City-scale impacts of PFAS from normal and elevated temperature landfill leachates on wastewater treatment plant influent

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HIGHLIGHTS

- First investigation of PFAS in elevated temperature landfill leachate.
- Both leachates contain high concentrations of ultra-short-chain PFAS and precursors.
- Thermal condition of landfills impact PFAS speciation.
- Leachate impacts on WWTP influent depends on size of the facility.

GRAPHICAL ABSTRACT
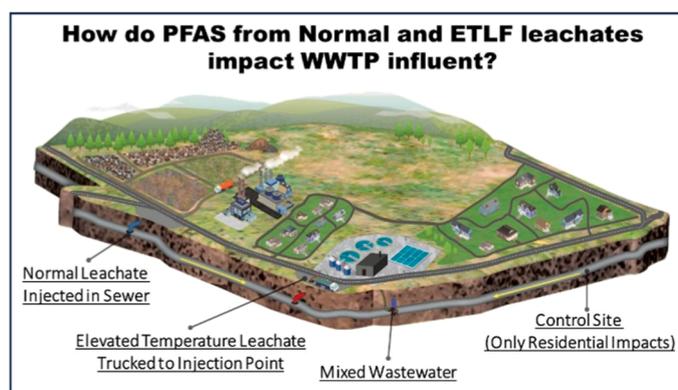
ABSTRACT

The influence of elevated temperatures on PFAS leaching in municipal solid waste (MSW) landfills has not been well characterized in the published scientific literature. This study systematically examined the compositions and concentrations of per- and polyfluoroalkyl substances (PFAS) and precursors content in both normal temperature landfill and elevated temperature landfill (ETLF) leachates and compared to a municipal wastewater and to a WWTP influent with and without introduced leachates. The characterization of the samples involved the analysis of 71 PFAS target compounds before and after applying the total oxidizable precursor (TOP) assay, along with measuring fluorotelomer alcohols (FTOHs) and adsorbable organofluorine (AOF) levels. Summed PFAS concentrations in leachates were driven largely by fluorotelomer carboxylic acids (FTCAs), short-chain and ultrashort-chain perfluorinated carboxylic acids and sulfonic acids. Summed PFAS concentrations in ETLF

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leachate were significantly higher than in normal leachate for precursors and terminal PFAS products. TOP assay data demonstrated that ETLF leachate contained significantly higher concentrations of oxidizable PFAS precursors than normal leachate. PFAS profiles in leachates were distinct from municipal wastewater and from WWTP influent, suggesting diverse PFAS inputs to the WWTP. The presence of unknown precursors revealed by the TOP assay and AOF analyses highlights the complexity of PFAS sources impacting sewer networks, warranting further study to better characterize PFAS inputs to the WWTP on a city-wide scale.

1. Introduction

Municipal solid waste (MSW) landfills receive a diverse array of non-hazardous solid wastes from local residential and commercial communities and represent a predominant form of waste management in the United States. Engineered to facilitate anaerobic decomposition, these landfills foster waste breakdown in the absence of oxygen. The temperature profiles within conventional MSW landfills generally conform to mesophilic (30–40 °C) or thermophilic (50–60 °C) conditions due to exothermic decomposition of organic materials in wastes. [1] In contrast, elevated temperature landfills (ETLFs) are characterized by even higher temperatures, up to or exceeding 100 °C [2], due to more strongly exothermic reactions from heat-generating waste materials such as aluminum dross or coal ash. [3,4] ETLFs are *not* landfills affected by fires. Landfill fires usually occur near the surface, where oxygen is available, impact a small area, and are quickly managed [5,6]. Although ETLFs are rare, approximately 1 % of active MSW landfills could be considered ETLFs, the reactions persist for decades and have detrimental impacts on landfill operations by requiring significant investment to mitigate or manage [7]. Conditions in ETLFs can compromise the integrity of liner systems [8], and potentially lead to melting of landfill gas collection infrastructure, in turn diminishing air pollution control efficacy. [3] Furthermore, the combination of rapid mass loss within the landfill and elevated temperatures condenses water in cooler portions of the landfill, leading to a rapid increase in leachate production rates at ETLFs and potentially remaining at above-average rates for years following the initiation of the conversion to ETLFs. [9] Leachates from ETLFs are characterized by elevated levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia (NH_3^+), volatile organic compounds (VOCs), and other organic components. Coupled with increased leachate volume, the properties of ETLF leachate render it much more challenging and expensive to treat compared to typical MSW landfill leachates [2,9].

One concern related to disposal of wastes containing per- and poly-fluoroalkyl substances (PFAS) in landfills is that these compounds can transfer into leachates and present an exposure risk to surrounding ecosystems and water resources. [10] PFAS, characterized by their persistence and potential adverse health effects, have garnered considerable attention in environmental research aimed at identifying and tracking their sources.[11,12] MSW landfills can serve as a reservoir and source of PFAS due to the disposal of consumer products containing these compounds, such as non-stick cookware, waterproof clothing, paper products, cleaning products, electronics and stain-resistant fabrics [13]. Furthermore, industrial waste, encompassing manufacturing byproducts and wastewater treatment plant sludges, can contribute significantly to PFAS concentrations in MSW landfill leachates. [14] Additionally, although liquids are generally banned from disposal in landfills, AFFF-treated debris from structure fires can end up in landfills and leach PFAS. Small quantities of containerized liquids containing PFAS such as firefighting foams and cleaning products if the container integrity is compromised can also end up in landfills and ultimately landfill leachates. [15] Terminal PFAS are known to be persistent in the environment and can accumulate in soil, water, and biota. Moreover, the complex chemical structures of PFAS make them particularly challenging to remediate effectively, further exacerbating concerns about their environmental impact. Given these multifaceted issues, addressing the sources and pathways of PFAS contamination in landfills is

paramount to mitigating the broader environmental and public health risks associated with these persistent pollutants [16].

