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Presence of per- and polyfluoroalkyl substances in untreated leachate from regional municipal waste landfills: A first assessment for Bulgaria

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ABSTRACT

Bulgaria is lagging behind in its investigation of per- and polyfluoroalkyl substances (PFAS) and consequently in its contribution to the global database and knowledge. This study constitutes the first assessment of PFAS in untreated leachate from regional landfill sites, which are a customary source of PFAS to the environment. A total of ten landfill sites, selected to represent a range of characteristics, were analysed. The requisite chemical analyses were meticulously conducted in an accredited scientific laboratory in Rome, Italy (Acea Infrastructure SpA). Utilising state-of-the-art instrumentation such as liquid chromatography-mass spectrometry (LC-MS/MS), along with a comprehensively formulated analytical procedure tailored to the study's specific needs, ensured the highest standards of scientific rigor. The results reveal that merely eight out of the thirty PFAS analysed exhibited concentrations above the limit of quantification (LOQ). It was found that the total PFAS concentration (i.e. the sum of the PFAS that were determined) varied between a minimum of 1.1 µg/L and a maximum of 14.0 µg/L between the landfills. This range falls within the reported values in the scientific literature for other landfills internationally. The majority of the identified PFAS belonged to linear, short-chained perfluoroalkyl acids (PFAAs). The most prevalent PFAAs with a carboxyl group were perfluorohexanoic acid (PFPHxA; C6), detected in nine landfills at concentrations ranging from 0.9 to 5.0 µg/L, perfluoropentanoic acid (PFPeA; C5), detected in seven landfills landfills at concentrations ranging from 0.6 to 1.7 µg/L, and perfluorobutanoic acid (PFBA; C4), detected in six landfills landfills at concentrations ranging from 0.4 to 3.0 µg/L. The predominant PFAA with a sulfonate group was perfluorobutane sulfonic acid (PFBS; C4), which was detected in eight landfills landfills at concentrations ranging from 0.8 to 8.0 µg/L. The study also provides an overview of the potential environmental and human health implications of the short-chain PFAS, drawing on a review of international literature. As the first investigation of its kind in Bulgaria, this research contributes to the understanding of PFAS contamination in landfill leachate and highlights the need for further studies to assess associated risks.

Keywords: landfill, leachate, liquid chromatography-mass spectrometry (LC-MS/MS), solid waste, PFAS.

INTRODUCTION

According to the latest definition by the Organisation for Economic Co-operation and Development (OECD), PFAS are defined as fluorinated compounds containing at least one fully fluorinated methyl or methylene carbon atom (i.e., without attached hydrogen, chlorine, bromine, or iodine atoms). This means that, with minor exceptions, PFAS encompass all chemical compounds containing at least one perfluorinated methyl group (–CF3) or perfluorinated methylene group (–CF2) (OECD, 2021).

As of 2018, the number of PFAS registered with a CAS number and potentially available on the global market amounted to 4730. In addition to their large number, PFAS exhibit significant diversity in their molecular structures, as well as in their physicochemical and biological properties (OECD, 2021). The majority of registered PFAS are of anthropogenic origin, although some, such as trifluoroacetic acid (TFA), can form naturally in the environment (Rustum, 2021). The industrial production of PFAS can be traced back to the late 1940s. The exceptional strength of the carbon-fluorine (C-F) bond endows these compounds with a number of noteworthy properties, including high thermal stability, fire resistance, hydrophobicity, lipophobicity, corrosion resistance, and electrical insulation. These characteristics allow them to be highly versatile and widely applicable in various industrial and consumer products, including but not limited to: firefighting foams, non-stick cookware, textiles, paper and food packaging, paints, inks, electronic equipment (printers, scanners, cameras, and mobile phones), construction materials (glass coatings and solar cells), etc. (Brun et al., 2023; Rustum, 2021).

Conversely, the elevated chemical stability of PFAS, attributable to the strength of the C-F bond, renders them resistant to degradation under natural conditions, thereby leading to their accumulation in the environment. This has led to their categorisation as “forever chemicals” (Propp et al., 2021). This poses significant environmental and health challenges. The initial indications of the potential risks associated with PFAS contamination and accumulation emerged in the late 1990s. Over the past two decades, there has been a notable increase in research interest concerning the toxicity and impact on human health of these substances (OECD, 2021). Research has indicated that PFAS has the potential to induce a range of significant health concerns, including reproductive disorders, delayed developmental outcomes in children, an elevated risk of specific forms of cancer, immune system dysfunction, and other adverse effects. However, determining the precise effects of PFAS accumulation in the human body is complicated by multiple factors, including the diversity of PFAS compounds, their different toxicological profiles, the emergence of new representatives of this class of substances, and the varying physiological sensitivity of individuals (EPA, 2024).

Perfluorooctanoic acid (PFOA) and PFOS were the first two PFAS compounds whose production and use have been globally restricted or banned (Podder et al., 2021). However, the European Environment Agency (EEA) has reported that between 2018 and 2022, 51–60% of rivers, 11–35% of lakes, and 47–100% of transitional and coastal waters in Europe exceeded the annual average environmental quality standards (EQS) for PFOS (EEA, 2024).

