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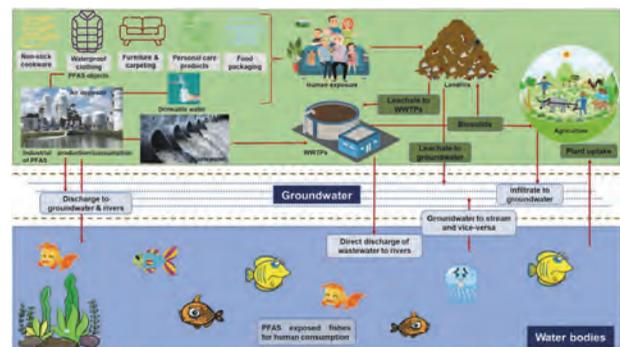
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THE “GREAT DROUGHT” OF 2022 AND HOW IT AFFECTED FARMERS IN BÉKÉS COUNTY

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ABSTRACT

This paper investigates the historically large so called “great drought” of 2022 and how it affected the farmers in our local Békés County area. We worked with those individuals who previously provided me with information that we needed to complete our research papers “Agriculture and the Climate Change” and “Love for the land inherited by our ancestors”) through interviews (10-30 minutes long, due to dialect differences no transcription was made). After showcasing the gathered evidence from these sources, that proves our thesis correct, the effects of this drought were real and noticeable in the local area, we would highlight the problems it caused and what steps did the farmers take and will do in the future to mitigate the damages.

keywords: great drought, devastation, damage, historical

INTRODUCTION

We made similar research earlier (Vigh and Rákóczi 2021; 2022). The “great drought” of 2022 is already considered historical in its devastation, in the last 160 years only twice did we have a drought of such magnitude 1863 and 1952.

The National Meteorological Service summarized the following about the great drought affecting Hungary (OMSZ 2023):

“On the day of Medárd (June 8th) and the days before, there were showers and thunderstorms in many places in the country, but this did not mean the beginning of a long rainy period. In the first third of June, significant precipitation irrigated the western and southwestern regions of the Transtisza and the Great Plain, and then the second and third decades of the month were drier than

usual in most of the country, with only 5-25 mm falling in the Transtisza during the month. The moisture content of the soils decreased below the critical value of 40% in proportion to the usable water content for plants in an increasingly large area and in an increasingly deep layer. In many places in Transztisza and in the northern part of the country, the moisture content of the upper one-meter layer became critically dry by the end of the month, and the soil layer near the surface contained almost no moisture. Favorable soil moisture conditions were found almost only in the western and southwest portions of Lake Balaton, while there were signs of severe drought in a large area east of the Danube, and severe drought in more and more places in Transtisza. The adverse effects of the drought were exacerbated by high temperatures, sometimes over 35 degrees in large areas, which were accompanied by very low humidity in the Great Plains. The ripening of the autumn crops accelerated significantly in the second half of June in the hot, dry weather, so the harvest started earlier than usual. In the eastern part of the country, the drought that occurred during the period of flowering and grain development severely affected the stocks of autumn-sown plants, which was reflected in the quality and quantity of the crop.”

MATERIAL AND METHODS

We collected the data of our scientific student work in the county of Békés. The county is located in the Southern Great Plains region, its seat is in Békéscsaba. It has an area of 5,631.05 km² and has 9 districts (békéscsabai, békési, szeghalmi, gyomaendrőd, szarvasi, orosházi, mezőkovácsházai, gyulai, sarkadi) in which there are 75 settlements (1 city with county rights and 21 other cities) according to the 2022 census surveys 2022- approximately 315,000 people live in Békés County with an average population density of 56 people/km² (KSH 2013,

