant reports found online or provided by the landfill operator. Upgradient groundwater, usually considered as representative of background by the landfill operator, was collected from documented high-water elevation. Downgradient groundwater was collected from documented lower water elevation and is used to monitor for possible groundwater impacts. Among these samples, 15 samples for upgradient and downgradient were collected respectively for landfills without leakage control systems and 8 samples for upgradient and downgradient groundwater were collected respectively for landfills were lined with synthetic systems. Remaining paired groundwater samples were collected outside and inside the slurry wall systems (8 samples were collected for each).

2.2. Sampling and analysis methods

After receiving permission for sample collection from landfill operators, an initial landfill sampling plan was developed based on publicly available information (e.g., public repositories associated with permitting and reporting requirements from public utilities) (FDEP, 2020). These initial plans were then shared and discussed with landfill operators during at least two conference calls, who then provided suggestions for specific sampling locations that targeted gas condensate, groundwater, stormwater ponds, and landfill leachates at their sites. Efforts were made to identify landfill sites that would be representative of different types of leachates (MSW, CDD, MSWI ash and/or combinations) and different ages of landfill cells.

At each sampling location, leachate was collected into an HDPE primary collection bottle (1 L or greater). The primary collection bottle was then used to split the leachates among sample analysis bottles which included two 250 ml HDPE bottles for PFAS analysis. Additional details about sample collection including the collection of quality control samples are provided in the supplemental text section 3.

The 26 evaluated PFAS (\sum_{26} PFAS) in this study were categorized into 18 perfluoroalkyl acids (PFAAs, including 11 PFCAs and 7 PFSAAs) and eight of their precursors. Definition of acronyms and chemical structures of the 26 species analyzed are given in Supplement Table S4. In this study, the 18 analyzed PFAAs were further separated short-chain PFCAs ($C_4 - C_7$, \sum_4 short-chain PFCAs), long-chain PFCAs ($C_8 - C_{14}$, \sum_7 short-chain PFCAs), short-chain PFSAAs ($C_4 - C_5$, \sum_2 short-chain PFCAs), and long-chain PFSAAs ($C_6 - C_{10}$ PFSAAs, \sum_5 long-chain) (Brendel et al., 2018; Buck et al., 2011; Kwiatkowski et al., 2020; Lindstrom et al., 2011; Organization for Economic Cooperation and Development Environment Directorate, 2020). The eight analyzed PFAA-precursors

(\sum_8 PFAA-precursors) included fluorotelomer carboxylic acids (FTCAs, including 5:3 and 7:3 FTCA), perfluorooctane sulfonamides (FOSAs, including PFOSA, NMeFOSAA, and NEtFOSAA), and fluorotelomer sulfonic acids (FTSAs, including 4:2 FTS, 6:2 FTS, and 8:2 FTS). These PFAA-precursors, especially 5:3 FTCA, are usually high in concentration under anaerobic processes (Lang et al., 2017) or strong methanogenic (Allred et al., 2015; Zhang et al., 2013) conditions. These evaluated precursors are considered as intermediates in the conversion of other PFAA-precursors such as fluorotelomer alcohol (FTOH) to terminal PFCAs and PFSAAs (Hamid et al., 2020; Huset et al., 2011; Liu et al., 2020; Zhang et al., 2013). Additional details about PFAS analysis and quality control analysis are provided in the supplemental text.

2.3. Data analysis

For statistical analysis comparing different liquid types, the values below the limit of detection (LOD) were replaced with the $\text{LOD}/\sqrt{2}$ as recommended by Verbovšek (2011). Results from Shapiro-Wilk tests (Yap and Sim, 2011) indicated that PFAS data were not normally or lognormally distributed, and thus nonparametric tests were used to compare the different types of aqueous landfill samples having at least five data points. As shown in Table S2, a Mann-Whitney U test (Noether, 1992) was used to identify the difference between two separate data sets, like the comparison of different types of aqueous landfill samples (e.g., MSW leachate and groundwater). This test was also used to compare different waste types, waste proportions (amount of accepted MSW, CDD and MSWI ash divided by total accepted solid waste), waste age and landfill operational status, and different gas condensates based on their sources. A Wilcoxon signed rank test (Wilcoxon, 1992) was used for comparison of the means between two paired data sets, including different stormwater sets based on their upstream or downstream status, and groundwater sets based on the leakage control system employed (Table S2). The statistical software package, SPSS (Statistics 26) was used to complete these tests. Statistical differences between datasets were set at p -values less than 0.05.

Associations between PFAS groups and individual species were assessed through a nonparametric Spearman's rank correlation (Sedgwick, 2014). Correlation coefficients greater than 0.7 ($|r_s| = 0.7$) were considered strong and less than 0.5 were considered weak ($|r_s| = 0.5$). Correlations were considered significant for p -values less than 0.05. The relationships were evaluated between the PFAS concentrations of the landfill leachates (MSW, CDD and MSWI ash leachate) and landfill characteristics, including waste proportions, waste ages, operational status, and rainfall (Table S2). Results of r_s and p -values of Spearman's rank correlation were provided by SPSS (Statistic 26). To indicate these r_s values, the package "corrplot", Visualization of a Correlation Matrix (Version 0.92) (Wei and Simko, 2021), was used in R Statistical Software (Version 4.0.2) to generate heatmaps of Spearman's correlation matrices. In addition, as shown in Table S2, Pearson's correlation (Sedgwick, 2012) was also evaluated through SPSS (Statistics 26) to identify the relationship between the PFAS in landfill leachates and the proportion of accepted MSWI ash.

Overall results were first analyzed by liquid type for \sum_{26} PFAS, the sum of perfluorooctanoic acid and perfluorooctane sulfonic acid (\sum PFOA + PFOS), and fractions of different PFAS groups. Results presented in this manuscript emphasize \sum PFOA + PFOS because of the regulatory guidelines established in 2016 at the federal level which recommend less than 70 ng L⁻¹ for the sum of these two species (Hamid et al., 2018; US EPA, 2016). In 2022, the US EPA updated this advisory and suggested that PFOA and PFOS should be less than 0.004 ng L⁻¹ and 0.02 ng L⁻¹, respectively (US EPA, 2022). Considering the health advisory updated in 2022 for PFOA and PFOS are lower than detection limits in this study, only the health advisory issued in 2016 was used for comparisons. Correlations between PFAS and landfill characteristics (waste proportions, age, operational status, and rainfall) were considered only for leachates. Details of landfill liquids other than leachates (gas condensates, stormwater, and groundwater) were evaluated independently given differences in their management. When comparing the different categories of most samples using significance tests, the median was used to reduce the impact of extreme values due to the high variability in environmental samples. The exception corresponds to the comparison of the different categories of gas condensate, where the average was used because only three samples were collected for two out of four evaluated categories of gas condensate. The average was also used when describing the percentage of each PFAS group based on the \sum_{26} PFAS.

3. Results and discussion

3.1. Detected PFAS in aqueous samples within landfills

3.1.1. Comparison of \sum_{26} PFAS in aqueous samples within landfills—Results (Fig. 1) show that \sum_{26} PFAS concentration was usually larger than 1,000 ng L⁻¹ in landfill leachates (MSW, CDD, MSWI ash) and gas condensate based on median values. Among three types of landfill leachates, the median \sum_{26} PFAS concentration was highest for MSW leachate (10,000 ng L⁻¹), followed by CDD leachate (6,200 ng L⁻¹) and the lowest \sum_{26} PFAS concentration was observed for MSWI ash leachate (1,300 ng L⁻¹). These results are similar to the observation of MSW, CDD and MSWI ash leachates in previous studies (Solo-Gabriele et al., 2020). Statistical differences were observed between MSW and MSWI ash leachate ($p < 0.01$); however, leachate from MSW was not statistically different than leachate from CDD ($p = 0.19$), and leachate from CDD was not statistically different than leachate from MSWI ash ($p = 0.65$).