Numerous investigations have been undertaken to elucidate the composition and environmental repercussions of typical landfill leachates stemming from conventional landfill operations. [10,15,17] In stark contrast, no data exists regarding the levels and speciation of PFAS in leachates from ETLFs. The distinctive thermal conditions in ETLFs can result in unique biogeochemical transformations and degradation kinetics relative to ambient systems. [9] These temperature-driven differences suggest PFAS profiles in ETLF leachates could diverge substantially from conventional facilities. Specifically, accelerated reactions due to elevated temperatures and the anoxic environment present within the landfill may lead to an enhanced breakdown of PFAS precursors and can alter the fate of existing compounds through alternative transformation or release pathways. [18] An investigation is needed to determine how thermal conditions impact PFAS transformation and transport within ETLFs. Developing an in-depth understanding of similarities and divergences between leachates generated under the range of temperature conditions found in landfills is paramount for optimizing waste management strategies, environmental monitoring protocols, and treatment approaches tailored to address specific PFAS challenges.

This study aims to bridge existing knowledge gaps by conducting a comprehensive investigation into the characteristics and implications of both normal and ETLF leachates concerning PFAS. Specifically, the research delves into elucidating the fate of PFAS within landfill environments, their subsequent transport to sewer systems, and their consequential impact on influents at wastewater treatment plants (WWTPs) at the city-wide scale. Analytical tools used for this examination included targeted PFAS analysis methods encompassing 71 PFAS compounds, including pretreatment using the total oxidizable precursor (TOP) assay as a proxy for total PFAS as well as adsorbable organofluorine (AOF) analysis. Fluorotelomer alcohols (FTOHs) were also analyzed including: 4:2, 6:2, 7:2, 8:2, and 10:2 FTOHs. To the best of our knowledge, this is the first study to assess PFAS occurrences in normal and ETLF leachates and to delineate their influence on WWTP influents. Given the intricacy of urban landscapes wherein diverse sources may contribute to PFAS contamination in waste and wastewater, a nuanced characterization of PFAS contributions from these varied sources is paramount to managing associated risks. The results from this investigation stand to inform the evaluation of challenges encountered by treatment operators grappling with PFAS contamination and how to determine risk assessments and management protocols.

2. Materials and methods

2.1. Municipal sewer district and landfill characteristics

The district collects and treats an average of 185 million gallons a day (MGD) of wastewater from 80 Significant Industrial Users (>25,000 GPD), 92 Non-Significant Industrial Users (<25,000 GPD), roughly 10,000 Commercial Users, and 232,000 households in a 290 square mile area conveyed through 3000 miles of sewer pipe. For the sewer-shed examined in this study, typical dry weather flow is 110 MGD, however during wet weather, the combined sewers can convey up to 430 MGD through the treatment processes. Flow above that capacity is lost from the system through designed overflow points.

The MSW landfill described in this investigation in Ohio, USA, receives an estimated 6000 metric tons of waste daily. Operating since the 1940s, the landfill spans approximately 150 ha of waste-in-place. Beginning in 2009, a sector of the landfill manifested elevated temperatures, diminishing methane gas concentrations, and surface seepage and geysers of leachate. Notably, sections of the northwestern slopes experienced rapid settlement and failure. The origin of this subsurface exothermic reaction is hypothesized to have originated from self-heating waste or water-reactive waste. This sustained smoldering has resulted in a substantial loss of airspace, affecting approximately 30 ha of the landfill, due to thermal degradation of waste. [3] Because of its large footprint coupled with the additional production of leachate from the elevated temperature sector, the landfill generates a significantly larger volume of leachate compared to standard MSW landfills, contributing on the order of 0.1–0.2 % of the District's typical dry weather wastewater flow. To manage leachate disposal effectively, two separate mechanisms are employed: direct injection of normal leachate (~150,000 gallons per day) into the sewer system linked to the landfill cell, and indirect injection involving hauling trucks to transport ETLF leachate (30,000–50,000 gallons per day) from on-site storage to an off-site injection point within the sewer system, distant from the wastewater treatment plant.

2.2. Sampling plan

Samples were collected over a 3-day span in October 2023 with the aim of sampling in dry days to avoid precipitation diluting influent samples. By coordinating with the operators at both the landfill and the WWTP, the injection of leachates into the sewer was controlled to capture different scenarios (Fig. 1), including: 1) normal leachate before injection into the sewer system, 2) ETLF leachate from transport trucks prior to off-site injection into the sewer system, 3) municipal wastewater taken from a residential pumping station at an intermediate point in the sewer system, 4) WWTP influent collected while no landfill leachate was being introduced to the sewer system, 5) WWTP influent collected while only normal leachate was introduced to the sewer system, and 6) WWTP influent collected while normal and ETLF leachates were introduced. All wastewater influent samples were taken at the post-grit location in the WWTP. Leachate-free wastewater samples were collected by shutting down normal or ETLF leachate injection into the sewer system for 24 h,

which was enough time to flush leachate out of the system based on calculated hydraulic conditions. Similarly, wastewater influent samples with normal and ETLF leachates were captured at the influent using the same hydraulic calculations. A total of 18 samples were collected in triplicate for each of the six different scenarios for testing by the respective analytical procedures. Wastewater and leachate samples were collected in polyethylene sample containers at 125 mL volume for targeted PFAS analysis pre- and post-TOP assay and for AOF analysis, while samples collected for FTOH analysis were collected in 250 mL containers. Extra replicate bottles were collected for re-analysis for each sample.

