

PFAS Chain Length Impact on **Landfill Leachate Treatment Efficiency**

by Lingke Zeng, Stephen Zemba, and Sarah Pope

Recent regulation changes could require a more complete reduction of PFAS. The chain length of PFAS can greatly affect the treatment efficiency. Therefore, when selecting the treatment technology for landfill leachate, one should understand applicable regulations, leachate water chemistry, and PFAS characterization.

Per- and polyfluoroalkyl substances, collectively known as PFAS, have become an urgent environmental concern in recent years. In June 2022, the U.S. Environmental Protection Agency (EPA) issued updated Drinking Water Health Advisories for two PFAS (0.004 parts-per-trillion [ppt] for perfluorooctanoic acid [PFOA] and 0.02 ppt for perfluorooctane sulfonate [PFOS]), as well as new Health Advisories for two other PFAS (10 ppt for GenX chemicals and 2,000 ppt for perfluorobutane sulfonic acid [PFBS]).¹ Also, a number of states have independently established groundwater and drinking water standards for PFAS in the low parts-per-trillion range. Most of the state standards have typically targeted long-chain PFAS, which are known to bioaccumulate in the bloodstream of humans. However, regulatory focus is shifting to include short-chain compounds as well, as evidenced by the inclusion of two of these PFAS in the Health Advisory Levels.

PFAS have been detected in municipal solid waste (MSW) landfill leachate at levels two to three orders of magnitude above drinking water standards.² Although PFAS treatment is not currently required for landfill leachate, some states have developed or are moving forward with surface water criteria likely to either directly (through discharge permits) or indirectly (through industrial pretreatment requirements of wastewater treatment plants that accept leachate) require substantial reductions of PFAS concentrations in leachate. Anticipated surface water standards will likely be set at levels equal to or lower than drinking water standards based on criteria to protect human health (and drinking water supplies). In expectation of these broader, lower standards, regulators are looking to establish effluent limitations under the National Pollutant Discharge Elimination System (NPDES) program, and landfills that send leachate to wastewater treatment plants should consider planning for limits on PFAS and/or pretreatment requirements.³ Thus, continued progress in PFAS regulation at the national level will likely lead to widespread landfill leachate treatment.

In the recent article, “PFAS Leachate Treatment – Breaking Down the Bond Barrier,”³ the authors discuss “off-the-shelf” technologies, such as sorption and filtration, that can remove high percentages of PFAS from landfill leachate, as well as

innovative technologies with the potential to sequester PFAS from the environment and destroy the compounds. PFAS encompass a wide variety of compounds; however, not all PFAS contaminants behave in the same way. Probably the most important physicochemical characteristic that differentiates PFAS is the size of the molecule, or simplistically, the length of the alkane chain in the case of perfluorinated compounds.

This article builds upon the previous discussion of leachate treatment methods by examining the implications of PFAS chain length on technology-dependent treatment efficiency, and how these factors should be considered in the selection of treatment processes based on landfill-specific factors and leachate characteristics. Consideration of PFAS chain length will help to identify which compounds require additional treatment to eliminate impacts on the environment, pending the extent and nature of forthcoming PFAS regulations.

PFAS Chain Length Significance

A perfluoroalkyl acid (PFAA) consists of a fully fluorinated alkyl chain except for a functional group attached to the end carbon of the chain—a hydrophilic head, which is typically a carboxylic or sulfonic group. Depending on the ater/leachate pH, PFAAs can dissociate to either cationic or anionic compounds.⁴ Based on the carbon chain number, PFAAs can be divided into short-chain and long-chain compounds (see Figure 1).⁵ The classification of short- and long-chain PFAS is not an absolute division, but affords a general framework for categorization.

Long-chain PFAS typically show higher bioaccumulation potential and partitioning to organic solids. For perfluoroalkyl carboxylic acids (PFCAs) with a carboxylic functional group, long-chain PFAS include compounds with a carbon number of more than six or seven. For perfluoroalkyl sulfonic acids (PFSAs) with a sulfonic functional group, long-chain PFAS include compounds with a carbon number of more than five. Polyfluoroalkyl substances are similar in structure to PFAAs, with the difference being that not all carbon atoms of the alkyl chain are attached to fluorine atoms. The chain length of polyfluoroalkyl substances is not well defined but generally follows a similar trend as PFAAs.