Although significant differences were not observed between CDD and MSW leachates in the current study, Gallen et al. (2016, 2017) found opposite results; that CDD leachates have higher PFAS levels than MSW leachates. This may be caused by the variability of PFAS levels with the landfill category and the number of PFAS-containing products disposed of in Florida, US (current study) and Australia (Gallen et al., 2016, 2017) landfills. Specifically, when comparing the sum of nine PFAS evaluated in the Australian landfills (Gallen et al., 2016, 2017), detected PFAS in MSW leachate from landfills in Australia (~3,500 ng L⁻¹) was similar with that in Florida landfills (~3,300 ng L⁻¹), which is consistent with the similar waste composition (major portion is household waste) disposed in MSW

landfills in Florida and Australian landfills. However, for CDD leachates, detected PFAS from Australian landfills ($\sim 12,000 \text{ ng L}^{-1}$) (Gallen et al., 2016, 2017) was higher than that in Florida landfills ($\sim 2,400 \text{ ng L}^{-1}$). CDD landfills in Florida accept yard trash, CDD, processed tires, asbestos, carpet, cardboard, paper, glass, plastics, and furniture other than appliances (Solo-Gabriele et al., 2020); and CDD landfills in Australia accepted CDD, cardboard, glass, paper, concrete, solid metals, timber, and plastics (Gallen et al., 2017). Yard trash disposed of in Florida landfills may dilute the PFAS concentrations in CDD leachate compared with the Australian landfills. More details about the difference between the Florida and Australian landfills (landfill materials and climate conditions) are provide in the Supplement Table S8.

For MSWI ash leachate, PFAS is detected significantly lower than that in MSW leachates, which is consistent with the previous study (Liu et al., 2022). However, Liu et al. (2022) also showed that detected PFAS in pure ash monofills was 290 ng L^{-1} which was lower than the median found in the current study. The difference between the current study and the pure ash evaluated by Liu et al. (2022) is likely due to the co-disposal of MSW with MSWI ash in landfill leachates sampled in the current study. The unburned MSW co-disposed of with MSWI ash could preferentially leach PFAS resulting in an increase in concentration. The co-disposed unburned MSW could also explain the lack of statistical differences in $\sum_{26}\text{PFAS}$ levels between MSWI ash and CDD leachates.

There was no statistically significant difference ($p > 0.18$) between the $\sum_{26}\text{PFAS}$ in gas condensate (median of $7,000 \text{ ng L}^{-1}$) and the $\sum_{26}\text{PFAS}$ in any type of landfill leachate in this study. However, a prior study in Canada showed that detected PFAS in condensate was lower than that in landfill leachate from the same site (Li, 2011). The lack of statistical difference between $\sum_{26}\text{PFAS}$ in leachates (MSW, CDD, MSWI ash) versus gas condensate in the current study may be due to the mixing of gas condensate with leachate in some samples, this mixing would drive the median detected PFAS to be higher than that in pure gas condensate thereby reducing the differences in $\sum_{26}\text{PFAS}$ between gas condensate and leachates evaluated.

Evaluating other aqueous samples found within the landfill boundary, stormwater and groundwater, $\sum_{26}\text{PFAS}$ was significantly lower than gas condensate and all landfill leachate types ($p < 0.01$). Although some comparatively high $\sum_{26}\text{PFAS}$ ($> 1,000 \text{ ng L}^{-1}$) were detected in 12 out of 77 collected groundwater samples, $\sum_{26}\text{PFAS}$ in the groundwater (collected from landfill with and without lined systems, 140 ng L^{-1}) was statistically lower than that in the stormwater (470 ng L^{-1} , $p < 0.01$) based on median values.

3.1.2. Comparison of $\sum \text{PFOA} + \text{PFOS}$ in aqueous samples within landfills

—For $\sum \text{PFOA} + \text{PFOS}$ specifically, among the three types of landfill leachate based on the median, MSW leachate had the highest level of $\sum \text{PFOA} + \text{PFOS}$ ($1,300 \text{ ng L}^{-1}$); CDD leachate had intermediate levels of $\sum \text{PFOA} + \text{PFOS}$ (980 ng L^{-1}); MSWI ash leachate had the lowest level of $\sum \text{PFOA} + \text{PFOS}$ (430 ng L^{-1}). Significant differences were only observed in $\sum \text{PFOA} + \text{PFOS}$ between MSW and MSWI ash leachate ($p < 0.01$). As observed in

\sum_{26} PFAS, all remaining differences for \sum PFOA + PFOS among landfill leachates were not significant ($p > 0.20$). Comparing the \sum PFOA + PFOS of landfill leachate against prior studies, results from this work were in the same order of magnitude for US landfills (Lang et al., 2017; Solo-Gabriele et al., 2020), but were higher than landfill leachate from landfills in Australia and Germany (Busch et al., 2010; Gallen et al., 2017). As observed in \sum_{26} PFAS, higher \sum PFOA + PFOS was also detected for MSWI ash leachates in the current study compared with the pure ash monofills in the Liu et al. (2022) previous study (37 ng L⁻¹). Again, the higher levels of \sum PFOA + PFOS in the current study may be due to co-disposal of unburned MSW.

Median \sum PFOA + PFOS in gas condensate (410 ng L⁻¹) was lower than that in MSW (1,300 ng L⁻¹) and CDD leachate (980 ng L⁻¹) and was similar to \sum PFOA + PFOS in MSWI ash leachate (430 ng L⁻¹). Although these differences were not significant ($p > 0.30$), lower \sum PFOA + PFOS in gas condensate compared with the MSW and CDD leachate was influenced by gas condensates collected from CDD gas wells which generally had lower PFAS levels compared to other types of gas condensates (more details described below). In addition, \sum PFOA + PFOS in the current study was also similar with the median of gas condensate in an existing study (360 ng L⁻¹, Smallwood et al., 2023).

Levels of median \sum PFOA + PFOS in stormwater (65 ng L⁻¹) and groundwater (20 ng L⁻¹) were significantly lower than landfill leachate and gas condensate ($p < 0.01$), and the level of \sum PFOA + PFOS in groundwater was significantly lower than that in stormwater based on the median ($p = 0.02$). These detected \sum PFOA + PFOS in stormwater and groundwater were lower than the 70 ng L⁻¹ guideline level for drinking water issued by EPA in 2016 (Hamid et al., 2018; US EPA, 2016).

3.1.3. Fraction of PFAS groups in aqueous samples within landfills—

For the fraction of PFAS groups within the MSW, CDD, and MSWI ash landfill leachates (Panel b of Fig. 1, details of distribution for these PFAS groups shown in Supplement Fig. S1), PFAA-precursors and short-chain PFCAs usually had the highest fraction (\sum_8 PFAA-precursors/ \sum_{26} PFAS = 39%, 25% and 30%; \sum_7 short-chain PFCAs/ \sum_{26} PFAS = 31%, 36% and 32%, respectively) compared to the other PFAS groups. Fractions of other PFAS groups in landfill leachate were usually less than 20%, except for long-chain PFSAs (\sum_5 long-chain PFSAs/ \sum_{26} PFAS = 23%) in CDD leachate. The higher fractions of PFAA-precursors in the leachates is consistent with studies that have shown high fractions of PFAA-precursors in samples under anaerobic and/or strong methanogenic conditions (Allred et al., 2015; Lang et al., 2017; Zhang et al., 2013). In the study of vehicle-derived leachates at transfer stations (Liu et al., 2020), PFAA-precursors composed up to 70% of the total PFAS fraction. Although MSW leachate had the highest fraction of PFAA-precursors among landfill leachates in the current study, the proportion was low compared to vehicle-derived leachate suggesting that very new leachate may preferentially carry precursors. These precursors may degrade to terminal species in the leachate.

In gas condensate, PFAA-precursors were dominant ($\sum_8 \text{PFAA-precursors} / \sum_{26} \text{PFAS} = 51\%$), which was consistent with Smallwood et al.'s (2023) study who found that PFAA-precursors represented a large fraction in gas condensate. Fractions of other PFAS groups in gas condensate were all less than 20% of $\sum_{26} \text{PFAS}$. The higher fraction of PFAA-precursors in gas condensate may also have been associated with specific gas condensate categories evaluated in this study, which would be discussed later. This also suggested that PFAA-precursors may preferentially be distributed in the gas condensate compared with landfill leachates.

For stormwater and groundwater, short-chain PFCAs were dominant ($\sum_7 \text{short-chain PFCAs} / \sum_{26} \text{PFAS} = 68\%$ and 63%) and their fractions were much higher than that in gas condensate and landfill leachate. Fractions of other PFAS groups in stormwater and groundwater were all less than 20% of $\sum_{26} \text{PFAS}$, especially for $\sum_8 \text{PFAA-precursors}$ which were 1.6% and 2.7% of $\sum_{26} \text{PFAS}$ in stormwater and groundwater, respectively. Existing studies showed that PFAA-precursors, including 5:3 FTCA, may further convert into short-chain PFCAs (Liu and Mejia Avendaño, 2013; Wang et al., 2012). Therefore, lower fractions of PFAA-precursors in stormwater and groundwater may suggest that when liquids leave anaerobic environments, like landfills, PFAA-precursors are lost and possibly converted into terminal short-chain PFCAs.