2.3. PFAS analysis

Detailed descriptions of all PFAS analytical methods used in the study are listed in **Section S1** in the supporting information (SI) file. Briefly, aqueous samples were prepared for targeted analysis by solid phase extraction with a weak anion exchange sorbent, and sample extracts were analyzed using LC-MS/MS with isotope dilution or extracted internal standard calibration targeting 71 analytes. In combination with the targeted PFAS analysis, replicate samples were also pretreated via the TOP Assay technique as developed by Houtz and Sedlak [19]. Aqueous sample results with and without TOP Assay pretreatment were compared to estimate PFAS precursors content that could form oxidized transformation products during or after wastewater treatment processes. To assess potential impacts from unknown PFAS or other fluorinated chemicals beyond the targeted PFAS analytes with and without the TOP Assay pretreatment procedure, samples were also analyzed for Adsorbable Organic Fluorine (AOF) where a sample aliquot is passed through a carbon adsorbent, washed with a dilute nitrate solution to remove inorganic fluorine, and analyzed by combustion ion chromatography (CIC).

2.4. Conventional wastewater quality analysis

All samples were analyzed following standard methods listed in Table S2 for basic water quality parameters, including dissolved organic carbon (DOC), biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total kjeldahl nitrogen (TKN),
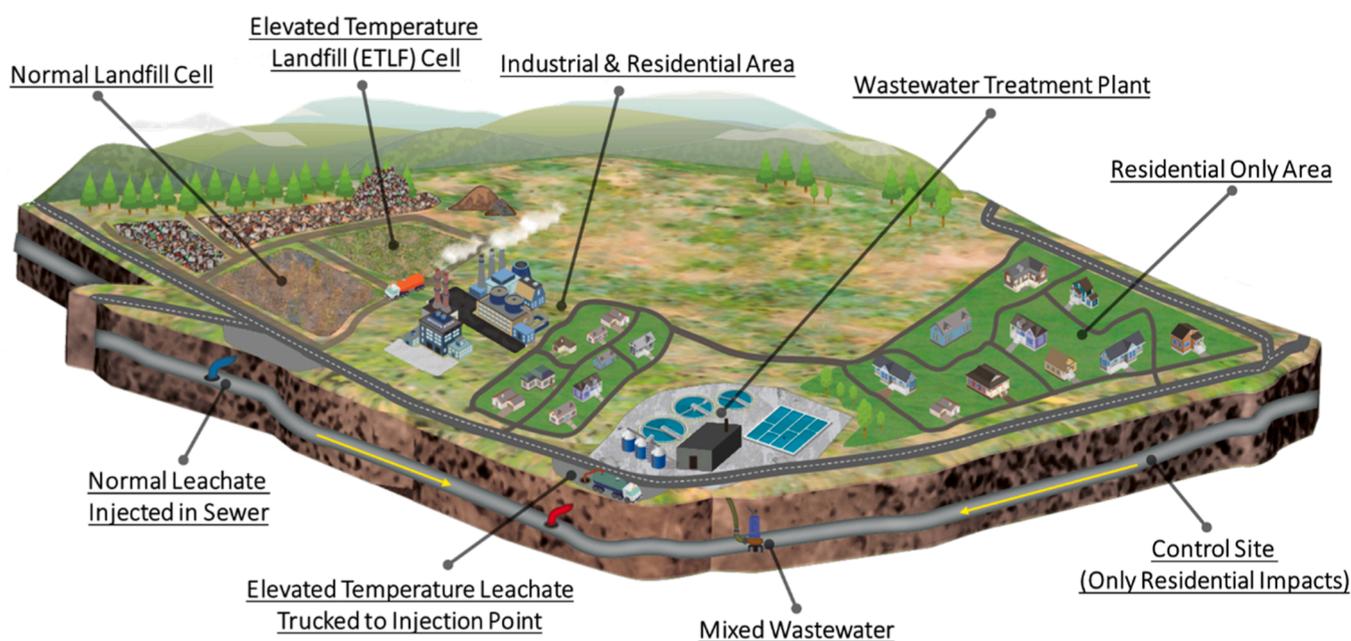
Fig. 1. Graphical illustration of the different scenarios and sample types captured in this study, including normal leachate, elevated temperature landfill (ETLF) leachate, municipal-only wastewater, and wastewater treatment plant (WWTP) influent samples with and without leachate impacts.

nutrients, and cyanides. Samples for basic water quality analysis were collected only once per operation scenario. Available historical data on BOD, COD, TKN, and TSS was also reported from the operator for a comparison to ensure that water quality during sampling was comparable to historical trends.