KSH 2018, KSH POP 2022) Békés County is located in the Great Plain, its area is flat. The plain between the Körös-Maros and the Körös-Berettyó region is almost perfect. The altitude of the county fluctuates around 81-106 meters above sea level. The area of the county is covered with a thick layer of sandy-loess sediment. The most significant mineral treasure of the county is natural gas. The continuity of the plain is divided by the relatively dense river network. The county has 8 rivers by number: the Körös (Fehér, Fekete -, Kettős -, Sebes - and Hármaskörös), Berettyó, Száraz-ér, Hortobágy-Berettyó. (KSH 2013, KSH 2018)

To collect this information we conducted semi-structured interviews in February 2023 with 6 farmers (Table 1). The interviews were also audio-recorded using a dictaphone for later processing. They range in length from 15 to 30 minutes. A literal transcript of the interviews was not made. We based the interview on the methodology described in the book made by Heltai and Tarjáni (Heltai and Tarjáni 1999). The completed interviews were subjected to quantitative evaluation and content analysis based on the methodological suggestions of Babbie (2003) and Newing (2011). The data of the interviews with the farmers concerned are illustrated in the table below:

Table 1: The data of the interviews

Surname	Age	Profession
Mihály	79	Primary producer
Pál	69	Primary producer/ Primary Family Farm
György	50	Family maintained Limited company.
Tibor	49	Primary producer/Site manager
Zsombor	24	Family maintained Limited company.
Lénárt	42	Primary Producer

Two major changes can be noted compared to the previous research conducted concerning this topic, firstly the obvious passing of time, that although this research has been going on for years now, as new interviews were made a new age is displayed, Secondly Zsombor (43) and Pál (78) could not participate due to outside factors.

RESULTS

Examining the interviews it can be seen that the local farmers suffered due to the effects of the "great drought" and it's been more than a few decades since a drought of this proportion manifested itself in the area. We would like to highlight the following words from the interview to further illustrate this (please note, that the original language of the interviews was Hungarian and the interviewed farmers mostly spoke with dialects).

"... we were not prepared for this, we noticed the lack of rainfall at the beginning of the year, but we were optimis-

tic about the harvest. Around the middle of that year, it became clear that it was going to be a year of drought... the water level in the soil also decreased, the plants could not replace the water from the soil through their roots, when we were faced with this, it was bad. There hasn't been a year previously where we couldn't even harvest corn,... I would also highlight the sunflower because it is a plant that doesn't need much water, but the drought was so devastating, that even on average, we only harvested one fifth of it... We had to irrigate twice as much as the usual amount to keep the average level..." (György 50 and Zsombor 24, they were interviewed at the same time, due to outside circumstances)

"...There was such a meteorological drought that, in the case of corn, that until the corn pollen reaches the seed, it burns away and cannot fertilize..." (Lénárt 42)

"...despite the use of fertilizers and such, the number of seedlings was rare and the rainfall was low. It grew weakly... irrigation was not possible, we could only wait for the rain, yet it did not come. The crop was scrapped... If we look at it from the point of view of harvesting, then only a quarter of it was profitable, which, to be honest, was complete failure...it didn't even return the cost of the year-round work..." (Mihály 79)

"... even before the year of 22, there was hardly any precipitation during the winter... the wheat did not bloom in the autumn, only in the spring... the year also started with a windstorm in January, the fasting winds were felt...then. 22 came, there was practically no precipitation... that a person can't irrigate and can only watch the regression of his crops is one thing, but the scenario where he can irrigate without care concerning costs and spends the summer watering his crops and see that his plants have a nice stem, yet bear no produce... the real drought is when the farmer does everything and even then nothing succeeds...the sunflower plates shrunk to the size of a pocket watch, one fifth of it could be hardly processed..." (Tibor 49)

Another memorable thing about the interviews was the conformation, that this drought was historical in its desolation, as it has been more than a decade, since the farmers suffered losses of this magnitude.