3.2. Relationship between PFAS in landfill leachate and landfill characteristics

Spearman's coefficients between PFAS categories and landfill characteristics (Fig. 2) indicate some statistically significant ($p < 0.05$) but generally weak correlations ($|r_s| = 0.5$). Overall, evaluating all landfill characteristics collectively, $\sum_{26} \text{PFAS}$ is usually higher when the landfill's solid waste had a higher proportion of MSW and lower proportion of MSWI ash, consistent with recent findings (Liu et al., 2022). Higher $\sum_{26} \text{PFAS}$ was also associated with active landfills and lower short-term rainfall. The $\sum \text{PFOA} + \text{PFOS}$ was generally higher in the older landfills, especially for those landfills which accepted less MSWI ash and under lower short-term rainfall. Details about some of these correlations are explored further in the subsequent sections.

3.2.1. Relationship with waste proportion—Further expanding upon the Solo-Gabriele et al.'s (2020) study which focused on PFAS in different types of landfill leachate, this section was able to establish correlations between the detected PFAS and proportions of accepted wastes given that more samples and landfills were evaluated. For waste proportions (Fig. 2), positive and significant correlations were observed between $\sum_{26} \text{PFAS}$ and the proportion of MSW ($|r_s| = 0.19$, $p = 0.03$), which was primarily driven by the correlation with ($\sum_5 \text{long-chain PFASs} / \sum_{26} \text{PFAS} = 23\%$) ($|r_s| = 0.19$, $p = 0.03$) and $\sum_8 \text{PFAA-precursors}$ ($|r_s| = 0.36$, $p < 0.01$). This suggests that $\sum_{26} \text{PFAS}$ increases when the proportion of MSW increases. No significant correlation was observed between $\sum_{26} \text{PFAS}$ and the proportion of CDD ($|r_s| = 0.15$, $p > 0.13$), suggesting that $\sum_{26} \text{PFAS}$ was not affected by the proportion of CDD significantly. This suggests that MSW was a larger reservoir of PFAS and tended to impact the detected PFAS concentration more than CDD. The negative correlation between

\sum_{26} PFAS and proportion of MSWI ash was also significant ($|r_s| = 0.22$, $p = 0.01$), and driven by significant correlations with all PFAS groups ($|r_s| = 0.20$, $p < 0.03$), with the exception of \sum_{2} short-chain PFCAs ($|r_s| = 0.01$, $p = 0.88$). This suggests that both \sum_{26} PFAS and \sum PFOA + PFOS increased when the proportion of the MSWI ash decreased. Therefore, it is worthwhile to discuss more details about the relationship between PFAS and related MSWI ash proportion for landfill leachate generated from landfill cells accepting MSWI ash specifically.

Comparing the \sum_{26} PFAS against the MSWI ash proportion of related landfill cells (panel a of Fig. 3), the median \sum_{26} PFAS in landfill leachate generated from landfill cells having MSWI ash proportions larger than or equal to 50% ($2,000 \text{ ng L}^{-1}$) was significantly lower than those having a MSWI ash proportion of less than 50% ($10,000 \text{ ng L}^{-1}$, $p < 0.01$). A moderate trend (shown in Supplement Fig. S2) was observed between the MSWI ash proportion of landfill cells and the \sum_{26} PFAS (Pearson's coefficient = 0.66, $p < 0.01$). Such results were consistent with other studies that showed that detected PFAS in unburned MSW leachate was higher than leachate from fly and bottom ash (Liu et al., 2021). The decrease in \sum_{26} PFAS in landfill leachate with higher MSWI ash proportions was also consistent with a recent finding for MSWI ash leachate collected at the site (Liu et al., 2022), and this result may be due to different processes. First, considering that MSWI ash is derived from MSW through incineration, two possibilities may explain this result. Incineration destroys some PFAS into HF and short-chain fluorocarbons when temperatures exceed 1200°C (Altarawneh et al., 2022). The range of incineration temperature was $820\text{--}1400^\circ\text{C}$ in this study, and this may suggest that incineration reduced the \sum_{26} PFAS in the landfill leachate with high MSWI ash proportions. In addition, the other possibility is that some PFAS, like 5:3 FTCA, may be lost by volatilization during the incineration process based on an existing study (Solo-Gabriele et al., 2020), which showed that lower PFAS was detected in landfill leachates from MSWI ash produced from higher incineration temperatures. Alternatively, with the exception of the incineration process, another explanation is due to the density and porosity of ash. Density of compacted ash ($1300\text{--}1800 \text{ kg m}^{-3}$, Millrath et al., 2008) tends to be higher than that of compacted MSW ($470\text{--}600 \text{ kg m}^{-3}$, Hunt et al., 1990), and, as such, compacted ash tends to be less porous. The smaller pore volume of ash can prevent moisture from flowing through the landfill, which means greater runoff is produced with less infiltration. Another possibility is that the chemical properties of the ash prevent the loss of PFAS from MSWI ash waste. However, regardless of the processes, MSWI ash leachate showed lower levels of PFAS relative to the other waste leachates based on the results in the current study.

For PFAS fractions shown in the Panel b of Fig. 3, when MSWI ash proportions became higher, the PFAS fraction of \sum_8 PFAA-precursors/ \sum_{26} PFAS decreased from 42% to 14%. In a prior study (Liu et al., 2022), results showed that \sum_8 PFAA-precursors were under detection limits in pure ash monofills, and \sum_8 PFAA-precursors/ \sum_{26} PFAS was 27% in the landfill dominated by unburned waste. This increase was consistent with the change of \sum_8 PFAA-precursors fraction in the current study. For other PFAS groups in the current study, \sum_4 short-chain PFCAs/ \sum_{26} PFAS increased from 24% to

50%; and \sum_2 short-chain PFCAs/ \sum_{26} PFAS increased from 11% to 24%. A decrease of \sum_7 long-chain PFASs/ \sum_{26} PFAS and \sum_5 long-chain PFASs/ \sum_{26} PFAS also occurred in landfill leachate for landfills with high MSWI ash proportions, although the difference was within 5.0%. Therefore, the results suggest that the more MSWI ash disposed in the landfills, the less PFAA-precursors and more short-chain PFCAs and PFASs may be detected in the landfill leachate.

3.2.2. Relationship with waste age—Considering waste age, which was split into young waste (waste age ≤ 15 years), moderate age waste (15 years $<$ waste age ≤ 30 years) and old waste (waste age > 30 years), no significant correlation between \sum_{26} PFAS and waste age ($|r_s| = 0.02$, $p = 0.83$) was observed (Fig. 2). However, waste age was significantly and positively correlated with \sum PFOA + PFOS ($|r_s| = 0.21$, $p = 0.02$) and \sum_3 long-chain PFASs ($|r_s| = 0.27$, $p < 0.01$). The positive correlation between \sum PFOA + PFOS and waste age is consistent with the history of PFAS manufacturing. Manufacturing PFOA and PFOS was initiated in the late 1940's (Prevedouros et al., 2006; Paul et al., 2009). In order to lower health risks, the US Environmental Protection Agency urged PFAS manufacturers to eliminate PFOA and PFOS (Oliaei et al., 2013; Zhou et al., 2021), but alternative substances, like short-chain PFAS and fluoroether compounds, took their place and are still widely used (Chambers et al., 2021; Gaballah et al., 2020; Janousek et al., 2019; Vorst et al., 2021). The significant correlation between waste age and \sum PFOA + PFOS or \sum_3 long-chain PFASs, with higher concentrations with older landfills, is consistent with this history of PFAS manufacture.