Recent progress in scientific research, coupled with the adoption of novel analytical methodologies for the detection and quantification of PFAS, has led to an enhanced comprehension of their environmental prevalence and the potential hazards they pose to human health and ecological systems. Presently, nations such as the USA, Canada, China, Australia, and certain Northern European states are at the forefront of research and database development on PFAS, while Southern European, African, and Middle Eastern countries are comparatively lagging behind (Hamid et al., 2018). Bulgaria falls into this latter category, with research on PFAS presence in the environment still in the early stages.

One of the primary sources of PFAS in nature is municipal solid waste landfills, where significant amounts of PFAS-containing products accumulate. Over time, and depending on multiple factors (climate, type of waste, biodegradation, sorption, etc.), some of these PFAS are released from the waste and enter the leachate. The increased mobility of PFAS from waste to leachate, as well as their partial biodegradation, is most often explained by changes in pH conditions during decomposition (Hamid et al., 2018). Recent scientific publications suggest that other transformation pathways are possible, such as the degradation of PFOS and PFOA through anaerobic ammonium oxidation under iron-reducing conditions (Huang and Jaffe, 2019) or the increased mobility of anionic PFAS due to competition with inorganic anions (Wei et al., 2019). However, a comprehensive scientific explanation of the transformation processes of PFAS in landfills and their release into leachate remains unelucidated fully (Wei et al., 2019).

The present study aims to provide the first quantitative and qualitative analysis of PFAS content in leachate from regional municipal solid waste landfills in Bulgaria. This research constitutes an inaugural phase in evaluating the potential risks associated with landfill operations and ascertaining the necessity for measures to restrict the dispersal of PFAS from disposed waste. The assessment incorporates a comparative analysis with data from international scientific publications. Furthermore, this study provides an overview of the potential environmental and human health implications of short-chain PFAS, drawing on a review of international literature.

MATERIALS AND METHODS

Selection of landfills

According to data from the National Statistical Institute (NSI), the number of registered landfills and facilities for municipal waste treatment in Bulgaria is 75 as of 2023 (NSI, 2024). However, the available data on these sites is limited and often contradictory. An initial review of the published annual reports of regional operators was conducted for the selection of the landfills included in the study. This review was aimed at finding landfill operators whose reports indicated the presence of total fluorine in the treated leachate which is usually associated with presence of PFAS in the leachate. However, due to the refusal of some operators to participate in the study, the initial list was expanded. Consequently, deliberations were undertaken with approximately half of the total landfills in Bulgaria, and consent for participation was obtained from 10 of them (Fig. 1).

The selected landfills can be regarded as a representative sample for Bulgaria in terms of geographical location, age and capacity. The majority of landfills in the country have been constructed within the last 15 years, with financial support from the government and the EU Cohesion Fund. The selected sites were commissioned between 2009 and 2019, covering an age range of 4 to 15 years (ExEA-Government, 2024). Furthermore, the capacity of these landfills varies significantly, with estimated populations ranging from 20 000 to 1 300 000 individuals. Collectively, these landfills account for approximately 35% of Bulgaria's annual waste landfilling capacity. In the presented results, the landfills are identified by numbers (L1 to L10), as not all operators have consented to the publication of specific data.

Sampling

Grab samples for chemical analysis of PFAS content were obtained from equalization tanks located at the inlet of the treatment facilities, where available, or from retention tanks designated for recirculating leachate back into the landfill in cases where on-site treatment was not conducted. The samples were collected in high-density polyethylene (HDPE) plastic containers with caps that had no polytetrafluoroethylene (PTFE) sealing. The containers were pre-rinsed three times with the sampled water. Subsequent to the collection, the samples were stored at a temperature of 4 °C until their analysis.

For each landfill site, two sampling campaigns were conducted, with the exception of landfill L7, where only a single sample was obtained in October 2023 due to a delayed agreement with the operator. The first sampling campaign was conducted in September 2023, while the second was conducted between October and December 2023.

Analytical method and procedure

The chemical analyses were conducted in an accredited scientific laboratory in Rome, Italy (Acea Infrastructure SpA), using liquid chromatography-mass spectrometry (LC-MS/MS) in multiple reaction monitoring (MRM) mode with

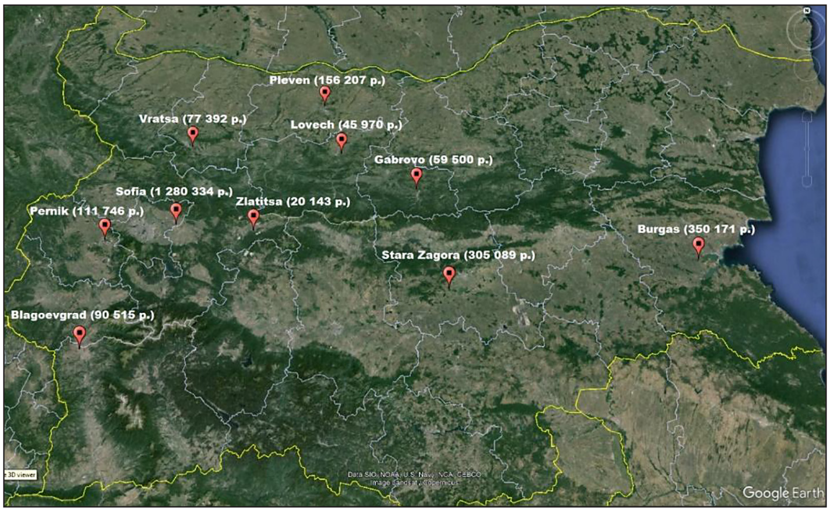


Figure 1. Regional landfills included in the study (the number of residents served is indicated in parentheses)

negative ionisation. The concentrations of all samples were determined using isotope dilution, with isotope-labelled compounds added to the samples prior to injection. The target compounds were identified by comparing the retention times of the samples with those of the isotope-labelled surrogates, or with the retention times of the target analytes in standard solutions, where applicable. Additional identification was performed by comparing product ion ratios with those in the standards. This method was employed to analyse 30 target PFAS in the leachate (Table 1). The limits of quantification (LOQ) were set at 1 µg/L for all analyses, except for:

- measurements for 4-2 FTS, FOSA, NaDONA, GEN X, PFBS, PFHpA, PFHxA, which had an LOQ of 0.1 µg/L from the first campaign;
- measurements for 4-2 FTS, FOSA, NaDONA, GEN X, PFBS, PFHpA, PFHxA, PFDS, N-etFOSAA, N-meFOSAA, which had an LOQ of 0.1 µg/L from the second campaign;
- In both campaign C6O4 had an LOQ of 5 µg/L

Table 1. Acrocym, names, molecular formulas, and CAS number of the target PFAS in the study (CAS Registry, 2025)

Acronym	Name	Molecular formula	CAS No.
Perfluoroalkyl carboxylic acids (PFCAs)			
PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$	375-22-4
PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$	2706-90-3
PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$	307-24-4
PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$	375-85-9
PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$	335-67-1
PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$	375-95-1
PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$	335-76-2
PFUnDA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	2058-94-8
PFDoDA	Perfluorododecanoic acid	$C_{12}HF_{23}O_2$	307-55-1
PFTrDA	Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$	72629-94-8
PFTreA	Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	376-06-7
Perfluoroalkane sulfonates (PFSAs)			
PFBS	Perfluorobutanesulfonic acid	$C_4HF_9O_3S$	375-73-5
PFPeS	Perfluoropentanesulfonic acid	$C_5HF_{11}O_3S$	2706-91-4
PFHxS	Perfluorohexanesulfonic acid	$C_6HF_{13}O_3S$	355-46-4
PFHpS	Perfluoroheptanesulfonic acid	$C_7HF_{15}O_3S$	375-92-8
PFOS	Perfluorooctanesulfonic acid	$C_8HF_{17}O_3S$	1763-23-1
PFNS	Perfluorononanesulfonic acid	$C_9HF_{19}O_3S$	68259-12-1
PFDS	Perfluorodecanesulfonic acid	$C_{10}HF_{21}O_3S$	335-77-3
PFUDS	Perfluoroundecane sulfonic acid	$C_{11}HF_{23}O_3S$	749786-16-1
PFDoS	Perfluorododecanesulfonic acid	$C_{12}HF_{25}O_3S$	79780-39-5
PFTrDS	Perfluorotridecane sulfonic acid	$C_{13}HF_{27}O_3S$	174675-49-1
Fluorotelomer sulfonic acid (FTSAs)			
4:2 FTS	1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	$C_6H_5F_9O_3S$	757124-72-4
6:2 FTS	1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	$C_8H_5F_{13}O_3S$	27619-97-2
8:2 FTS	1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	$C_{10}H_5F_{17}O_3S$	39108-34-4
Perfluorooctane sulfonamide (FOSAMs)			
FOSAA	Perfluorooctane sulfonamidoacetic acid	$C_{10}H_4F_{17}NO_4S$	2806-24-8
N-MeFOSAA	N-methyl perfluorooctanesulfonamidoacetic acid	$C_{11}H_6F_{17}NO_4S$	2355-31-9
N-EtFOSAA	N-ethyl perfluorooctanesulfonamidoacetic acid	$C_{12}H_8F_{17}NO_4S$	2991-50-6
Others			
HFPO-DA	Hexafluoropropylene oxide dimer acid	$C_6HF_{11}O_3$	13252-13-6
NaDONA	4,8-dioxa-3H-perfluorononanoic acid	$C_9HF_{17}NO_4$	958445-44-8
C_6O_4	Acetic acid, 2,2-difluoro-2-[[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl]oxy]-	$C_6H_4F_9NO_6$	682-238-0

The following analytical procedure outlines the systematic steps involved in the processing and quantification of PFAS from leachate samples. The procedure developed in the current study ensures accurate identification and quantification of target compounds while minimizing errors associated with contamination and matrix interference:

1. Sample collection and homogenization – the sample was meticulously collected to ensure it accurately represents the leachate under study. After collection, the sample was manually homogenised in glass bottles to ensure even distribution of PFAS within the matrix.
2. pH verification and adjustment – the pH of the leachate sample was verified using litmus paper. If necessary, the pH was adjusted to a range of 2–10, specifically to facilitate the extraction and analysis of PFAS compounds, using either formic acid or ammonium hydroxide solution.
3. Sample dilution – to mitigate the potential loss of PFAS due to adsorption onto the surface of the container an aliquot of the sample was diluted at least 10 times in methanol prior to the separation of suspended solids from the liquid phase by means of centrifugation. This dilution step aids in minimizing matrix effects and ensures that PFAS remain in the liquid phase. At this juncture, the sample can be prepared for instrumental analysis.
4. Separation of suspended solids and sample processing – a maximum of 50 mg of solids is contained within the total volume of the sample that is to be processed by dilution (corresponding to 0.5% TSS in the matrix). The sample was manually agitated prior to processing. The sample was then transferred into a polypropylene or glass centrifuge tube, following which it was subjected to centrifugation at 4000 rpm for a period of 5 minutes.
5. Preparation of water-methanol mixture – the next step involved the preparation of a water-methanol mixture by further diluting an aliquot of the sample. Subsequently, an isotope dilution (NIS) at a known concentration was added to this mixture within the range of the calibration curve. Additionally, 0.1% v/v of formic acid was introduced. To ensure effective control of the filming process on the container walls, the dilution was performed at least 100 times (including the initial dilution step previously mentioned), and the resulting mixture must contain a minimum of 30% methanol.
6. Quantification – the concentration of PFAS in the sample was determined using NIS, a technique that compensates for matrix effects and provides accurate quantification., Isotopically labelled compounds were incorporated into the samples prior to instrumental analysis, ensuring the integrity of the quantification process.
7. Instrumental analysis – LC-MS/MS. The prepared sample was analyzed using LC-MS/MS in MRM and negative ionisation mode.
8. Identification and quantification of target compounds – the target PFAS compounds were identified in the samples by comparing the retention times (RTs) to those of isotopically labelled surrogates in the same samples or to the RTs of target analytes in standards, as applicable. The product ion ratios obtained from the samples were then compared to those in standards to confirm compound identification. The target compounds were then quantified based on their primary product ion responses, using NIS to correct for any variations in the sample matrix.

This analytical procedure ensures accurate and reproducible results for PFAS determination in leachate, addressing potential issues such as matrix interference, and providing a robust methodology for PFAS analysis in environmental matrices.

Equipment

Instrumental system details

As previously stated, the analytical procedure utilized a UHPLC-MS/MS system comprising the following components: (i) UHPLC UltiMate 3000 (Thermo Scientific), which is equipped with essential components including pumps, a refrigerated autosampler, a thermostated column compartment, and a degasser; (ii) TSQ Altis Thermo Scientific triple quadrupole mass spectrometer equipped with ESI source; (iii) Chromatographic column: a Luna Omega 1.6 µm PS C18 100Å column (100 × 2.1 mm), Phenomenex or equivalent. For accurate sample handling, micropipettes were used and calibrated in accordance with the UNI EN ISO 8655-2 standard. The mobile phases employed consisted of; mobile phase A (Ammonium acetate 5 mM in Water), and Mobile Phase B (Acetonitrile, LC-MS grade).

Reagents

Solvents used included Acetonitrile, water, and methanol, all of LC-MS grade, and were supplied by Biosolve. These solvents were used for the preparation of the mobile phases and sample dilutions. Formic acid (≥ 99%, LC-MS grade) was obtained from VWR. This reagent was used to acidify the mobile phase and facilitate optimal ionization during mass spectrometry analysis. Ammonium acetate, LC-MS grade > 99%, supplied by VWR was used to prepare the mobile phase buffers.

Reference materials

Standard working mixtures are prepared from commercially available certified reference materials (CRMs). Standard solutions employed for quantitative purposes are assayed periodically (e.g. every six months) against certified standard reference materials (SRMs) from the National Institute of Science and Technology (NIST), if available, or certified reference materials from a source accredited under ISO Guide 17034 that attests to the concentration, in order to assure that the composition and concentrations have not changed.

Calibration standard solution

The calibration standard solution (CAL) is freshly prepared for each analytical session and injected at the commencement of the analysis. It is imperative to quantify a compound with a minimum of five concentration levels, with each CAL having a concentration no greater than three times the previous one. In instances where the target analyte concentration exceeds the measure range of the calibration standard solution, the prepared sample or sample extract should be diluted using a water-methanol mixture, maintaining the same ratio utilised in the preparation of the calibration standard solutions. A minimum of 30% methanol is recommended for this purpose. Following this dilution, 0.1% v/v of formic acid should be added to the sample, which can then undergo re-analysis.

RESULTS AND DISCUSSION

Analytical method performance

The PFAS target analysis is conducted using conventional analytical instrumentation, with a particular emphasis on coupled chromatography with mass spectrometry (LC-MS/MS), a hyphenated technique. This approach is both selective and quantitative, with detection limits in the low ppt range. The EPA and ISO have both approved methods that involve the use of direct injection or solid-phase extraction (SPE) to concentrate the sample, followed by LC-MS/MS analysis. These methods provide information regarding the occurrence and concentrations of compounds based on multiple lines of evidence (i.e. MS spectra, MS2 spectra, MRM transition, Mass exact, retention time, etc.).

Conventional chromatographic methods have been demonstrated to offer the requisite sensitivity and selectivity for analysis purposes. However, the complex analysis procedure, specifically for complex matrices (sludge, leachate, waste), the need for specialised equipment and trained personnel, and the high price per sample (150 –250 €) significantly hinder the available testing capabilities.

The term “complex matrices” is employed to denote matrices that are solid and/or highly cross-contaminated. These matrices contain substantial amounts of other contaminants and/or high amounts of harmless (yet analytically problematic) matrix constituents, such as dissolvable or solid organics, salts, or particulate matter. The complex matrices under consideration in this study are leachates. The present study has focused on leachates from various landfill sites in Bulgaria. Leachate is defined as the solution (or suspension) that forms when liquid travels through a solid and removes some components of that solid with it. These components may be dissolved or suspended within the liquid.