"...The last time we experienced something like this was around 2000, 2004, around that time there was a similar six-month drought, then various grain farmers had something similar to this, but even then the corn and sunflowers still managed to turn profit..." (György 50)

"...I can say that there has never been such a drought in my lifetime, nor in my father's lifetime... but every 9 and 11 years there is always an intense drought year, the last such drought was in 2011, but it was only local, it occurred only on clay loam soils. There has never been a year like this, when crops failed everywhere regardless of the soil" (Lénárt 42)

"The "seven-year drought" was a drought like this one in

the 60s, even then hardly anything was produced...the values were near 0" (Pál 69)

"In such sprawling areas so far from each other, there has never been a drought like this, even irrigation was impossible for our region, because the water canals dried up..." (Tibor 49)

"...I don't remember anything similar like this in the last few years, maybe something was close to this 30-35 years ago...but even then at least something was produced..." (Mihály 79)

Even if this is not fully perceptible in the text format, the farmers were noticeably proud of their farms during the interviews (body language, emphasis). They felt that they have years of experience, they actually know the lands they cultivate, their land is important to them. It was noticeable that they care about their lands, they aim to improve it and protect it from harm. They were devastated by the damages caused by the "great drought", they were not prepared for such an all-encompassing drought. It should be noted however, that all of them began seeking various solutions to mitigate future problems from catastrophes. *"the farmer can only be protected by standing on more than one foot, many farmers have gone bankrupt, they have thrown in the towel because they have no money to cultivate in the future... the farmers who deal with land have to make reserves if they wish to make things work"* (Pál 69)

"...people try to make friends with drought-tolerant plants, but this is just a concept... because there is no plant without water..." (Tibor 49)

"...we have to experiment with how well we can withstand the drought, if one of these comes again, how can we reduced losses..." (Mihály 79)

"... the areas that were irrigated in the previous years, the subsoil was in better condition, it was less dry, and the reserve was better. The plant could be protected with less watering. Where they only started irrigating the plant in 2022, practically what was watered was completely absorbed by the soil, the soil had a much greater suction power than that of the plant..." (Lénárt 42)

"...it appeared that the stock was profitable only in the areas of irrigated crops, where we were able to distribute the required amount for growth, to avert future problems it could be possible that we should turn to minimum tillage...perhaps the planting of drought-tolerant plants..." (Szombor 24)

DISCUSSION

The last drought that was devastating to such an extent and was recorded in history was in 1863 and 1952, most farmers fear that there might be more problems ahead as the effects of the climate change worsen.

CONCLUSIONS

The main goal of our hypothesis was, that the effects of the great drought were truly devastating for the farmers in the area around Szarvas, it was an actual phenomenon, not just a baseless reason hiding human errors occurring in the area of farms, but a real problem, and it can be perceived based on what the interviewees said, caused damage to agriculture. Our hypothesis was confirmed, the interviews with the farmers and the data from the pilot plant confirmed that they perceive the phenomenon of the drought and connected to it climate change during their own production and everyday life, and that they actively and consciously act to reverse these harmful processes and prepare countermeasures to prevent further deterioration of the current state against the elimination of damages.