Number of Carbons	4	5	6	7	8	9	10	11	12
PFCAs	Short-chain PFCAs			Long-chain PFCAs					
	PFBA (214.0)	PFPeA (264.1)	PFHxA (314.1)	PFHpA (364.1)	PFOA (414.1)	PFNA (464.1)	PFDA (514.1)	PFUnA (564.1)	PFDoA (614.1)
PFSAs	PFBS (300.1)	PFPeS (350.1)	PFHxS (400.1)	PFHpS (450.1)	PFOS (500.1)	PFNS (550.1)	PFDS (600.1)	PFUnS (650.2)	PFDoS (700.2)
	Short-chain PFSAs			Long-chain PFSAs					

Figure 1. PFAA short- and long-chain classification, as adapted from ITRC.⁵

Notes: Molecular weight indicated in parentheses; individual PFAS defined in Glossary.

Glossary of PFAS Acronyms

PFBA	perfluorobutanoic acid	PFBS	perfluorobutane sulfonic acid
PFPeA	perfluoropentanoic acid	PFPeS	perfluoropentane sulfonic acid
PFHxA	perfluorohexanoic acid	PFHxS	perfluorohexane sulfonic acid
PFHpA	perfluoroheptanoic acid	PFHpS	perfluoroheptane sulfonic acid
PFOA	perfluorooctanoic acid	PFOS	perfluorooctane sulfonic acid
PFNA	perfluorononanoic acid	PFNS	perfluorononane sulfonic acid
PFDA	perfluorodecanoic acid	PFDS	perfluorodecane sulfonic acid
PFUnA	perfluoroundecanoic acid	PFUnS	perfluoroundecane sulfonic acid
PFDaA	perfluorododecanoic acid	acid	

Landfill Leachate Composition

Our discussion of the effects of chain length focuses on PFAAs, or perfluorinated compounds, since they have garnered the greatest attention to date. However, it should be noted that PFAAs account for a little less than half of the PFAS mass identified in a national study of leachate.² Landfill leachate also contains a variety of *poly*fluoroalkyl substances (indicated in Figure 2, as “other PFAS”) that have been introduced into commerce more recently as substitutes for

Consistent with the present regulatory focus, many landfills have been primarily collecting data on PFAAs, with limited inclusion of poly-fluoroalkyl substances. Focusing on PFAAs, the distribution of long- and short-chain PFCAs and PFSA is illustrated in Figure 3. Results based on the national study are depicted in Figure 3a. As shown, short-chain PFCAs represent more than half of the PFAA mass. Figures 3b and 3c illustrate the composition of PFAAs in leachate with low and high total PFAA concentrations, respectively, based on a study at a specific MSW landfill. The distribution of PFAAs roughly follows national average data represented in Figure 3a, but there are notable differences that reflect the variability of a specific landfill. Interestingly, the profile is similar at low and high PFAA concentrations. At either the upper or lower limits of the total concentration range, the short-chain PFAS are the dominant group.

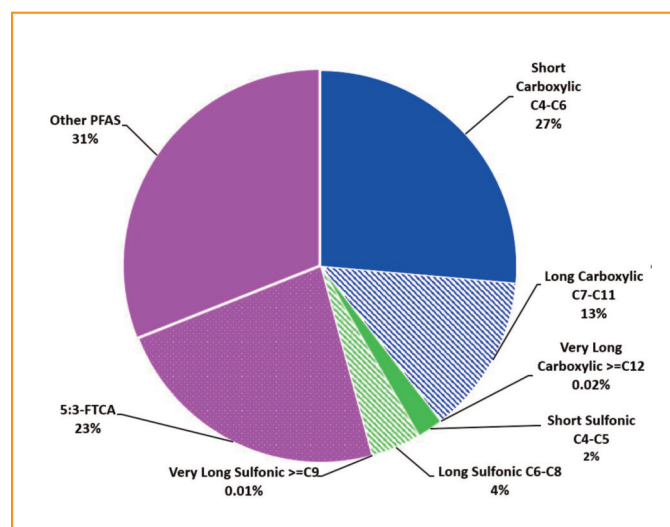


Figure 2. Average PFAS concentrations identified in landfill leachate.²

long-chain PFAAs. Some of these “other PFAS” partially degrade in the environment and convert to stable PFAS.⁶ One example is the 5:3 fluorotelomer carboxylic acid (5:3 FTCA)—a compound formed from the partial degradation of a fluorotelomer alcohol.⁶ These “other PFAS” could receive increased scrutiny, as a number of them (including 5:3-FTCA) are included as analytes in the EPA draft analytical Method 1633.⁷ Landfill leachate contains only small percentages of PFCAs and PFSA with chain lengths of more than 11 and 8 carbon molecules, respectively (see Figure 2).