Analytical methodologies for complex matrices (e.g. leachate) are not primarily concerned with achieving the lowest attainable limit of quantification; rather, their primary emphasis is on ensuring the robustness and ease of use of the analytical process. It is imperative to prioritise replicability across diverse research laboratories and to minimise analytical costs, thereby facilitating the augmentation and propagation of controls.

The method developed is an optimised direct injection (DI) of a diluted sample to prevent matrix effect. The method enables the quantification of thirty PFAS by means of isotope dilution, utilising 19 Non-Extracted Internal Standard (NIS), which is incorporated prior to the injection process, within the leachate matrix. In terms of production time and analytical costs, the DI method has proven to be simpler, to perform, to achieve optimal recoveries, to reduce analysis times and to incur lower costs, making it suitable for routine use in both screening analyses and for legal purposes. The selection of target PFAS and the determination of quantification limits were based on the following criteria:

- analytical feasibility – PFAS for which established chemical analysis methods are available were included,
- toxicological significance – PFAS with proven toxicity, as recognized by global scientific knowledge, were selected,
- regulatory requirements – PFAS included in at least one regulatory document were covered.

As a result of these considerations, the list comprises of the 20 PFAS referenced in the Drinking Water Directive (Directive (EU) 2020/2184) with additional 10 PFAS that have been identified as likely to be present in the environment (Table 1).

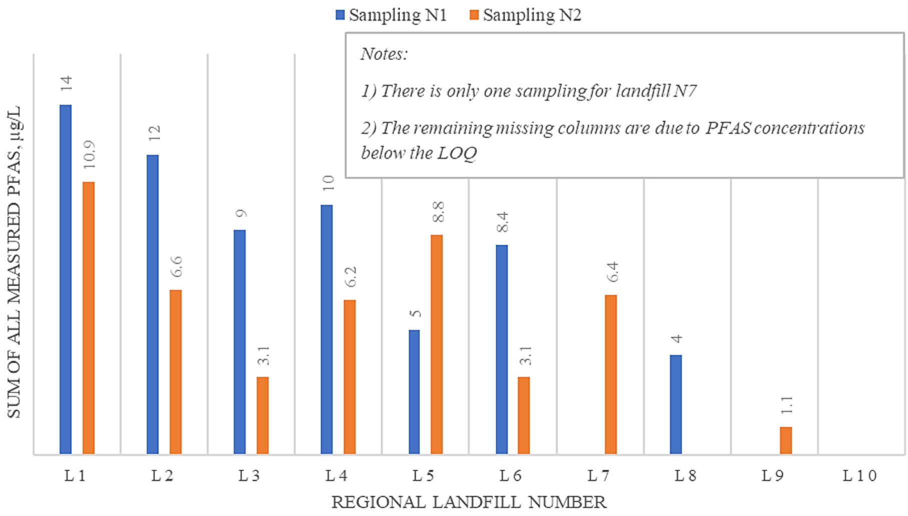
Sum of the concentrations of the measured PFAS in the samples

The sum of the measured PFAS concentration (> LOQ) for each sampling campaign and each landfill is presented in Figure 2. As demonstrated by the figure, the total concentration of measured PFAS fluctuates both between different landfills in Bulgaria and between the two sampling campaigns at each landfill. This variation indicates the necessity for more regular monitoring in order to achieve more reliable concentration assessments. A clear correlation has not been demonstrated between the total PFAS concentration and parameters such as landfill capacity or age. For instance, in the oldest landfill, where leachate is continuously recirculated through the deposited waste, resulting in an expected accumulation of persistent, non-biodegradable contaminants over time, the total PFAS concentration is not the highest. The total PFAS concentrations determined in this study for the 10 regional landfills in Bulgaria fall within the range of values reported in the scientific literature for other countries (Table 2).

PFAS content by type

The substantial number of registered PFAS compounds (4730) and their considerable diversity necessitate classification (OECD, 2021). According to the classification proposed by the OECD, PFAS are divided into four main groups (Table 3).

The 30 target PFAS included in the study belong to three main groups. The most numerous are the representatives of perfluoroalkyl acids (Table 1). In the untreated leachate of the ten studied landfill sites, only 8 out of the 30 analyzed



Notes:

1) There is only one sampling for landfill N7

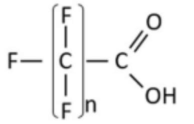
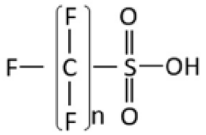
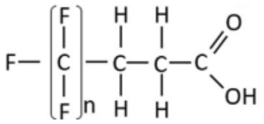
2) The remaining missing columns are due to PFAS concentrations below the LOQ

Figure 2. Sum of all measured PFAS (> LOQ) in untreated leachate from the 10 studied landfills

Table 2. Total PFAS concentration (in µg/L) compared to international data

PFAS	Bulgaria	North America	Europe	Australia	China	Reference
Total PFAS	< 14.0	< 31.4	<17.6	<16.8	< 300	(Wei et al., 2019)
		15.6 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
		-	-	-	< 290	(Travar et al., 2021)
		-	-	-	11.4–68.6	(Chen et al., 2025)

Table 3. Main groups of PFAS according to the OECD classification (OECD, 2021)