Median \sum_{26} PFAS in landfill leachate (Fig. 4) generated from recent, moderate-aged, and old waste were 6,900 ng L⁻¹, 7,600 ng L⁻¹ and 8,900 ng L⁻¹, respectively. Although, there were no significant differences among these three categories of leachates ($p > 0.14$), prior studies showed that higher PFAS was usually observed in the recent waste. For example, Lang et al. (2017) showed that six PFAS (PFNA, PFBS, 5:3 FTCA, MeFBSAA, MeFOSAA, 8:2 FTCA) had significantly higher concentrations in the more recent waste (waste age < 10 years) compared with the older waste (waste age > 10 years). Gallen et al. (2017) also showed that PFAS decreased with the increasing waste age. The differing results in terms of waste age observed in these studies suggest regional differences and also support the lack of statistical differences in PFAS levels for landfills categorized by different ages as observed in the current study.

\sum PFOS + PFOA and \sum_3 long-chain PFASs in the current study, on the other hand, were correlated with waste age, which may be due to the history of manufacture and the characteristics of wastes disposed of in various localities. To further identify the relationship between PFAS in the leachate and waste age, the fraction of different PFAS groups were evaluated (Fig. S3) and results of the current study are consistent with the correlations. The fraction of short-chain PFAS (\sum_4 short-chain PFCAs + \sum_2 short-chain PFCAs) decreased with the increasing waste age, which were 60%, 39%, and 32% in the leachate from recent, moderate-aged, and old waste. The fraction of long-chain PFAS (\sum_7 long-chain PFASs + \sum_5 long-chain PFASs) increased with the increasing waste age, which

were 15%, 22%, and 28% in the leachate from recent, moderate-aged, and old waste. Considering that PFOA and PFOS both belong to the long-chain PFAS, these results suggested that after PFOA and PFOS were banned after 2000s (Oliaei et al., 2013; Zhou et al., 2021), short-chain PFAS replaced long-chain PFAS in product manufacturing and this change is reflected in the leachates. Also of interest is that although PFOA and PFOS had been banned, they were still detected in landfill leachate from recent waste based on the current and the existing studies (Lang et al., 2017; Solo-Gabriele et al., 2020). The presence of PFOA and PFOS in the leachate from recent waste may be due to disposal of legacy consumer products containing these compounds, importation of products containing these compounds, or from conversion from the replacements of long-chain PFSA (e.g., fluoroether compounds) (McCord and Strynar, 2019).

In addition, although the fraction of PFAA-precursors was only 25% of \sum_{26} PFAS in recent waste, PFAA-precursors were dominant in the landfill leachate from moderate-aged waste (\sum_8 PFAA-precursors/ \sum_{26} PFAS = 39%) and old waste (\sum_8 PFAA-precursors/ \sum_{26} PFAS = 40%). Evaluated PFAA-precursors in this study, like 5:3 FTCA, are considered intermediate precursors and can be converted from original precursors, like FTOH (Hamid et al., 2020; Huset et al., 2011; Liu et al., 2020; Zhang et al., 2013). These evaluated intermediate PFAA-precursors may further convert into terminal PFCAs and PFSA within the landfill after prolonged periods or when they leave the anaerobic environment (Allred et al., 2015; Liu and Mejia Avendaño, 2013; Wang et al., 2012; Zhang et al., 2013). Therefore, higher fractions of intermediate PFAA-precursors, like 5:3 FTCA, were found in moderate-aged and old waste in comparison to recent waste. These results suggest that the transformation among PFAS was not fully completed in the moderate-aged and old landfills resulting in a greater proportion of intermediate precursor species. In summary, the distribution of PFAS in leachate generated from different waste ages may be caused by a combination of the history of manufacture and transformation among different PFAS.

3.2.3. Relationship with landfill operational status—Waste leachates (including MSW, CDD and MSWI ash leachates) were also classified based on the operational status of landfills (active or inactive, Fig. 4). Active landfills would have been expected to have received more recent waste compared to inactive landfills, and inactive landfills would have been expected to have received more moderate-aged and old waste than active landfills. Although the correlation between \sum_{26} PFAS and waste age was not significant ($|r_s| = 0.02$, $p = 0.83$), positive correlation between \sum_{26} PFAS and operational status was significant ($|r_s| = 0.27$, $p = 0.06$) (Fig. 2). In addition, with the exception of \sum PFOA + PFOS and \sum_5 long-chain PFSA, all evaluated PFAS groups were significantly correlated with the operational status of landfills ($|r_s| = 0.17$, $p < 0.05$). The correlation between operational status and \sum PFOA + PFOS ($|r_s| = 0.16$, $p = 0.07$) or \sum_7 long-chain PFSA ($|r_s| = 0.17$, $p = 0.06$) was significant based on a 90% confidence interval. Therefore, results suggest that active landfills have higher \sum_{26} PFAS when compared to inactive landfills.

Although there were no significant differences among detected PFAS in different categories of waste age ($p > 0.14$), results of landfill operational status (Fig. 4) also show that

the median \sum_{26} PFAS in landfill leachate from active landfill cells (10,000 ng L⁻¹) was significantly higher than that from inactive disposal areas (3,800 ng L⁻¹, $p < 0.01$). Although Gallen et al. (2017) did not find significant differences of PFAS in the different operational status of Australian landfills, this result is consistent with their other study that showed that short-chain PFCAAs in active landfills were significantly higher than that in inactive landfills (Gallen et al., 2016). Higher \sum_{26} PFAS in active landfills than that in inactive landfills may be explained by the top liner systems. Once a landfill becomes inactive, it usually initiates the closure process which involves the placement of the final top liner. The placement of this top liner may impact the rate at which PFAS is released from the disposed waste into the leachate. Results suggest that the placement of the top liner in landfills (inactive landfills) may cause the lower \sum_{26} PFAS concentrations in leachate compared with the landfills without top liner (active landfills), but similar distribution of different PFAS groups based on their fractions were detected in the leachate from both active and inactive landfills.

Considering the fraction of PFAS groups between these two kinds of operational status (shown in Supplement Fig. S3), these fractions were similar and the difference between fractions for each class was within $\pm 5.0\%$. Among these fractions, \sum_8 PFAS-precursors/ \sum_{26} PFAS was 40% in inactive landfills, which was higher than that in active landfills (\sum_8 PFAS-precursors/ \sum_{26} PFAS = 35%). This result was similar to higher PFAS-precursors detected in moderate-aged and old waste than recent waste in the current study mentioned before. Therefore, the reason for slightly higher PFAS-precursor fractions in inactive landfills may be because of incomplete transformations among PFAS.

3.2.4. Relationship with rainfall—For cumulative 14-d antecedent rainfall (Fig. 2), significant and negative correlations were observed for \sum_{26} PFAS ($|r_s| = 0.19$, $p = 0.04$) and \sum PFOA + PFOS ($|r_s| = 0.19$, $p = 0.04$). With the exception of \sum_2 short-chain PFCAAs ($|r_s| = 0.15$, $p = 0.11$) and \sum_3 long-chain PFCAAs ($|r_s| = 0.12$, $p = 0.18$), significant and negative correlations were also observed for the remaining PFAS groups ($|r_s| = 0.18$, $p < 0.05$). For cumulative 30-d antecedent rainfall (Fig. 2), significant and negative correlations were observed for \sum_{26} PFAS ($|r_s| = 0.39$, $p < 0.01$), \sum PFOA + PFOS ($|r_s| = 0.35$, $p < 0.01$) and all remaining PFAS groups ($|r_s| = 0.26$, $p < 0.01$). However, for cumulative one-year antecedent rainfall (Fig. 2), a significant and positive correlation was observed for \sum_{26} PFAS ($|r_s| = 0.31$, $p < 0.01$), \sum PFOA + PFOS ($|r_s| = 0.29$, $p < 0.01$) and all remaining PFAS groups ($|r_s| = 0.19$, $p < 0.05$). Florida is subject to considerable climate differences given its peninsula and areas adjacent to the continental US. As a result, there are significant annual differences in rainfall due to the differences in climate. We suspect that the positive correlation with rainfall reflects these different climate conditions with wetter warmer climates in the State towards the south and drier cooler climates to the north. Since PFAS samples were collected at one point in time, we believe that the instantaneous measurements observed are a combination of short-term rainfall effects combined with broader climate differences that are better reflected by annual rainfall values. Therefore, results suggest that lower PFAS concentrations were detected in the leachate for higher short-term rainfall amounts (for 14 and 30 d before the sampling date). This change can be explained by the dilution from rainfall, which was similar with the results from some previous studies (Benskin et al., 2012; Gallen et al., 2017;

Wreford et al., 2000). Similarly, the higher PFAS concentrations associated with higher annualized rainfall reflect broader climate impacts with warmer wetter climates resulting in higher PFAS concentrations from landfills. This is also consistent with the literature (Lang et al., 2017).