3. Results and discussion

3.1. Conventional wastewater quality of leachates

The measured concentrations of TSS, BOD, COD, and TKN in this study demonstrate that the sampled leachates are representative of both normal and ETLF leachate types and fall within the range of data collected by operators over the past decade (see Table 1 and Fig. S1). Overall, the results indicate notable disparities between the two leachate types, with ETLF leachate consistently exhibiting significantly higher levels of both organic and inorganic constituents compared to unaffected areas generating normal leachate, i.e., at a lower temperature range. [9] Specifically, the difference in concentrations of DOC, BOD, and COD between normal and ETLF leachates measured in this study can be as high as an order of magnitude, while solids and nutrient concentrations can vary by a factor of 2–5. This marked distinction can be attributed to thermal reactions within the landfill, which in turn lead to accelerated chemical degradation of waste. Moreover, elevated temperatures within the landfill environment typically diminish microbial activity, thereby impeding biodegradation of leachate as it permeates through the waste mass. The increasing temperature could also facilitate aqueous dissolution, resulting in higher concentrations of chemicals in the ETLF leachates. Exothermic reactions from increased temperatures were first observed at this location in 2009 and have persisted for over a decade. The high standard deviation in recoded historical data between 2011 and 2023 might be due to the shift from normal to higher temperature conditions. These elevated concentrations may pose a significant challenge for operators of municipal WWTPs tasked with managing influent source concentrations to prevent adverse impacts on the treatment trains and their efficacy.

3.2. PFAS in normal vs. ETLF leachates

3.2.1. Targeted PFAS analysis

Elevated concentrations of PFAS were identified in both normal (ΣPFAS = 49,069 ± 4398 ng/L) and ETLF (ΣPFAS = 67,088 ± 1268 ng/L) leachates ($p \ll 0.05$ via a two-tailed t-test with equal variances). Among the 71 targeted PFAS, 15 were measured at concentrations above

their respective minimum reporting levels including PFAS representing various classes and carbon chain lengths (see Fig. 2). The notably higher ΣPFAS concentrations observed in this study compared to previous investigations can be ascribed to the expanded list of targeted analytes, including PFPrA and the FTCAs (Table S3). Fluorotelomer alcohols (4:2, 6:2, 8:2, and 10:2 FTOHs) were also targeted but were all below the method reporting limit (Section S1), and the results are not further analysted here. Concentrations of PFPrA, PFBS, and 5:3 FTCA were found at the highest levels in both leachate types, with concentrations approaching or exceeding 10,000 ng/L, followed by PFBA, and PFHxA at concentrations on the order of 3000–5000 ng/L. These ultrashort- and short-chain PFAS are highly water soluble, rendering them more mobile and prone to partitioning into landfill leachates than their longer-chain counterparts. [20] Isotopically labeled FTOH surrogates showed low recovery rates ranging from 14 % to 29 % in normal leachate samples, and were not recovered in ETLF leachate samples. As a result, all FTOH results were below the Lower Limits of Quantitation. These findings suggested that further optimization of sampling procedures and holding times and improvements in recovery during extraction would improve the usefulness of the FTOHs analysis for landfill leachate. Addressing these challenges is crucial for accurately assessing the presence and fate of FTOHs and their transformation products, such as FTCAs, in landfill environments. [21] FTOHs may have been present but due to matrix interferences, poor stability or poor recovery they were not detected in the samples.

Fluorotelomer carboxylic acids (FTCAs) and fluorotelomer sulfonates (FTSs) are among PFAS precursors that were found in both normal and ETLF leachates at varying concentrations (see Fig. 2). Notably, 5:3 FTCA was measured at the highest concentration among all PFAS precursors, exceeding 10,000 ng/L in both normal temperature and ETLF leachates. 5:3 FTCA has been identified as an oxidative transformation product of PFAS precursors such as FTSs and FTOHs, and it has also been linked to leaching from treated carpets and textiles. [14,22] While normal leachate contained 3:3 FTCA, 6:2 FTCA, and 7:3 FTCA at concentrations on the order of 300- 1100 ng/L, these compounds were not positively identified in ETLF leachate. However, the FTCA results in the normal leachates were near or below the LOQs in the ETLF leachates due to extraction of smaller ETLF leachate sample volumes, so it was not clear whether these apparent compositional differences in the PFAS profiles from these sources was in fact due to differences in sensitivity (File S2). Further investigations may be warranted to better understand the influence of temperature on PFAS precursor transformation processes and on fate and transport mechanisms of PFAS within and from

Table 1
Water Quality Results measured in this study and historical data collected over the past decade for both leachate types.

Water Quality Parameter	This Study (mg/L)		Historical Trends 2011-2023 (mg/L) (± Std Dev)	
	Normal Leachate	ETLF Leachate	Normal Leachate	ETLF Leachate
TSS	307	1473	410 (± 318)	917 (± 797)
BOD	1330	30,455	829 (± 619)	29,700 (± 6620)
COD	5760	53,200	12,800 (± 25,200)*	56,100 (± 25,300)*
TKN	1400	2560	1300 (± 594)	2540 (± 674)
DOC	1560	16,400	N.A.	N.A.
Nitrite as N	0.091	0.194	N.A.	N.A.
Nitrate + Nitrite	0.031	0.00	N.A.	N.A.
Ammonia as N	1360	2340	N.A.	N.A.
Oil and Grease	19.9	150	N.A.	N.A.
Cyanide	0.017	0.036	N.A.	N.A.

N.A.: Not available because not measured.
* Historical data is from 2011–2017

Fig. 2. Total concentration in ng/L of detected PFAS analytes in normal and ETLF leachates. The values represent the mean from triplicate samples with standard deviation. N.D.: Not Detected.

these significant sources.