PFAS		
Group	Definition according (TemaNord., 2022)	Example Formulas according (Solo-Gabriele et al., 2020)
Per-fluoroalkylic acids (PFAAs)	They consist of a perfluoroalkyl chain linked to a charged functional group (one of the following three): • Carboxyl (PFCA), • Sulfonate (PFSA) or • Phosphonate (PFPA)). Perfluoroalkylether acids (PFEAAs) are also included. They are not polymers.	 with a carboxylic group  with a sulfonate group
Poly-fluoroalkyl acids (PolyFAAs)	In these (as opposed to the above) at least one of the carbon atoms in the alkyl chain of the substance carries an atom other than the fluorine atom (usually hydrogen, chloride, bromine or iodine). Polyfluoroalkylether acids (PolyFEAAs) are also included. They are not polymers.	 fluorotelomeric acid
PFAA precursors	These are substances that can transform and form PFAA. They include fluorinated side-chain polymers as well as fluorotelomer compounds and perfluoroalkanesulfonyl fluoride (PASF-based) substances.	Fluoromethane
Other PFAS	A number of widely known fluoropolymers.	Polytetrafluoroethylene (Teflon) (PTFE)

PFAS exhibited concentrations above the LOQ. A more detailed description of these eight compounds can be found in Table 4. A review of scientific publications indicates that these compounds are among the most commonly found in landfills in many other countries. In addition to them, reviewed studies have reported the presence of PFNA (C9), PFDA (C10), PFUnA (C11), PFDoA (C12), FTSA (Wei et al., 2019), as well as PFHxS (C6) (Gallen et al., 2017; Solo-Gabriele et al., 2020; Wei et al., 2019). The presence of specific PFAS in the untreated leachate of a given landfill site is contingent on numerous factors, including:

- chemical analysis method,
- type of target compounds being analyzed,
- sampling location,
- type and quantity of waste in the landfill,
- age of the landfill,
- climatic conditions (precipitation frequency, temperature).

The initial three factors refer to the study methodology (subjective factors), while the subsequent three are objective and independent of the specific study. The following discussion will address these objective factors.

Impact of waste type and quantity

PFAS present in waste are the primary source of these compounds in leachate. Changes in the PFAS used in commercial products (e.g., a shift

Table 4. PFAS detected in the leachate of the investigated landfills

Group PFAS	Acronym	Full name	Chemical formula
Per-fluoroalkyl acids with a linear carbon chain and a carboxyl group (-COOH)	PFBA	Perfluorobutanoic acid	$C_4HF_7O_2$
	PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$
	PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$
	PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$
	PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$
Per-fluoroalkyl acids with a linear carbon chain and a sulfonate group (-SO_3H)	PFBS	Perfluorobutane sulfonic acid	$C_4HF_9SO_3H$
	PFOS	Perfluorooctane sulfonic acid	$C_8HF_{17}SO_3H$
Poly-fluoroalkyl acid with linear carbon chain and sulfonate group. Four fully fluorinated carbons and two non-fully fluorinated carbons containing hydrogen atoms	4-2 FTS	4-2 Fluorotelomer sulfonic acid	$C_6H_5F_9O_3S$

to PFBS and fluorotelomers instead of PFOS and PFOA) are expected to influence the PFAS content in leachate (Lang et al., 2017). However, Lang et al. found similarities in PFAS detected in landfills built in different decades, likely due to the persistence of these compounds and their slow release into leachate (Lang et al., 2017).

Impact of landfill age

The conclusions regarding the influence of landfill age on PFAS content in leachate are contradictory. Some authors have found no direct correlation between landfill age and PFAS concentration or composition (Solo-Gabriele et al., 2020). Conversely, other studies have indicated a trend of increasing concentrations of certain PFAS with landfill age (Gallen et al., 2017). Conversely, some reports suggest higher concentrations of specific PFAS in younger landfills (Lang et al., 2017). Finally, it has been observed that PFAS concentrations in closed landfills fluctuate within narrower ranges when compared to those observed in active landfills (Travar et al., 2021).

Impact of climatic factors

In the context of landfill sites situated within humid climates, there is a notable proclivity for heightened levels of PFAS leaching when compared to those operating within temperate and arid regions. This may be due to the fact that heavy rainfall facilitates the leaching process (Wei et al., 2019). Table 5 presents a comparison of the PFAS concentrations identified in this study with data from scientific literature.

A comparison with data from other scientific publications indicates that PFAS concentrations in Bulgaria are within the same order of magnitude and a similar range as those reported in other studies. Concentrations of PFPeA, PFHxA, and PFBS in Bulgaria are marginally elevated compared to the European average yet remain within the range observed in non-European countries.

The predominant PFAS detected in Bulgaria, as indicated by the analysis of more than half of the studied landfills, are short-chain compounds, as outlined below:

Table 5. Concentration of PFAS detected (in µg/L) in the present study compared with international data