PFAS Chain Length and Physicochemical Characteristics

All PFAS, being surfactants, contain a hydrophobic tail and a hydrophilic function head. Long-chain PFAS show more hydrophobicity (dislike of water), and short-chain PFAS show more hydrophilicity (affinity for water). Characteristics and behavior resulting from these structural properties are noted below.

- Higher solubility is often observed for a compound with high hydrophilicity. Solubility typically increases when the carbon chain number decreases and is generally higher for PFCAs than PFSA for similar carbon numbers.⁴
- Sorption efficiency is high for a compound with high hydrophobicity. Sorption typically increases when the carbon chain number increases.⁸
- Surfactants can form foam when gas is applied to the water. The ability to form foam increases when the carbon chain number increases. Short-chain PFAS are less effective at forming foams.⁹
- PFAAs are generally not volatile, though short-chain compounds have demonstrated some degree of volatility.^{10,11}

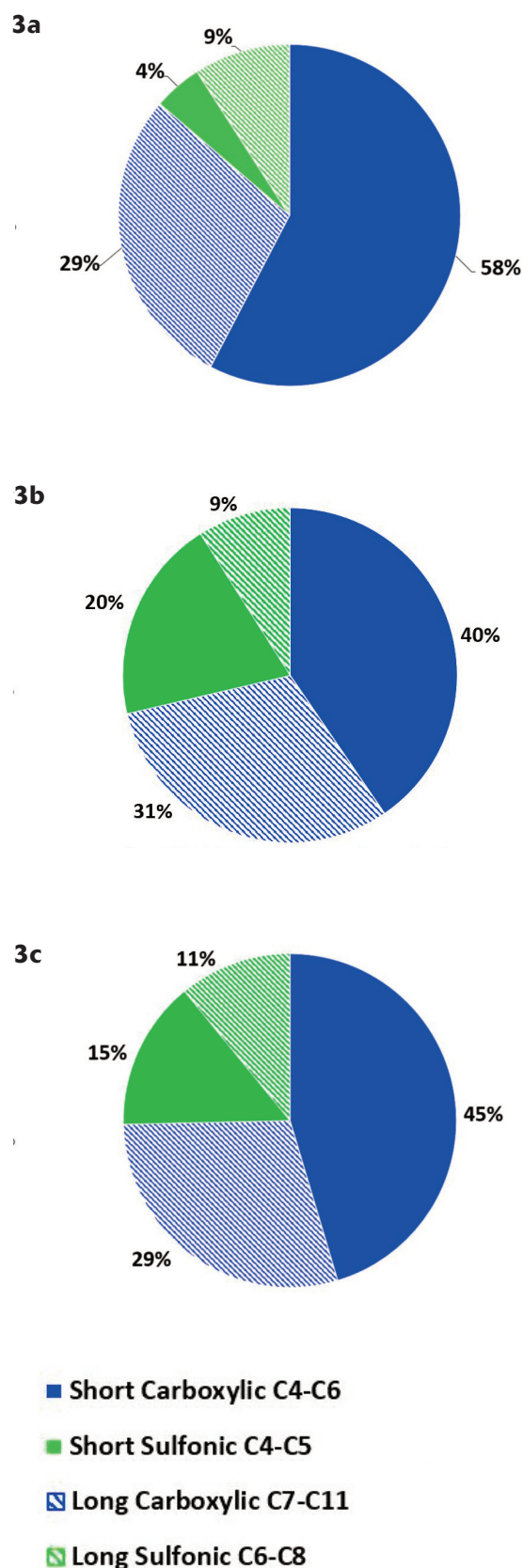


Figure 3. Distribution of PFAs (average concentrations) in landfill leachate.²

Impact of PFAS Chain Length on Treatment Options

Variability of the physical and chemical properties among PFAS, as well as differing characteristics of leachate among landfills, presents a complex set of challenges for effective treatment. Further, all available treatment technologies are generally less effective for short-chain PFAS. Note that none of the technologies can readily achieve EPA's recently recommended Lifetime Health Advisories for PFAS.¹ Various treatment options are discussed below.