3.2.2. TOP assay analysis

The application of the TOP assay indicated the presence of elevated levels of PFAS precursors in both normal and ETLF leachates, with ETLF leachate exhibiting markedly higher precursor concentrations than normal leachate (p ≪ 0.001 via a two-tailed t-test with unequal variances) (Fig. 3) [23]. The identification of specific precursors, including FTCAs and their PFAA transformation products from the TOP assay, provide valuable insights into the PFAS profile within landfill leachates. [24] The measured FTCA precursors are expected to oxidize during TOP assay treatment to PFCAs such as PFPrA, PFBA, PFPeA, and PFHpA, all

of which were monitored in this study, and even TFA, which was not monitored. [25] Post-TOP assay samples of normal (Fig. 3A) and ETLF leachates (Fig. 3B) exhibited complete oxidation of FTCA precursors and elevated concentrations of PFCAs, with PFBA yielding the highest levels post-oxidation, followed by PFPeA. Both PFPrA and PFBA tended to have a higher and more variable baseline and signal-to-noise ratios compared to the longer-chain PFCAs, especially in the pre-TOP assay sample chromatograms. In this study, the concentrations of PFBA and PFPeA in the pre-TOP assay leachate samples were high compared to other measured PFAS in the samples, and the TOP assay still produced higher concentrations of these short chain PFCAs. Other recent studies have highlighted the variability in conversion of FTCAs to PFCAs during
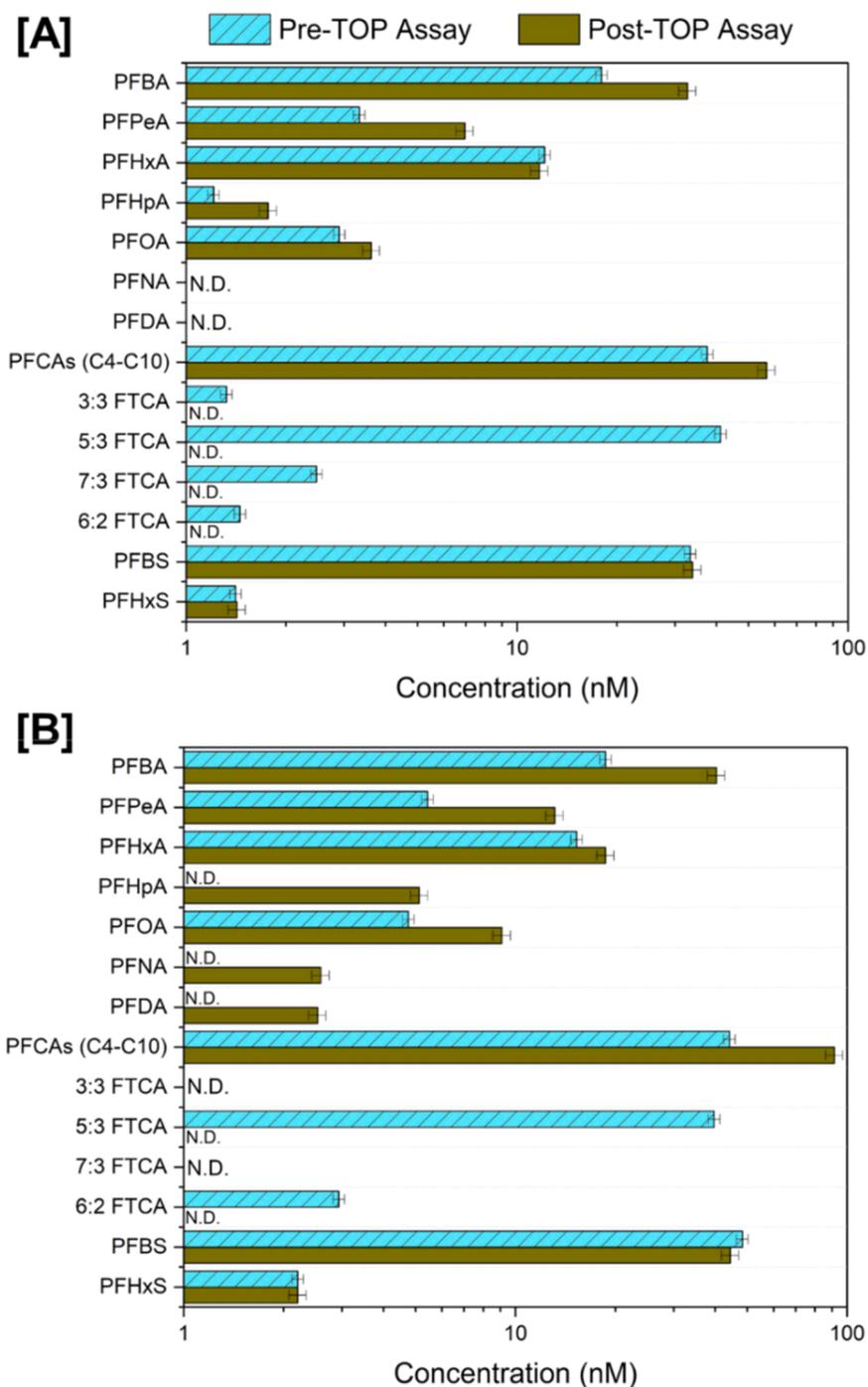
Fig. 3. Concentration all detected PFAS and precursors in normal (A) and ETLF (B) leachates for pre- and post- TOP assay. The values represent the mean value from analysis of triplicate samples with standard deviation. N.D.: Not Detected.

the TOP assay, suggesting the potential for the generation of diverse PFAS mixtures under different experimental conditions. [26] Notably, the concentrations of PFHpA, PFOA, and PFNA were also elevated in post TOP assay ETLF leachate samples relative to the pre-TOP assay, while these analyte concentrations were more similar in pre-and post--TOP assay normal temperature leachate samples. These results suggest precursors of longer chain PFAS may be more mobile in ETLF leachate, possibly due to the elevated temperatures entraining more dissolved organic carbon and/or particulates.