ACKNOWLEDGEMENTS

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PFAS IN COMPOSTS – NEW CONCERNS IN COMPOST APPLICATION

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ABSTRACT

Per- and polyfluoroalkyl substances (PFASs, $C_n F_{2n+1}-R$) refer to a family of anthropogenic chemicals created in the 1940s and used in a myriad of industrial applications and consumer products due to their properties such as hydrophobicity, oleophobicity and high chemical and thermal stability. There is no single definition of PFAS. Several authorities, non-governmental organizations, scientists, and other entities have developed class-based PFAS definitions for regulatory and non-regulatory uses which may create confusion and conflicts of interest. PFAS can be classified into long-chain ($\geq 8C$) and short-chain ($\leq 7C$) substances in accordance with the number of carbon atoms in the molecular chain and can be further classified into three subcategories; perfluoroalkyl acids (PFAAs), polyfluoroalkyl substances, and polymers. Due to their toxicity, persistence, and potential for bioaccumulation, PFASs have received global attention from the scientific and regulatory communities and the general public. The transformation of precursor compounds in designed and environmental systems can contribute to the presence of PFAS in composts, however, only a few studies investigated the existence and concentration of PFAS in composts and no such studies were carried out in Hungary. Therefore we carried out a preliminary PFAS analysis, investigating the occurrence and concentration of five different types of PFAS in 3 types of compost (biosolids, biopolymers and manure composts). Our results pointed out that the PFAS in the previously mentioned composts were below 5 ppb, hence PFAS do not represent a critical issue in Hungarian composts, however, further analysis is required to measure the concentration of PFAS in ppt and provide a scientifically robust database regarding PFAS in Hungarian composts. Finally; efforts and regulations are being established to ban PFASs in food packaging and other compounds which will eventually lead to a lower migration of PFASs from food packaging and PFASs-containing products into composts.

INTRODUCTION

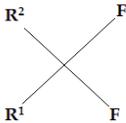
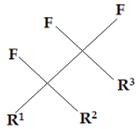
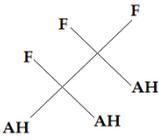
Per- and polyfluoroalkyl substances (PFASs, $C_n F_{2n+1}-R$) refer to a family of anthropogenic chemicals created in the

1940s and used in a myriad of industrial applications and consumer products due to their properties such as hydrophobicity, oleophobicity and high chemical and thermal stability (Wang et al.; 2017; Ma et al., 2021; Lyu et al., 2022). Hence, they are useful in grease-proofing agents used in packaging, stain repellents used in textiles and carpets, nonstick coatings used in nonstick cookware, aqueous film-forming foams (AFFF) found in firefighting foams, various ingredients used in cosmetics, etc. (Rice et al., 2021).

Due to their toxicity, persistence, and potential for bioaccumulation, PFASs have received global attention from the scientific and regulatory communities and the general public (OECD, 2018; USEPA, 2009). PFASs have been detected in various organisms worldwide, as they may be released into the environment at any stage of the life cycle of the goods they are contained in and eventually may be ingested by the biota (Evich et al., 2022). There has been a widespread observation of their bioaccumulation in both aquatic and terrestrial organisms (Evich et al., 2022; De Silva et al., 2021). Moreover, humans are exposed to PFAS in a variety of ways, including through food, drinking water, personal care, cosmetics items, inhaling dust, and breathing indoor air (Evich et al., 2022; De Silva et al., 2021). Human exposure to PFASs is linked to various adverse health effects such as endocrine disruption, hepatic, reproductive, and developmental toxicity, kidney and testicular cancer, neurotoxicity, immunotoxicity, and genotoxicity, particularly for pregnant women, fetuses, and children (Lyu et al., 2022).

Furthermore, the transformation of precursor compounds in designed and environmental systems can contribute to the presence of PFAS in subsurface habitats, hence indirect sources of PFAS include municipal sludge from wastewater treatment facilities, biosolids applied to the soils, MSW composts, potting mixtures, AFFF in firefighting foams and irrigation using PFAS-containing water (Choi et al., 2022, Hamid et al., 2018). Levels of PFAS in composts can increase through migration from food packaging and PFAS-containing products that are commonly disposed of by composting. However, there are only a few studies investigating the concentrations of PFASs in composts, and few restrictions on the thresh-