Sorption

Drinking water systems have mostly applied sorption media to remove PFAS based on widespread availability, and sorption systems could also be applied to landfill leachate or pre-treated landfill liquids. Three common sorption media are activated carbon, ion-exchange (IX) resin, and organoclay. All sorption media can sequester PFAS via hydrophobic sorption, although the sorption of short-chain PFAS is less effective because they generally show less hydrophobicity. IX resin and organoclay can also sorb PFAS via electrostatic charges. Therefore, IX resin and organoclay show higher sorption efficiency for short-chain PFAS, when compared with activated carbon.

Figure 4 shows the high effectiveness (in terms of operational times to breakthrough) ranges based on chain length for each different sorption material. However, the high total organic carbon (TOC) and high total dissolved solids (TDS) in landfill leachate can reduce the sorption capacity of PFAS, especially for short-chain PFAS. High TOC competes for hydrophobic sorption and high salinity competes for electrostatic charge sorption. Figure 5 provides a comparison of the three sorption media with various process and geochemical parameters and indicates the impact of these parameters on the treatment efficiency.

Reverse Osmosis

Reverse Osmosis (RO) filters water through a semi-impermeable membrane under high pressure. Larger molecules can typically be more readily filtered, and long-chain PFAS are larger molecules than short-chain PFAS. Thus, although RO can effectively filter all PFAS, the filtration efficiency of the short-chain is generally less than the long-chain. Because RO is prone to fouling and clogging, extensive pre-treatment processes are required to remove all total suspended solids (TSS), TOC, metals, and TDS. RO also concentrates PFAS into a reject stream that may require further treatment or disposal.

Precipitation

PFAS can be precipitated via coagulation and flocculation, the conventional wastewater treatment technology. PFAS generally show negative electrostatic charges at circumneutral pH conditions; therefore, cationic flocculant is more

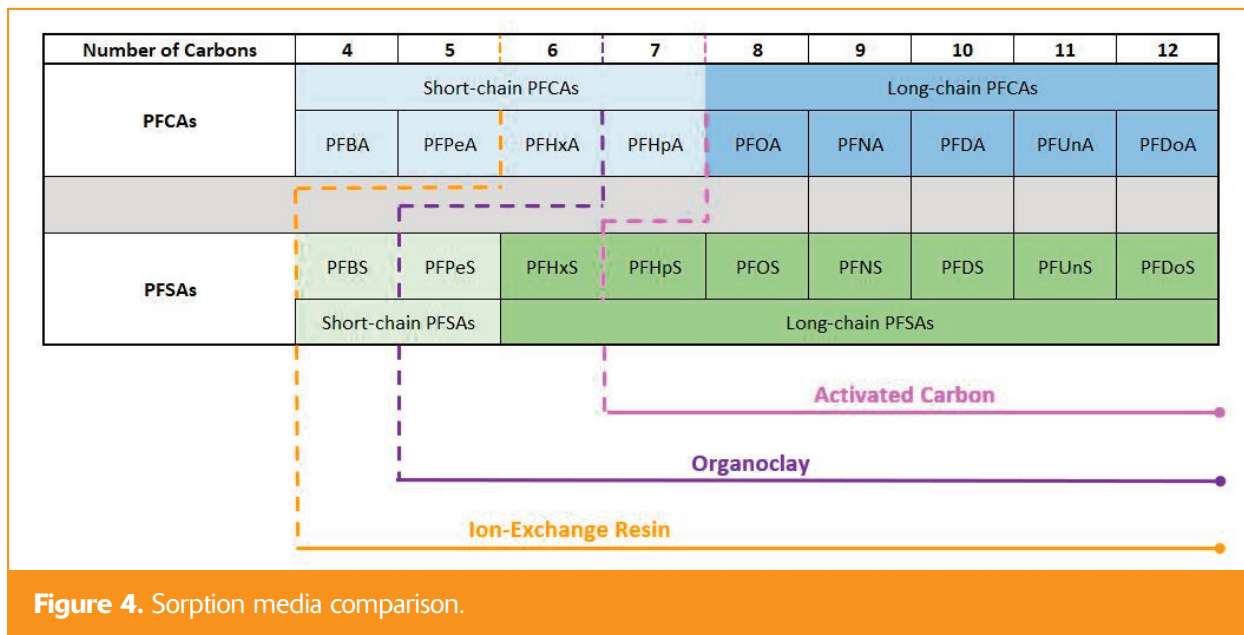
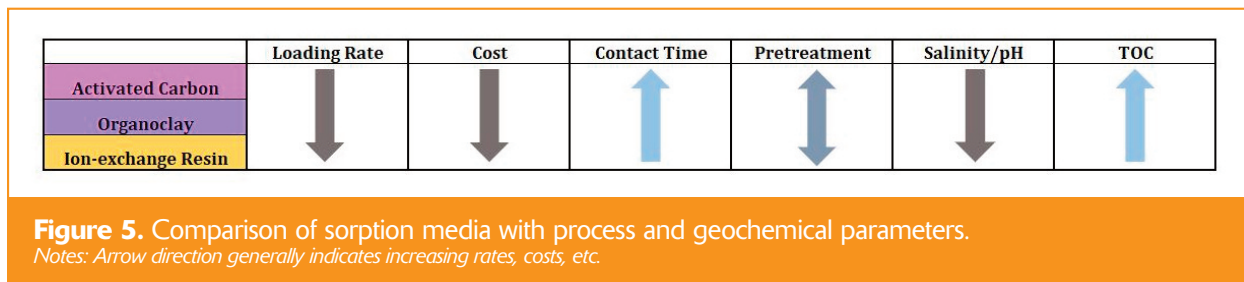