While the TOP assay serves as a valuable tool for assessing PFAS precursor content, it is essential to acknowledge its current limitations and potential sources of error. [27] For instance, the lack of a standardized method for TOP assay introduces variability in experimental conditions, such as oxidant concentration and reaction temperature, which may influence precursor conversion rates and subsequent PFAAs formation. [27] Additionally, the present study excluded PFPrA from TOP assay calculations due to high and variable background in the ion trace, particularly in pre-TOP assay landfill leachate samples. PFPrA also was not included toto avoid experimental artifacts from conversion of the isotopically labeled surrogate M2–4:2 FTS to PFPrA, as was observed in the post-TOP assay method blank. This is a major limitation for surrogates used in current TOP assay procedures, in which an isotopically labeled PFAS precursor can transform to a native PFCA, which is the case for M2–4:2 FTS, or it can oxidize to an the isotopically labeled internal standard used for quantitative analysis, as would occur with TOP assay conversion of $^{13}C_8$-PFOSA to form $^{13}C_8$-PFOA. Overall, these challenges highlight the need for continued refinement and validation of analytical techniques and potential cleanup steps to ensure comprehensive detection of PFAS precursors across all chain lengths. [28] It should be noted that high concentrations of background constituents have impacted both the oxidation and concentration steps of TOP assay resulting in repeated tests for some samples in this study due to the high oxidant demand and/or quenching of the radical generation reactions resulting in incomplete oxidization of the PFAS precursor molecules. Ultimately the TOP assay is useful to measure precursor conversion, but additional work is needed to improve robustness, build in additional quality assurance, and provide a more complete mass balance of oxidative PFAS transformation products [29]. It is still a powerful tool to screen for PFAS precursors that retains some structural information and can simulate potential conversions that may occur within the natural environment, ultimately affecting inputs into WWTPs.

The higher overall PFAS concentrations in ETLF leachate samples coupled with higher prevalence of longer-chain PFCAs in the post-TOP assay samples highlight the need for further research to determine the mechanisms driving these results and their implications for environmental health. Additionally, the development of advanced analytical methods capable of detecting a broader range of PFAS precursors and derivatives will be crucial for improving our understanding of PFAS fate and transport in landfill environments and informing effective remediation strategies. [28] Moreover, the observed differences between normal and ETLF leachates underscore the complex interplay of factors within landfill environments that influence oxidation processes. Factors such as pH variations, temperature fluctuations, and the magnitude of co-contaminants concentrations can significantly impact the efficiency of PFAS precursor oxidation and subsequent formation of PFAS intermediates and terminal PFAA transformation products, highlighting the need for a deeper understanding of the chemical dynamics within landfill settings.

3.2.3. AOF analysis

ETLF leachate exhibited a substantial elevation in AOF levels compared to normal leachate, with measured concentrations reaching 220 µg/L and 36 µg/L, respectively. This stark difference in AOF concentrations mirrors the observed trends in PFAS and precursor relative concentrations in both normal temperature and ETLF leachates discussed earlier. AOF analysis is expected to capture a broader range of

fluorinated compounds than the targeted PFAS analysis presented here, potentially capturing substances like fluorinated pesticides and pharmaceuticals that may contribute to the overall AOF levels. [30] Despite its broader applicability, the AOF method faces challenges, particularly in complex matrices such as landfill leachate. [31] Furthermore, the substantial difference in AOF concentrations between normal and ETLF leachates underscores the complex nature of fluorinated compound dynamics within landfill environments. The elevated AOF levels in ETLF leachate could suggest contributions from industrial or municipal sources; however, given the conclusion in the previous section that differences in PFAS distribution between normal and ETLF leachate are likely due to variations in oxidation processes, this hypothesis requires further evidence to establish a clear link between AOF levels and external waste streams.

Comparison of organofluorine content calculated from targeted PFAS analysis to AOF results provides valuable insights into the composition of the leachate and wastewater. For comparison, organofluorine concentrations were calculated from the PFAS target analyte concentrations by converting each concentration from a mass/volume to a molar basis and multiplying by the number of fluorine atoms per molecule. Calculated in this manner, the targeted PFAS analytical results for normal temperature landfill leachate converted to an organofluorine concentration of 23,224 nM, whereas the AOF results exhibited a significantly lower concentration of 1877 nM. Similarly, in the case of ETLF leachate, the targeted PFAS analysis demonstrated a higher fluorine concentration of 29,177 nM, while the AOF results displayed a reduced concentration of 11,488 nM. As noted earlier, the ultra-short chain and short chain PFAS may at least partially break through when loading samples onto the sorbent, so the AOF method might not comprehensively capture the total fluorine content present within the samples [32]. For ETLF leachate samples with the highest DOC concentrations, the AOF reporting limits are set at 200 µg/L due to the need for high dilutions to minimize competition from fluorinated organics for sorption sites on the carbon cartridge [33]. These factors likely contributed to low bias measurement of AOF in these landfill leachate samples. Conversely, AOF measurements in replicate WWTP influent samples were variable and higher than expected based on conversion of targeted PFAS concentrations to an equivalent fluorine-based concentration, even based on the post-TOP assay results in these samples that had higher summed PFAS concentrations. The causes of this observed variability were not identified in this study, but wastewater influent and landfill leachate are complex sample matrices, and AOF analysis does not include additional cleanup steps to mitigate those matrix effects. This level of variability was not observed for wastewater influent in the multi-laboratory validation study for EPA method 1621, but similarly high variability was observed in groundwater samples tested as a part of another recently published study [29,34]. An alternative approach for future research could be to investigate the use of extractable organofluorine methods for samples containing high levels of hydrophilic compounds [35].