Table 1: Regulatory and nonregulatory definitions of PFASs

Entity	Paper/Report/Act	Definition	Schematic representation of the PFAS definitions
Buck et al., (2011)	Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins.	"Aliphatic compounds comprising one or more C atoms on which all of the H substituents present in their non-fluorinated analogs have been replaced by F atoms, resulting in PFASs containing the perfluoroalkyl moiety C_nF_{2n+1} ".	C_nF_{2n+1}
OECD, 2021	Report: Reconciling terminology of the universe of per- and polyfluoroalkyl substances: recommendations and practical guidance	"PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e. with a few noted exceptions, any chemical with at least a perfluorinated methyl group (-CF ₃) or a perfluorinated methylene group (-CF ₂ -) is a PFA"	
EPA, 2021	Safe drinking water act	"PFAS is a structure that contains the unit R-CF ₂ -CF (R') (R''), where R, R', and R'' do not equal "H" and the carbon-carbon bond is saturated (note: branching, heteroatoms, and cyclic structures are included)."	
Barnabas et al., 2022	Extraction of chemical structures from literature and patent documents using open-access chemistry toolkits: a case study with PFAS DOI: https://doi.org/10.26434/chemrxiv-2022-nmnd-v3 .	"Each compound that contains an (AH)(AH)(F)C-C(AH)F ₂ group is considered a PFAS, where the AH groups could be hydrogen or any other atom and the bond between both aliphatic carbon atoms is a single bond."	

old concentration of PFAS in composts (O'Connor et al., 2022), hence, further scientific studies and investigations are required to establish maximum limits in compounds in composts around the world.

HOW TO DEFINE PFASS?

There is no single definition of PFAS. Several authorities, non-governmental organizations, scientists, and other entities have developed class-based PFAS definitions for regulatory and non-regulatory uses (Hammel et al., 2022). Table 1 contains the different regulatory and non-regulatory definitions of PFAS in chronological order generated by the different entities:

The term PFAS was first publicized by Robert C Buck and his team in 2011. They defined PFASs as substances containing one or more carbon atoms on which all hydrogen substituents are substituted by fluorine atoms and contain the perfluoroalkyl moiety C_nF_{2n+1} . It is important to highlight that this definition excludes aromatic compounds. Furthermore, the Organisation for Economic

Co-operation and Development (OECD) broadened the definition proposed by Buck and his team to define PFAS in 2021 as any substance that has at least one perfluorinated methyl group (-CF₃) or a perfluorinated methylene group (-CF₂-), this definition results in a huge number of chemicals that are regarded as PFASs, as the Buck team's definition of PFAS is expanded to encompass compounds that lack fluorines at either end of a carbon chain and instead have hydrogen or a functional group at both ends (OECD, 2021; Hammel et al., 2022; Barnabas et al., 2022). Aromatic compounds with at least one aliphatic side chain containing at least one completely fluorinated, saturated-carbon moiety are also included. As a result, the 2021 OECD definition includes 107 organofluorine pharmaceuticals whose use may be essential and are found in pharmaceuticals and wastewater compared to 8 fluorinated pharmaceuticals that would be classified as PFAS according to Buck's definition (Hammel et al., 2022). On the other hand, the United States Environmental Protection Agency (EPA) adopted a narrower definition than the one proposed by OECD. EPA's definition states that a

PFAS is any chemical that comprises an (R1)(R2)(F)C-C(R3)F2 group, where the R groups can be any atom except hydrogen and the bond between the two aliphatic carbon atoms is a single bond. In contrast with the OECD definition, EPA's definition results in a small number of chemicals regarded as PFASs. PFAS definitions continue to evolve. Recently, J Barnabas and his team (2022), comprised between the definitions proposed by OECD and EPA and proposed a new definition stating that a PFAS is any chemical that comprises a (AH)(AH)(F)C-C(AH)F2 group, where the AH groups can be hydrogen or any oth-

er atom and the bond between the two aliphatic carbon atoms is a single bond.