PFAS presence by landfills and samples	Bulgaria: Range and median	North America	Europe	Australia	China	Reference
PFBA in 6 landfills, in 9 samples	0.4–3.0 1.0	0.069–0.66	0 – 2.9	<1.6	1.1–9.2	(Wei et al., 2019)
		1.4 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
PFPeA in 7 landfills, in 8 samples	0.6–1.7 1.2	0.054–3.2	< 0.8	-	0.6–6.5	(Wei et al., 2019)
PFHxA in 9 landfills, in 15 samples	0.9–5.0 2.0	0.19–8.9	< 2.9	0.012–5.7	0.14–5.7	(Wei et al., 2019)
		3.6 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
		-	-	0.073–2.5	-	(Gallen et al., 2017)
PFHpA in 1 landfill, in 1 samples	0.1 0.1	0.062–3.1	< 0.6	< 3.5	0.075–5.8	(Wei et al., 2019)
		1.2 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
		-	-	< 4.4	-	(Gallen et al., 2017)
PFOA in 2 landfills, in 2 samples	0.2–1.7 1.0	0.042–5	< 4.2	0.019–2.1	0.281–214	(Wei et al., 2019)
		2.6 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
		-	-	< 7.5	-	(Gallen et al., 2017)
PFBS in 8 landfills, in 13 samples	0.8–8.0 3.0	0.028–3.2	< 1.3	< 0.8	1.6–41	(Wei et al., 2019)
		3.4 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
PFOS in 1 landfill, in 1 sample	1.0 1.0	< 4.4	< 1.5	< 1.1	1.1–6.0	(Wei et al., 2019)
		0.9 (USA)	-	-	-	(Solo-Gabriele et al., 2020)
		-	-	< 2.7	-	(Gallen et al., 2017)
4-2 FTS in 1 landfill, in 2 samples	0.2 0.2	-	-	-	-	

- perfluoroalkyl acids with a linear carbon chain and carboxyl group: PFHxA (C6) in 9 landfills, PFPeA (C5) in 7 landfills, PFBA (C4) in 6 landfills,
- perfluoroalkyl acids with a linear carbon chain and sulfonate group: PFBS (C4) in 8 landfills.

A global consensus on the classification of long and short-chain PFAS has yet to be achieved. However, a significant number of authors consider long-chain PFAS to be those with a carbon chain length greater than 8 (Sodani et al., 2025; Solan et al., 2023). A further division is proposed by Sodani et al. (2025), who utilise the term “ultrashort-chain” (C2-C3). In the USA, the classification system incorporates the functional group, categorising as short-chain PFAS those with a carbon chain length of less than six carbons when the functional group is sulfonate. In contrast, PFAS with less than six carbons classified as short-chain PFAS when the functional group consists of carboxyl groups (Coy et al., 2022).

Regardless of the applied classification, the predominant PFAS detected in Bulgaria belong to the short-chain PFAS category. The prevalence of short-chain PFAS in untreated leachate has been extensively documented in the scientific literature (Bush et al., 2010; Hamid et al., 2018; Wei et al., 2019). For instance, in six untreated leachates from Germany, 25 out of 43 studied PFAS were detected, with short-chain compounds being the most prevalent (Bush et al., 2010). A further study of four of the most common PFAS (contributing over 10%) reported in that study found that three of these match those identified in Bulgaria: PFBA (average contribution 27%), PFBS (24%), and PFHxA (15%). Gallen’s study of 27 landfill sites identified three short-chain PFAS (PFHxA, PFHpA, PFHxS), with PFHxA exhibiting the highest concentrations (Gallen et al., 2017). According to Wei and Hamid, the prevalence of short-chain PFAS can be explained by the following factors (Hamid et al., 2018; Wei et al., 2019):

- higher hydrophilicity and mobility of short-chain PFAS facilitate their release from waste,
- they are intermediate degradation products of long-chain PFAS,
- after the year 2000, industrial production of PFOA and PFOS has gradually been replaced by short-chain PFAS.

Despite the ban on PFOA use, this compound continues to be detected in landfill leachate, including in Bulgaria. This indicates that improper landfill management can lead to secondary PFOA contamination in the environment (Hamid et al., 2018). This conclusion is supported by studies of closed landfills in Canada, where PFOA and PFOS were found in leachate (Propp et al., 2021), as well as research on closed landfills in England, showing PFOS concentrations ranging from 0.016 to 0.3 µg/L (Neill and Megson, 2024).

The four compounds – PFHxA, PFPeA, PFBA, and PFBS – were detected in the majority of landfills in this study, and they exhibited the highest concentrations, as illustrated in Figure 3.

The present study’s findings are consistent with those reported in the study by Chen et al. (2025). PFBS was found to predominate over the other six short-chain compounds, with percentages ranging from 50.3% to 87.3% of their sum in all sites. This observation can be attributed to the fact that, following the prohibition of PFOS, PFBS-related products have been developed and

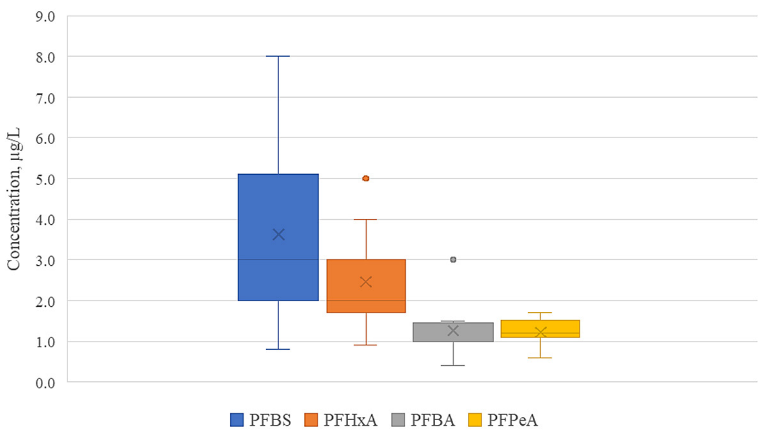


Figure 3. Concentration of the four PFAS compounds that are in the highest concentration and that are detected in the largest number of landfills

disposed of in landfills over the past few decades (Chen et al., 2025). Furthermore, the authors of the study hypothesise that the higher abundance of PFBA and PFHxA may be a result of the degradation of C6 or C8-based precursors.