3.3. Impact of leachates on WWTP influent

The examination of WWTP influent samples revealed no evident impact from both normal and ETLF leachates based on PFAS and basic water quality analysis (Fig. 4 and Table 2). However, analysis of samples collected from a residential pump station, utilized as a reference point for municipal-only impacts, detected 6:2-fluorotelomer phosphate diesters (6:2 FPD) at concentrations of 16–20 ng/L. This PFAS precursor, also known as 6:2 diPAP, [36] is commonly found in personal care and cosmetic products and can undergo microbial degradation to yield 6:2 FTOH, which may further degrade to 5:3 FTCA. [10,37,38] Interestingly, the WWTP influent samples, representing various scenarios of background municipal and industrial impacts with and without leachates, exhibited higher PFAS concentrations but within a close range of 60–100 ng/L of total PFAS, with contributions by PFBA, PFPeA, PFHxA,
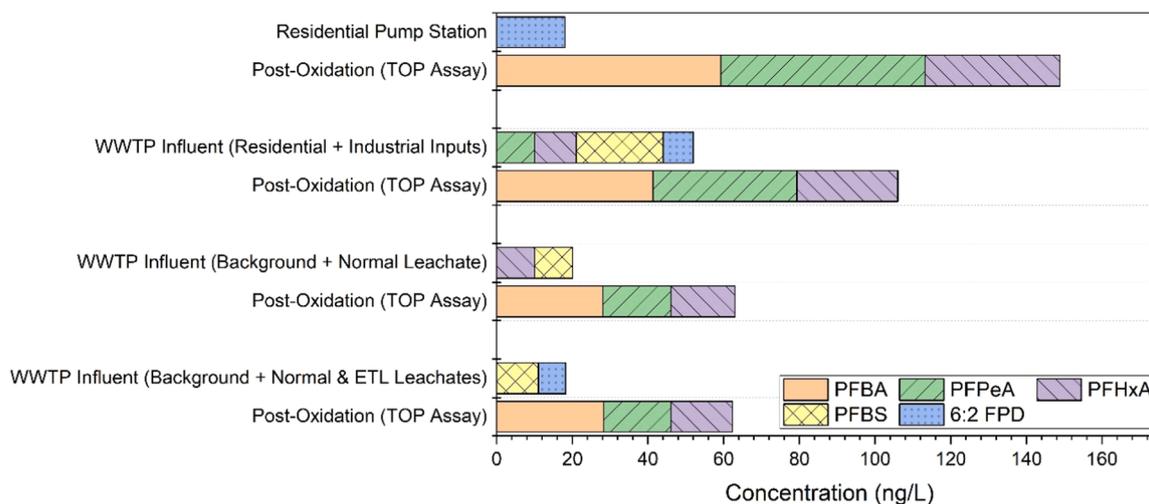
Fig. 4. Concentrations of targeted PFAS in residential pump station and WWTP influent samples with comparison to detected PFAS concentrations in post-oxidation step of TOP assay. The values represent the mean value from triplicate samples. Raw data is summarized in **File S2**.

Table 2
Tracking the impacts of different leachate types on AOF, FTOHs and basic water quality parameters. Raw data is summarized in **File S2**.

Sample Description	AOF	FTOHs	DOC	BOD	COD
	(μg/L)	(μg/L)	(mg/L)	(mg/L)	(mg/L)
Residential Pump Station	23.7 (± 12.5)[1]	<RL[**]	419	154	395
WWTP Influent (Residential + Industrial Inputs)	28[#]	<RL[**]	438	496	1024
WWTP Influent (Background + Normal Leachate)	73[#]	<RL[**]	410	133	337
WWTP Influent (Background + Normal & ETLF Leachates)	<RL[*]	<RL[**]	354	139	333

[1] Standard Deviation from triplicated samples
[#] Detected in one sample only of the triplicates
[*] Reporting Limit (RL): 8-40 μg/L
[**] RL: 4-50 μg/L

PFOA, PFBS, and 6:2 FPD. The difference in composition of the WWTP influent with and without the influence of leachates suggests that a diverse array of PFAS sources along the sewer system influence PFAS loading to the WWTP, in addition to contributions from landfill leachates. [38,39] Despite the absence of detectable PFAS precursors from the targeted FTCAs, FTSs, and other classes, TOP assay results consistently indicated an increase in PFCA concentrations post-oxidation. [28] This implies the presence of PFAS precursors beyond the scope of the PFAS target analytes than were measured in this study.

PFAS precursors also have the potential to undergo transformation into terminal compounds within the WWTP treatment train, thereby impacting the overall PFAS mass balance at the facility. A recent report [40] showed that PFAS concentrations may increase in the effluent relative to the influent concentrations for WWTP receiving municipal-only and leachate-impacted wastewater, as summarized in Table S4. Besides, the higher difference in total PFAS concentrations between pre- and post-oxidation samples from the residential pump station compared to influent samples underscores the dilution effect of precursors in wastewater at the influent relative to pump station samples. This highlights the need for further investigation into PFAS and precursors originating solely from municipal sources, which could not be adequately captured with only one pump station in this study [41].