Figure 4. Sorption media comparison.



suitable for PFAS precipitation for landfill leachate with a circumneutral pH range. PFAS precipitate through electrostatic charge sorption with cationic flocculant and also co-precipitate with flocs. Higher hydrophobicity of PFAS results in more removal efficiency via co-precipitation. Therefore, short-chain PFAS are typically less effective for precipitation. In addition, high TOC and high salinity in leachate can also reduce the precipitation efficiency when compared with the typical groundwater treatment efficiency. In general, precipitation is the least effective technology and unlikely to achieve the prospective standard.

Foam Fractionation

This technology removes PFAS using the ability of PFAS to form foams. Gases (often air) are injected into a liquid containing PFAS, and as the air bubbles rise to the top of the liquid layer, PFAS adhere to and travel with the bubbles,

resulting in a top foam layer with collected PFAS.⁸ This technology requires minimal pre-treatment and is not affected by high TOC, although high TDS can reduce the foamability of PFAS. Once formed, foam can be recovered as a waste concentrate, as has been shown during site demonstrations at several landfill sites. However, because the foamability of short-chain PFAS is significantly less than long-chain PFAS, this technology removal efficiency decreases with decreasing carbon chain number.

Oxidation

All oxidation methods initially break down long-chain PFAS to short-chain PFAS, so that the short-chain PFAS are essentially transient oxidation daughter products. Therefore, short-chain PFAS can be the most persistent PFAS in the oxidation treatment process. Many innovative methods using oxidation can be significantly hindered by high organic contents

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typical in landfill leachate. The high persistence of the short-chain PFAS would likely occur if the TOC level is high in the landfill leachate.

Summary

The question is not whether landfills will need to treat landfill leachate for PFAS, but rather when treatment will be required, and what the design goals will be in terms of the specific PFAS and concentration limits. A variety of techniques are being explored for treating leachate, ranging from established absorption media (activated carbon and

resins) to novel methods such as foam fractionation.

Treatment systems will be landfill/leachate-specific and may involve integrating methods to optimize high removal efficiencies and cost effectiveness. An impactful unknown is whether regulations will stay focused on the long-chain, bioaccumulative PFAS, or whether short-chain compounds will need to be considered as well. In the latter case, costs could rise dramatically if treatment for short-chain compounds is needed, and resilient designs may be prudent in anticipation of future changes to the PFAS regulatory landscape. **em**

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