3.3. Gas condensate from different sources

In this study, gas condensates were collected from MSW and CDD landfills. Although the volume of gas condensate generated is small relative to the amount of leachate, it is a potential source of concentrated PFAS. The estimated volume amount of gas condensate was publicly available for only one of the studied landfills (FDEP, 2020). The generation volume for the gas condensate (mixed source) for this landfill was 0.025 L s^{-1} (equivalent to 0.58 mgd), which was less than 1% of the generation volumes of related landfill leachate.

In this study, the configurations of the gas condensate collection systems also varied by landfill. These configurations included gas wells, flare stations and mixed sources (e.g., leachate management structure that receives both leachate and gas condensate). Given the distinct differences observed in gas condensates from MSW versus CDD gas wells, the discussion that follows further separated gas condensates from gas wells into MSW and CDD. Based on the average (Fig. 5), gas condensates from MSW gas wells had the highest $\sum_{26}\text{PFAS}$ (avg: 22,000 ng L^{-1} ; std: 28,000 ng L^{-1}); gas condensates mixed with some MSW leachate had moderate-values of $\sum_{26}\text{PFAS}$ (avg: 18,000 ng L^{-1} ; std: 4,100 ng L^{-1}); gas condensates from flare stations had lower $\sum_{26}\text{PFAS}$ (avg: 14,000 ng L^{-1} ; std: 9,200 ng L^{-1}); and gas condensates from CDD gas wells had the lowest $\sum_{26}\text{PFAS}$ (avg: 1,200 ng L^{-1} ; std: 2,300 ng L^{-1}).

As mentioned in the methods section, gas condensates from gas wells, mixed sources, and flare stations, were considered as liquids with low, moderate, and high proportions of pure gas condensate. Higher detected PFAS in gas condensate from MSW gas wells than that from flare stations was consistent with Smallwood et al.'s (2023) study. When comparing these three categories of gas condensate (MSW gas wells, mixed sources and flare stations), results (Fig. 5) suggest that when the proportion of true pure gas condensate was higher within the sample (higher for flare station samples compared to MSW gas wells), fractions of $\sum_4\text{short-chain PFCAs}$ ($\sum_4\text{short-chain PFCAs}/\sum_{26}\text{PFAS} = 7.1\%$, 19%, and 35%) and $\sum_7\text{long-chain PFCAs}$ ($\sum_7\text{long-chain PFCAs}/\sum_{26}\text{PFAS} = 13\%$, 15%, and 33%) were higher. Specifically, for $\sum_7\text{long-chain PFCAs}$ in gas condensate from the flare station, PFOA was predominant ($\sum \text{PFOA}/\sum_{26}\text{PFAS} = 24\%$). To explain this distribution, it is known that some PFAS are volatilized under specific environmental conditions (Sima and Jaffé, 2021). For example, PFOA was detected directly through volatilization in natural water bodies or landfill environments (Ahrens et al., 2011; Goss, 2008). In addition, short-chain PFCAs, like PFBA ($K_H = 1.2 \text{ Pa m}^3 \text{ mol}^{-1}$), are more volatile than PFOA ($K_H = 0.36 \text{ Pa m}^3 \text{ mol}^{-1}$) (Kotthoff and Bücking, 2018; Centers for Disease Control and Prevention, 2018) based upon Henry's Law gas constants. Considering that gas condensate is liquid condensed from warm gas evaporated from landfill leachate, preferential volatilization may explain the distribution of PFAS groups, including the dominance of short-chain PFCAs and PFOA in gas condensate

from flare stations. Smallwood et al. (2023) showed that PFAA-precursors were dominant in both MSW gas wells and flare stations, and PFAA-precursors in flare stations were higher than that in MSW gas wells. However, the current study showed that PFAA-precursors were only dominant in the gas condensate from MSW gas wells, which was higher than that in gas condensate from flare stations. The opposite results for gas condensate between these two studies may be due to having more PFAA-precursors analyzed in Smallwood et al. (2023) study, although 5:3 FTCA was the major contributor for PFAA-precursors in Smallwood et al. (2023) study and was also evaluated in the current study. Alternatively, this may be also explained by the variability of anaerobic process in different landfills as Smallwood et al. (2023) study was conducted at three MSW landfills whereas the MSW gas condensate and flare station data correspond to two CDD landfills and seven MSW landfills in the current study.

When only comparing the gas condensates from MSW and CDD gas wells (Panel b of Fig. 5), \sum_{26} PFAS in gas condensate from MSW gas wells was significantly higher than that in gas condensate from CDD gas wells ($p < 0.01$). In addition, similar with the \sum_{26} PFAS, \sum PFOA + PFOS in gas condensate from MSW gas wells (avg: 3,000 ng L⁻¹, std: 3,500 ng L⁻¹) was significantly higher than that from CDD gas wells (avg: 210 ng L⁻¹, std: 340 ng L⁻¹, $p = 0.04$). This may be reflective of the lower levels of PFAS in CDD leachates compared to MSW leachates mentioned earlier, although this difference was not significant in the leachates. For fractions of PFAS groups (Panel a of Fig. 5) in gas condensate from MSW and CDD gas wells, PFAA-precursors were dominant for MSW gas wells (\sum_8 PFAA-precursors/ \sum_{26} PFAS = 67%) and short-chain PFCAs were dominant for CDD gas wells (\sum_7 short-chain PFCAs/ \sum_{26} PFAS = 41%). This is also reflective of the distribution of PFAS groups in MSW and CDD leachate.

3.4. Stormwater from different sources

In all collected stormwater, 71% of results were below the detection limit (DL) or limit of quantification (LOQ). Based on the median, PFAS levels were relatively low in stormwater. Median \sum_{26} PFAS in stormwater (470 ng L⁻¹) was significantly lower than leachate and gas condensate ($p < 0.01$) and was significantly higher than groundwater ($p < 0.01$). The typical concentration of PFAS in rainfall ranges from 0.9 to 13 ng L⁻¹ (Kim and Kannan, 2007). Thus, the PFAS levels in the stormwater observed at the landfills were above what would be expected from rainfall suggesting that other sources of PFAS are impacting runoff. It is possible that when rainfall goes through the upper layers of the landfills, the infiltration encounters the disposed solid waste. This infiltration may avoid the leachate collection system by inadvertently contaminating runoff. Therefore, the PFAS released from the solid waste may impact PFAS in stormwater. More research is needed to confirm the source of PFAS in stormwater detention areas at landfills.

For PFOA and PFOS in all collected stormwater specifically, 17% of PFOA and 29% of PFOS were below the DL or LOQ. Median \sum PFOA + PFOS in stormwater (65 ng L⁻¹) was also significantly lower than gas condensate and landfill leachate ($p < 0.01$) and was significantly higher than groundwater ($p = 0.02$). A study of surface water in urban watersheds in the US (Bai and Son, 2021) showed that \sum PFOA + PFOS levels were 9.1 ng

L^{-1} and 40 ng L^{-1} . Another study conducted in Alabama US found that $\sum \text{PFOA} + \text{PFOS}$ levels were not detected in three of 14 selected natural water bodies, thereby confirming low natural background levels in the state. Among the 14 waters with detectable levels, the levels ranged from 0.19 ng L^{-1} to 44 ng L^{-1} (Viticoski et al., 2022). In our study, the levels of $\sum \text{PFOA} + \text{PFOS}$ in stormwater was higher than surface water in existing studies. More research is needed to evaluate the cause of the higher $\sum \text{PFOA} + \text{PFOS}$ in stormwater within landfill boundaries with an emphasis on evaluating whether such waters are impacted by inadvertent contamination of runoff by landfill leachate.

In addition, stormwater samples from the current study were usually collected from detention ponds that surround the landfills. As mentioned in the methods section, some stormwaters were collected in pairs based on inlets and outlets of detention ponds. Comparing the stormwater collected from inlets and outlets of the detention ponds, median $\sum_{26} \text{PFAS}$ in the stormwater outlet (590 ng L^{-1}) was lower than that in the stormwater inlet (990 ng L^{-1}), and the difference was significant ($p = 0.07$) based on 90% confidence interval. Although median $\sum \text{PFOA} + \text{PFOS}$ in the stormwater outlet (110 ng L^{-1}) was also lower than that in the stormwater inlet (210 ng L^{-1}), this difference was not significant for $\sum \text{PFOA} + \text{PFOS}$ ($p = 0.43$). In addition, the fraction of PFAS groups between the stormwater outlet and inlet were similar, and the difference of fraction was less than $\pm 5\%$. Results suggested that $\sum_{26} \text{PFAS}$ can be reduced when stormwater goes through the detention ponds before discharging into off-site receiving water bodies. This reduction may be caused by rainfall dilution, possible volatilization of PFAS from the water surface, and/or sedimentation of particulates containing PFAS.