This study provided a unique opportunity to control inputs to the sewer system at a city-scale, enabling the monitoring of the impacts associated with the two distinct leachates. However, it is imperative to recognize that the observed impacts outlined in this investigation are inherently influenced by the relative volume of generated leachate injected into the sewer system compared to the total volume of collected wastewater received at the WWTP. Considering the exceptionally high concentrations of PFAS and their precursors observed in both leachates, the permitted volume of leachates must be carefully evaluated, considering additional factors such as seasonal variations. Indeed, seasonal changes play a pivotal role, particularly during wet seasons, wherein increased precipitation levels facilitate the dilution of incoming wastewaters. This dilution effect serves to mitigate the potential impacts stemming from these significant sources of contamination. Therefore, a comprehensive understanding of the dynamic interplay between leachate temperature, leachate injection volumes, wastewater flow rates, and seasonal variations is paramount in devising effective strategies to mitigate PFAS contamination within municipal wastewater treatment systems.

4. Conclusions and environmental implications

The operational dynamics of ETLFs introduce unique challenges, with elevated temperatures accelerating waste decomposition and increasing leachate production rates. These conditions can overwhelm existing treatment systems, and the thermal environment within ETLFs may influence the fate and transport of PFAS compounds, potentially altering their behavior and environmental impact. Our findings shed light on the presence of PFAS in both normal and ETLF leachates, with significant differences observed in concentrations and composition. While targeted PFAS analysis revealed elevated levels of various PFAS compounds, including ultra-short- and short-chain species, the TOP assay identified additional PFAS precursors not captured by targeted analysis. These findings underscore the complexity of PFAS dynamics in landfill environments and emphasize the need for comprehensive analytical approaches to assess contamination risks effectively. Hence, the management of this diverse array of PFAS classes may necessitate adjustments to either on-site leachate treatment systems within landfills or the technologies deployed at WWTPs [23].

Based on observed results, future analytical methods should focus on enhancing sensitivity and specificity to accurately detect and quantify PFAS compounds and their precursors in landfill leachates. Targeted PFAS analysis with extended list of analytes coupled with TOP assay provide valuable insights, while current protocols for AOF and FTOHs with high organic background matrices in leachate are much more limited. Optimized protocols for sampling and sample preparation methods are warranted to improve the recovery, extraction efficiency

and reduce matrix effects, particularly in complex matrices such as landfill leachates.

PFAS contamination in landfill leachates poses significant environmental and public health challenges, necessitating proactive mitigation and management strategies. Improved waste management practices, including source reduction and segregation, can help minimize the introduction of PFAS-containing materials into landfills. Monitoring PFAS concentrations in potentially impacted soils and groundwater should be investigated. Additionally, the development of advanced treatment technologies capable of removing PFAS compounds from leachates is critical for safeguarding water resources and mitigating environmental risks.

While the analysis of influent samples from WWTP in this study did not reveal significant impacts from either normal or ETLF leachates, there remains a critical need for comprehensive source identification studies. This will allow a precise delineation of all PFAS contributors along collection systems, such as municipal, industrial, and urban runoff sources that may influence PFAS levels. States that have proactively addressed the PFAS burden on wastewater systems, including international examples such as Canada and Australia, have implemented source tracking measures. One notable instance is Michigan's Department of Environment, Great Lakes, and Energy Industrial Pretreatment Program (IPP), which requires industrial sources in the state to source track and eliminate PFAS sources from industrial users of their sewer systems, effectively reducing PFAS loading at their associated treatment plants. Similarly, Canada's Ministry of Environment and Australia's Department of Water and Environmental Regulation have implemented comparable source tracking initiatives to address PFAS contamination in their wastewater systems.[42].

Thorough evaluations of WWTP treatment processes are also essential to ascertain the efficacy of current methods in removing PFAS and precursors. Key factors include optimizing oxidation conditions, examining precursor conversion rates, and elucidating transformation product formation pathways. Scrutinizing these treatment performance factors will provide clearer insights into WWTP effectiveness for mitigating PFAS. Additionally, systematic seasonal assessments of PFAS concentrations in wastewater and leachates are imperative. Such studies can discern environmental influences, like precipitation and temperature, on PFAS transport and fate within these systems. Examining seasonal fluctuations will lend insights into the dynamic behavior of PFAS contaminants over time, aiding the development of robust mitigation strategies tailored to variable conditions. Continued research addressing these important knowledge gaps will help advance effective PFAS source control and management approaches.

Environmental implications

The operational dynamics of ETLFs introduce unique challenges, with elevated temperatures accelerating waste decomposition and increasing leachate production rates. These conditions can overwhelm existing treatment systems, and the thermal environment within ETLFs may influence the fate and transport of PFAS compounds, potentially altering their behavior and environmental impact. PFAS are present in both normal and ETLF leachates, with significant differences observed in concentrations and composition. While targeted PFAS analysis revealed elevated levels of various PFAS compounds, including ultra-short- and short-chain species, the TOP assay identified additional PFAS precursors not captured by targeted analysis. These findings underscore the complexity of PFAS dynamics in landfill environments.

CRediT authorship contribution statement

Mohamed Ateia: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Max J. Krause:** Writing – review & editing, Data curation. **Ashton Collins:** Writing – review & editing,

Visualization, Formal analysis, Data curation. **Troy Strock:** Writing – review & editing, Visualization, Validation, Investigation, Formal analysis. **Taryn McKnight:** Writing – review & editing, Validation, Resources, Methodology, Formal analysis. **Andrew Brougham:** Project administration, Formal analysis. **Scott M. Bessler:** Writing – review & editing, Investigation, Conceptualization.

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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.136270.

Data availability

Data will be made available on request.

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