Environmental and health impact of short-chain PFAS

Notwithstanding the conscious necessity and the scientific knowledge gained from the studies of PFAS and their impact on the environment and humans, there are still a considerable number of unresolved issues. These include the mechanisms and pathways of transformation and accumulation of PFASs in the environment and humans, and the critical allowable concentrations of individual PFAS for discharge to soils and waters.

Consequently, it is not possible to conclude definitively what the exact impact on humans and the environment of short-chain PFAS found in landfills in Bulgaria would be. To gain a general understanding, a brief review of publications on PFAS was conducted, which yielded the following findings:

Mobility PFAS

Short-chain PFAS exhibit enhanced water solubility and bioavailability, thereby facilitating their effective movement into water bodies when compared with long-chain PFASs (Chen et al., 2025). This phenomenon can be attributed to the distinct physicochemical properties inherent to short-chain PFASs. Consequently, short-chain PFASs pose significant risks of human exposure.

Human toxicity

It has been established that, due to protein affinity, higher concentrations of PFAS have typically been detected in blood and liver tissue (Bonato et al., 2025). The majority of studies conclude that short-chain PFAS are generally less toxic than long-chain PFAS (Bonato et al., 2025, Sodani et al., 2025, Solan et al., 2023). However, it should be noted that research on short-chain PFASs is comparatively limited.

Solan et al. (2023) are among the few authors who studied the effects of short-chain PFAS on human liver function. The researchers selected two critical PFAS concentrations for study: a low level (1 nM per PFAS), corresponding to those detected in population biomonitoring studies measuring serum, and a high level (1 μM), chosen to elicit a mechanistically driven response. The study revealed that short-chain PFAS influenced the expression of *ABCG2*, the gene encoding the breast cancer resistance protein, with all but one of the tested short-chain PFAS significantly upregulating its expression – by as much as fourfold.

Sodani et al. (2025) confirmed the elevated toxicity of long-chain PFAS in their study. They found that ultrashort-chain PFAS (C2-C3) did not exhibit cytotoxic effects within the tested concentration range (up to 10 mM). For HFBA (C4), a slight but statistically insignificant increase in cytotoxicity was observed at the highest concentration tested. In contrast, PFAS with chain lengths of C5 or greater demonstrated significant cytotoxicity (> 15% PI-positive cells) at concentrations starting from 100 μM.

Accumulation in biota

In view of the protein-philic nature of PFAS, some of these chemicals, upon reaching water bodies, may accumulate in the tissues and blood serum of water-dwelling organisms, including fish, birds and mammals (Coy et al., 2022). Research studies have demonstrated that the toxicity and bioaccumulation of PFAS decrease with decreasing carbon chain length in Daphnia magna, crayfish, and bluegill (Coy et al., 2022).

Accumulation in food

The bioaccumulation of short-chain PFAS in diverse food matrices remains a relatively understudied area. Research has hitherto been primarily focused on long-chain PFAS. However, mounting evidence suggests that short-chain variants may pose comparable risks due to their persistence and capacity to transfer through food chains. For instance, shorter-chain PFAS, such as PFBA (1.14–110 ng/g, accounting for 66.6% of the total), have been detected in rice (Bonato et al., 2025).

CONCLUSIONS

The present study constitutes the inaugural survey of the presence of PFAS in Bulgarian landfills, with the investigation focusing on 30 representative target PFAS compounds. The selection of these compounds was based on analytical capability, toxicological significance, and regulatory requirements. The study encompasses ten regional municipal waste landfills, selected to be representative of the country in terms of geographical distribution, age, and capacity. Collectively, these landfills process approximately 35% of the total municipal waste that is landfilled in Bulgaria on an annual basis. It is important to note that the study covers only untreated leachate. Most of the examined landfills recirculate treated leachate back into the landfill cells, while those that discharge into a water body treat the leachate in compliance with regulatory requirements and permissible limits.

The results and analysis reveal that the total PFAS concentration (i.e. the sum of the PFAS that were determined) as well as the concentrations of individual compounds in Bulgarian landfills fall within the range reported in scientific literature for other countries. Furthermore, the identified PFAS compounds primarily belong to the group of perfluoroalkyl acids with a linear structure and short carbon chains, which are commonly found in landfill leachate worldwide. No clear correlation was found between the PFAS concentrations and landfill parameters such as capacity or age.

A review of international literature on the environmental and human health impacts of the most commonly detected short-chain PFASs highlights a significant gap in comprehensive global knowledge. As a result, a definitive assessment of the specific effects of short-chain PFASs present in Bulgarian landfills on humans and the environment remains inconclusive. The higher water solubility and mobility of the short-chain PFASs compared to long-chain PFASs suggests that the risk of environmental contamination and human exposure may be higher. While long-chain PFAS tend to accumulate in blood and liver tissues and are generally associated with higher toxicity, research on the toxicological effects of short-chain PFAS remains limited. Studies indicate that short-chain PFAS can influence gene expression and may pose health risks, although their bioaccumulation in biota is comparatively lower. The bioaccumulation of short-chain PFAS in food matrices remains an under-explored area, but emerging evidence suggests their persistence and potential transfer through food chains.

The low and slow mobility of PFAS from waste to leachate poses a significant challenge in accurately assessing their content in landfilled waste. Consequently, landfills pose a serious long-term threat to the environment and human health and require effective management not only during their operation but also after their closure.

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