3.5. Groundwater from different sources

In terms of all collected groundwater, 78% of results were below the DL or LOQ. Median $\sum_{26} \text{PFAS}$ (140 ng L^{-1}) was significantly lower than landfill leachate, gas condensate, and stormwater ($p < 0.01$). As mentioned in the methods section, collected groundwater can be classified based on the type of solid waste accepted. When comparing the median $\sum_{26} \text{PFAS}$ in groundwater under MSW (130 ng L^{-1}), CDD (100 ng L^{-1}) and MSWI ash (180 ng L^{-1}) disposal areas, there were no significant differences among them ($p > 0.39$).

For the three types of leakage control systems mentioned in the methods section, background samples are typically upgradient groundwater from landfills without leakage control systems, with synthetic lined systems and for groundwater located outside the slurry wall systems. Results of background samples showed that median $\sum_{26} \text{PFAS}$ in upgradient groundwater from landfills without leakage control systems and with synthetic lined systems were 62 ng L^{-1} and 77 ng L^{-1} , respectively, and there was no significant difference between them ($p = 0.68$). Median $\sum_{26} \text{PFAS}$ was the highest in the groundwater outside the slurry wall systems (280 ng L^{-1}), which was significantly higher than $\sum_{26} \text{PFAS}$ in upgradient groundwater from landfills without leakage control systems and from landfills with synthetic lined systems ($p < 0.03$).

When comparing the upgradient and downgradient groundwater for landfills without leakage control systems and for landfills with synthetic lined systems (Fig. 6), different trends were observed between their \sum_{26} PFAS levels. For landfills without leakage control systems, median \sum_{26} PFAS in downgradient groundwater (210 ng L^{-1}) was significantly higher than that in upgradient groundwater (62 ng L^{-1} , $p = 0.01$). This suggests PFAS in leachate can impact the groundwater directly if there is no lined system. For synthetic lined systems, median \sum_{26} PFAS in downgradient groundwater (190 ng L^{-1}) was higher than that in upgradient groundwater (77 ng L^{-1}), but the difference was not significant ($p = 0.16$). This result makes the differences between the upgradient and downgradient groundwater for landfills with synthetic lined systems inconclusive. More samples should be collected from lined landfills to confirm potential trends. For slurry wall systems, median \sum_{26} PFAS in groundwater outside the slurry wall (280 ng L^{-1}) was similar with that in groundwater inside the slurry wall (280 ng L^{-1}) without a significant difference ($p = 0.26$). This suggests no difference between PFAS levels inside and outside slurry wall systems.

For PFOA and PFOS in all collected groundwater specifically, 32% of PFOA and 42% of PFOS were also below the DL or LOQ. Median $\sum \text{PFOA} + \text{PFOS}$ (20 ng L^{-1}) was significantly lower than landfill leachate, gas condensate, and stormwater ($p < 0.01$). In terms of the comparison of $\sum \text{PFOA} + \text{PFOS}$ between upgradient and downgradient groundwater, the results was similar with \sum_{26} PFAS. Significant differences were only observed for landfills without leakage control systems ($p = 0.02$) and no significant differences were observed for landfills with slurry wall systems ($p > 0.85$), nor for landfills with synthetic lined systems ($p > 0.16$). Based on the median, the groundwater that exceeded the drinking water health advisory ($<70 \text{ ng L}^{-1}$) issued by EPA in 2016 (Hamid et al., 2018; US EPA, 2016) were from the downgradient wells for landfills without leakage control systems (93 ng L^{-1}) and for groundwater inside the slurry wall systems (78 ng L^{-1}). All remaining groundwater had median $\sum \text{PFOA} + \text{PFOS}$ levels lower than 70 ng L^{-1} . For example, median $\sum \text{PFOA} + \text{PFOS}$ in upgradient groundwater from landfills without leakage control systems and from landfills with synthetic lined systems were both below 10 ng L^{-1} ; median $\sum \text{PFOA} + \text{PFOS}$ in groundwater downgradient from lined landfills was measured at 27 ng L^{-1} ; and median $\sum \text{PFOA} + \text{PFOS}$ in groundwater outside slurry walls was measured at 64 ng L^{-1} .

For PFAS groups in all categories of groundwater shown in Supplement Fig. S5, short-chain PFCAs were dominant (from 60% to 76% $\sum_4 \text{short-chain PFCAs} / \sum_{26} \text{PFAS}$) and the fraction of PFAA-precursors (from 0.83% to 6.7% $\sum_8 \text{PFAA-precursors} / \sum_{26} \text{PFAS}$) were less than that observed for leachates and gas condensates. For landfill without leakage control system, or with synthetic liners, the differences of the fraction of the five PFAS groups between the upgradient and downgradient were within 10% of \sum_{26} PFAS. These trends suggest that detected PFAS in all types of groundwater were dominated by short-chain PFCAs.

One limitation associated with the groundwater results for this study was high variability of \sum_{26} PFAS detected in some groundwater samples, as mentioned before. For the groundwater with high \sum_{26} PFAS, levels exceeded $1,000 \text{ ng L}^{-1}$, elevated levels may be due to the impacts

from leachate from older unlined solid waste disposal areas. Many of these landfills have been used historically to dispose solid waste and due to the long history, some of the disposal areas may not be entirely known, which may suggest impacts from unmanaged leachate. It is common for newer, properly managed landfills to be constructed near and/or above older waste sites for which leachate management may be lacking. For example, high \sum_{26} PFAS (10,000 ng L⁻¹) was detected in one of the groundwater samples. This sample corresponded to an unlined CDD disposal area with two lined MSW disposal areas stacked above. Due to the difficulties in choosing landfill sites, it is common for new landfills to be constructed atop old unlined landfills. In addition, PFAS sources from adjacent areas can possibly impact groundwater PFAS levels. These possibilities may also cause higher detected PFAS than expected in downgradient groundwater. Therefore, more work is needed to better understand possible sources of PFAS at landfills showing increases in PFAS within the groundwater.

4. Conclusions

This study focused on evaluating PFAS in landfill leachates, gas condensates, stormwater, and groundwater, and on identifying relationships between PFAS levels and landfill characteristics. Results are useful for prioritizing methods for leachate management systems and solid waste disposal facilities to reduce the impact of PFAS to natural water bodies and groundwater.

Among landfill leachates evaluated, municipal solid waste (MSW) leachate had the highest \sum_{26} PFAS and municipal solid waste incineration (MSWI) ash leachate had the lowest \sum_{26} PFAS. For landfill leachate generated from landfill cells having higher MSWI ash proportions, lower detected PFAS levels were observed suggesting that incineration can destroy some PFAS or volatilize shorter-chain PFCAs. Alternatively, the physical and chemical properties of MSWI ash could also influence the relative loss of PFAS.

For the fraction of PFAS groups in landfill leachate, short-chain PFCAs and PFAA-precursors were dominant. Long-chain PFASs were dominant in CDD leachates and PFAA-precursors were dominant in gas condensate, especially for gas condensate from flare stations at MSW facilities. Lower fractions of PFAA-precursors and higher fractions of short-chain PFCAs were observed in stormwater and groundwater. In addition, some PFAS groups in landfill leachate have been found to be associated with waste proportions, waste age, operational status of landfills, and antecedent short-term rainfall. Based on correlations, \sum_{26} PFAS was generally higher during times of lower short-term rainfall for landfills accepting more MSW and less MSWI ash. \sum PFOA + PFOS was generally higher in the older landfills accepting less MSWI ash.

For gas condensate specifically, pure gas condensate from the flare stations had lower \sum_{26} PFAS than gas condensate mixed with MSW leachate, and PFAA-precursors converted into PFCAs in the pure gas condensate. Also, gas condensate from CDD landfills were observed to have lower \sum_{26} PFAS than that from MSW landfills. However, the information about the generation volume of these gas condensates is limited. Based on the available

information, it seems that the impact of liquid-phase gas condensate is less than the impact of leachate generated for the study landfills due to the relatively small volumes of gas condensate. In addition, inhalation exposure of PFAS is another consideration, but volatile gas-phase PFAS data were not collected from landfills in this study. This data should be obtained through future work to further understand potential exposure routes of PFAS from landfills.

Comparison of stormwater between the inlets and outlets of detention ponds suggested that these ponds reduce PFAS levels. For groundwater impacted by landfills where leachate was not managed, PFAS levels increased in downgradient wells. Additional comparisons for groundwater were inconclusive. Statistical differences were not observed for groundwater impacted by lined landfills nor slurry-wall landfills. More research is needed to better understand the level of protection afforded by leachate management systems in protecting groundwater resources from PFAS.

In terms of landfill management of PFAS, results suggest that PFAS management should focus on MSW and CDD leachates and to a lesser extent, MSWI ash leachates, especially during the active phase of the landfill. Gas condensates, especially when mixed with leachates, can also be a significant source of PFAS. Given that \sum PFOA + PFOS in some stormwater and groundwater samples exceeded the drinking water guidance level, efforts are needed to manage these water sources at landfills.

An overall limitation of this study is that all samples were collected within a defined geographic region of Florida. Florida is generally characterized by a warm wet climate and results may be applicable to landfills in similar climates. Efforts should focus on expanding such research to include aqueous sample measurements for landfills throughout the US and globally to better evaluate the relationships between the PFAS concentration and waste composition, climate conditions and landfill design.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data availability

Data will be made available on request.

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HIGHLIGHTS

- \sum_{26} PFAS in gas condensate \approx landfill leachates $>$ stormwater $>$ groundwater.
- Among landfill leachates, \sum_{26} PFAS concentrations in MSW $>$ CDD $>$ MSWI ash.
- PFCAs dominant in all aqueous samples and precursors also dominant in leachates.
- \sum_{26} PFAS significantly correlated with some landfill characteristics.
- Results can be used to inform management of liquids at landfills.

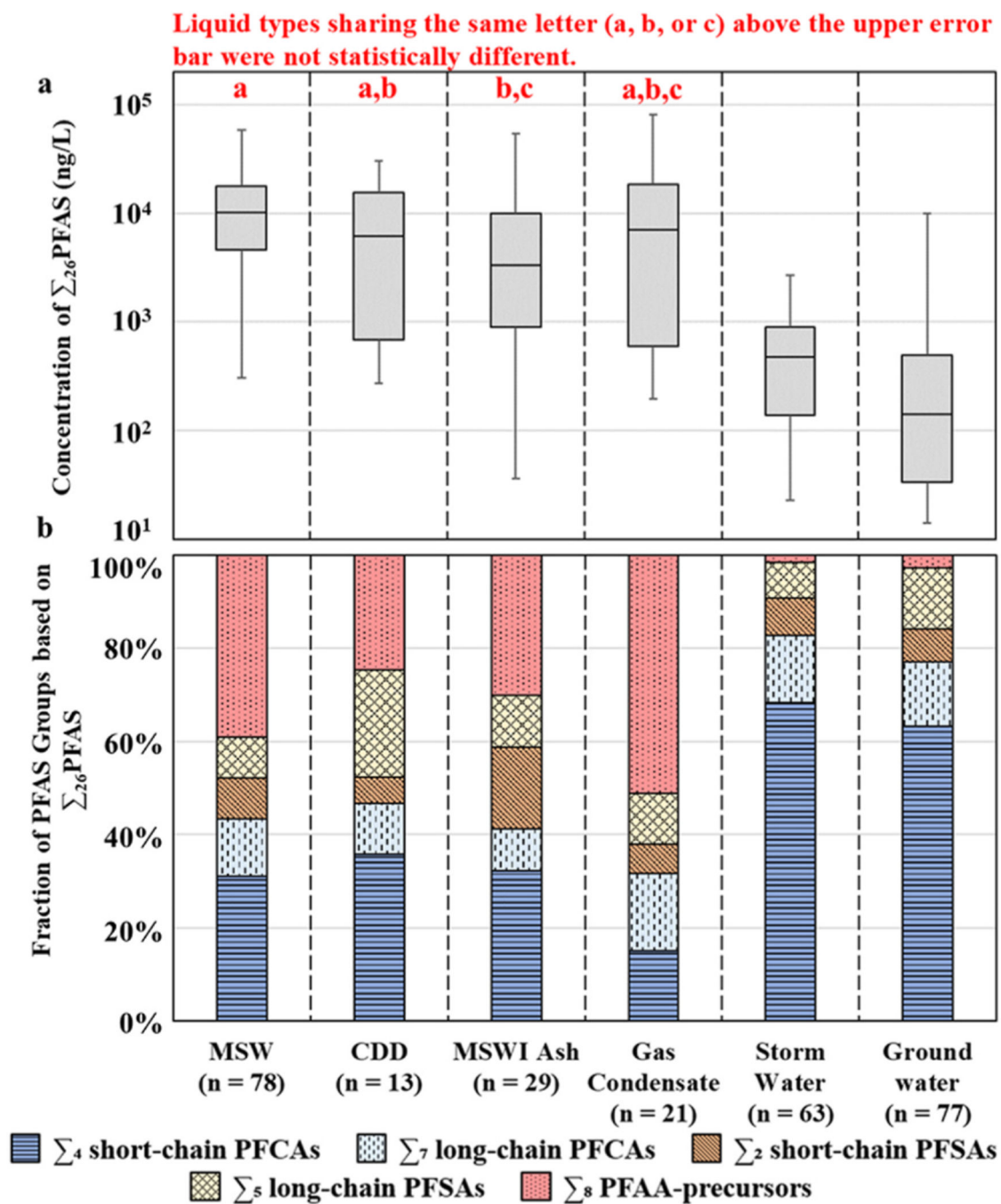
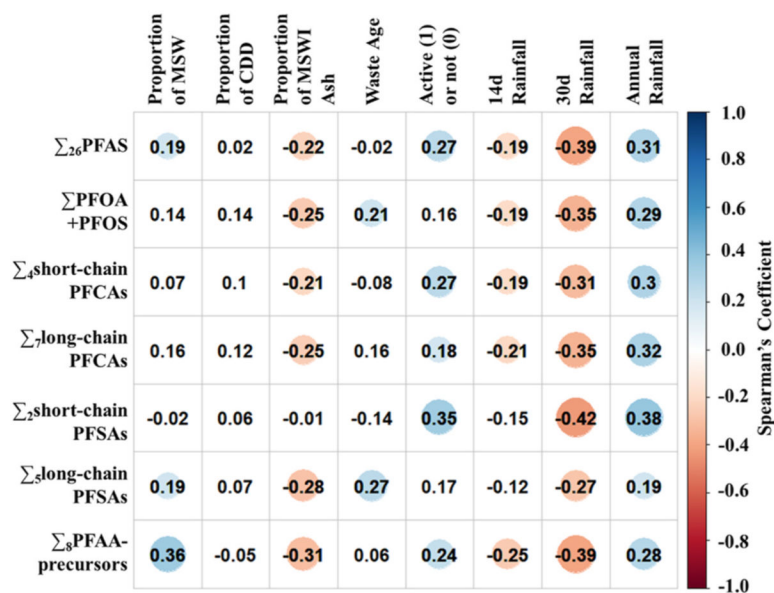
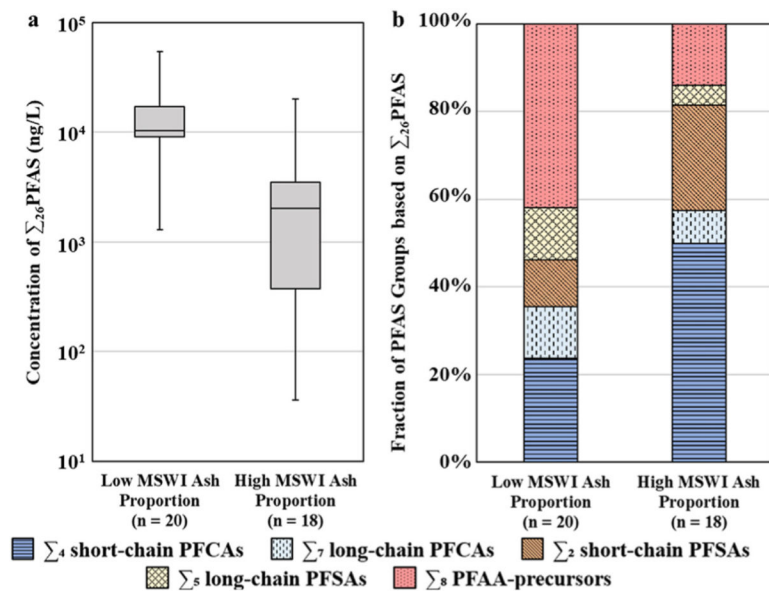


Fig. 1.

Panel a, measurements of Σ_{26} PFAS in six types of aqueous landfill samples. The median is the line within each box, the 25% and 75% quartiles are the lower and upper border of each box, the minimum and maximum are the lower and upper extremes shown in error bars. Panel b, detected PFAS groups, by fraction of Σ_{26} PFAS in six types of aqueous landfill samples based on the average.

**Fig. 2.**

PFAS correlation matrix between leachate (including MSW, CDD and MSWI ash) and landfill characteristics. Blue means significant positive Spearman's correlation ($p \leq 0.05$); Red means significant negative Spearman's correlation; blank background color means non-significant Spearman's correlation ($p > 0.05$). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Fig. 3.**

Panel a, measurements of Σ_{26} PFAS in leachate samples from disposal areas with low (< 50%) and high (> 50%) proportions of MSWI ash. Panel b, fraction distribution of detected PFAS groups in leachate with low and high proportions of MSWI ash.

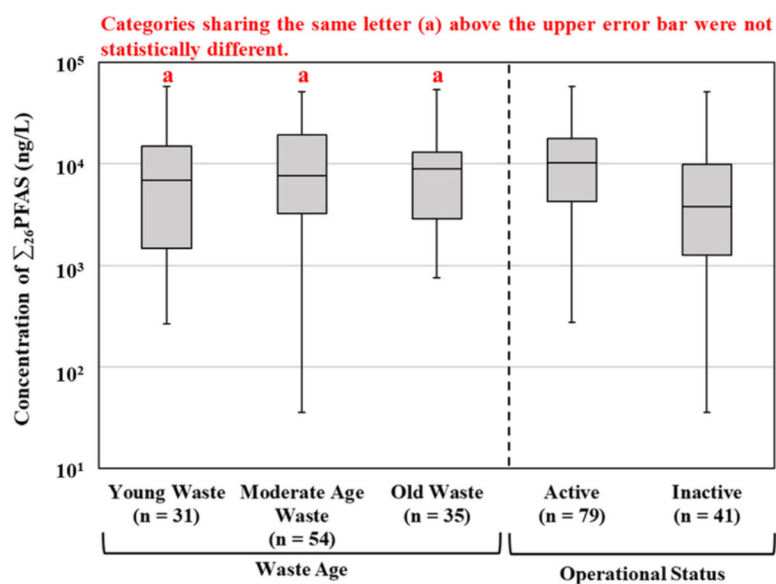


Fig. 4. Measurements of Σ_{26} PFAS in MSW leachate samples from solid wastes with different ages, or from landfills with different operational status.

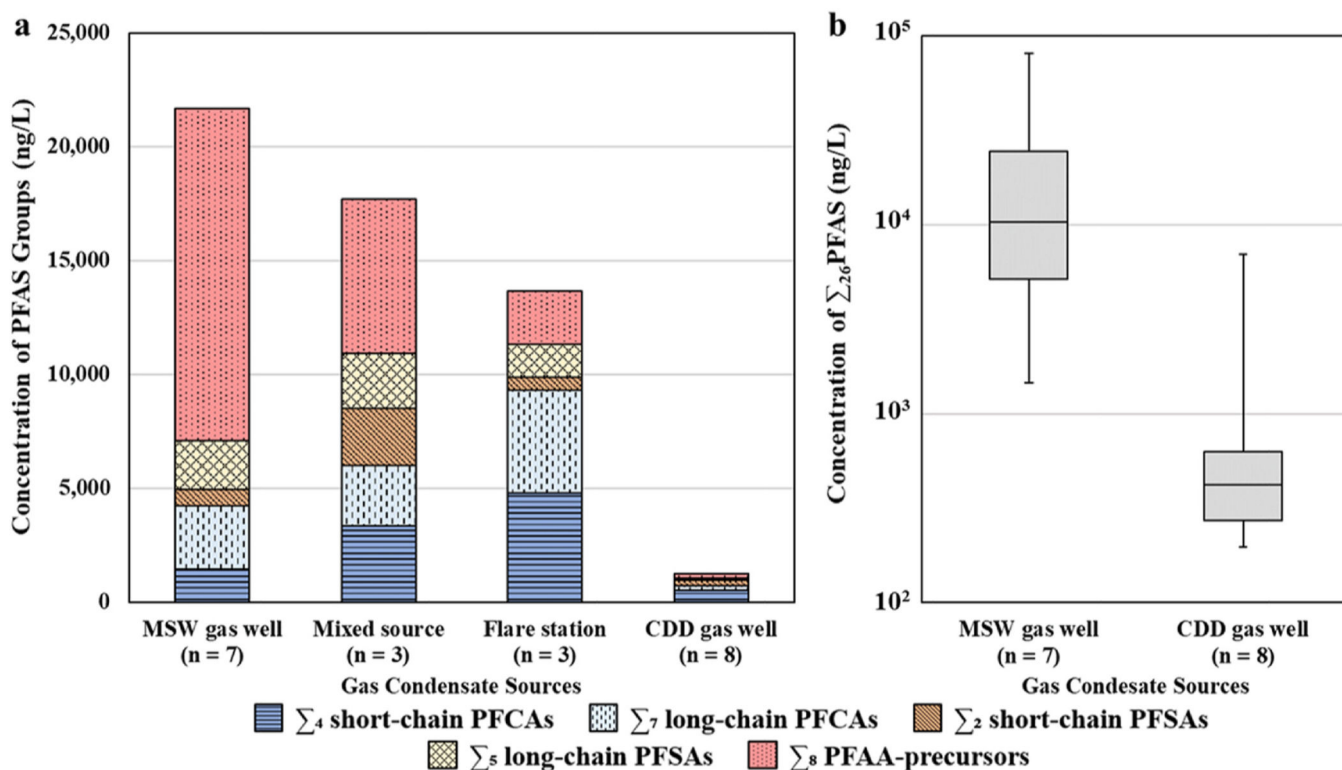


Fig. 5.

Panel a, measurement of detected PFAS groups in different types of gas condensate. Panel b, measurements of Σ_{26} PFAS in gas condensate samples from MSW and CDD landfills. The GC mixed with leachate and from the flare station did not have enough samples for plotting in panel b.

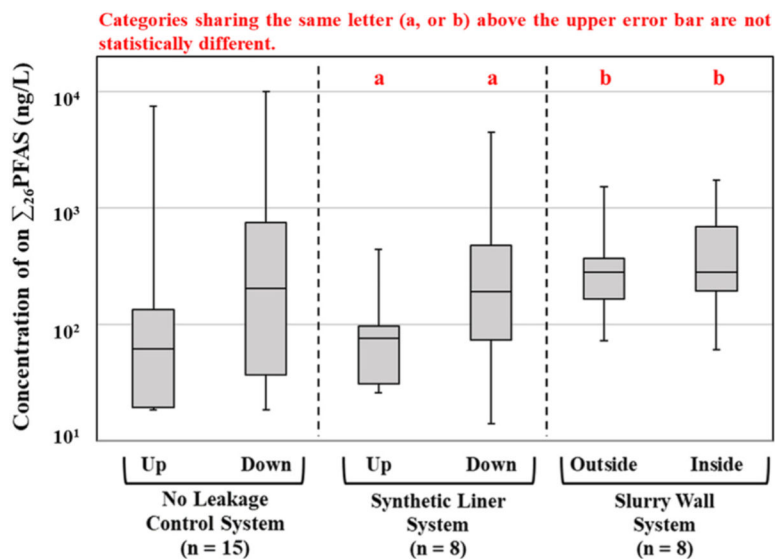


Fig. 6. Measurements of Σ_{26} PFAS in groundwater from landfills with different types of leakage control systems (Up = groundwater upgradient; Down = groundwater downgradient).