PFAS CLASSIFICATIONS AND PHYSICOCHEMICAL PROPERTIES

PFAS classifications

Per- and poly-fluoroalkyl substances (PFAS) are a class of fluorinated organic compounds having a wide range of physical, chemical, and biological characteristics. They

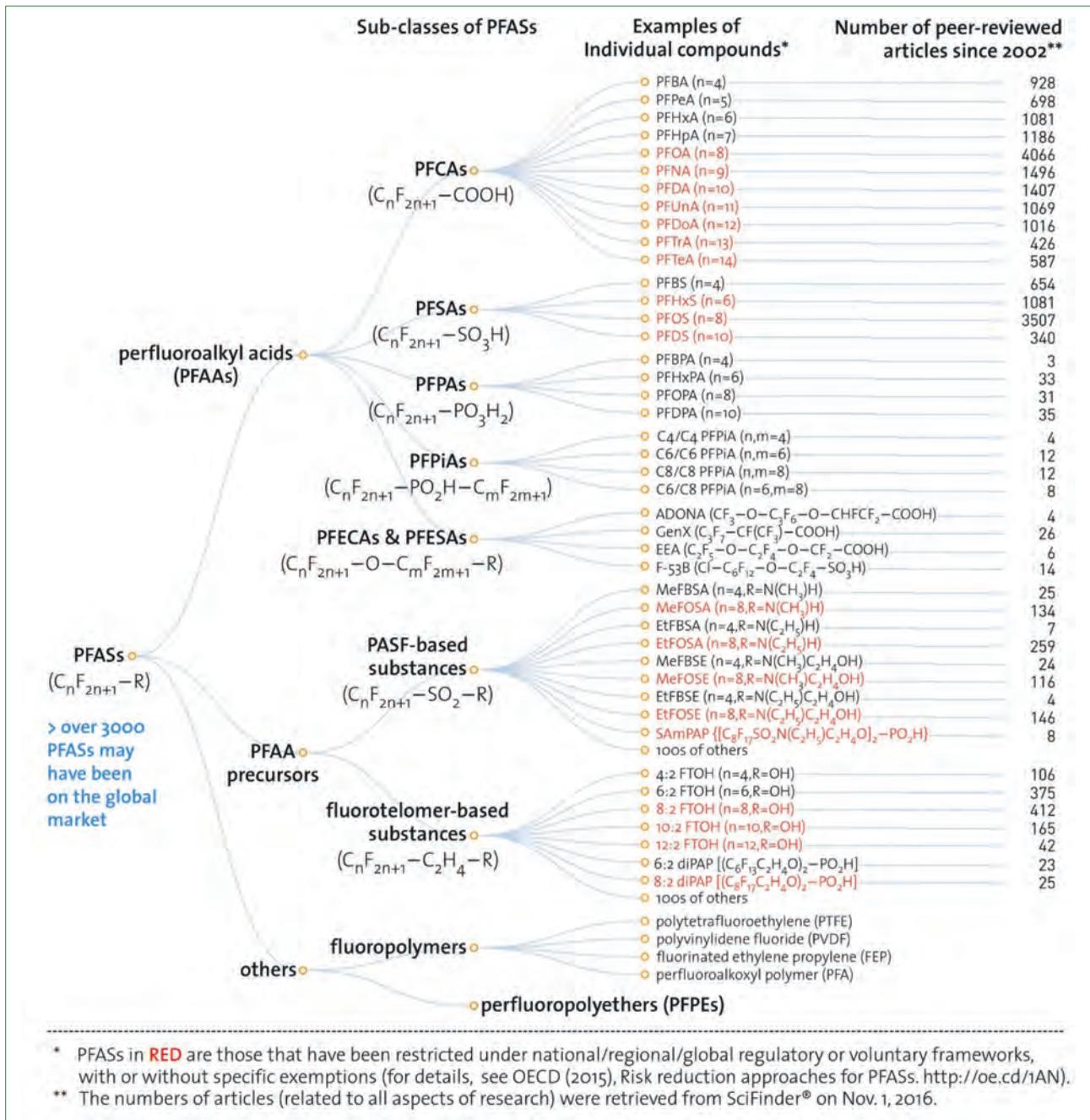


Figure 1: PFAS family tree (source: Wang et al., 2017) PFAS physicochemical properties

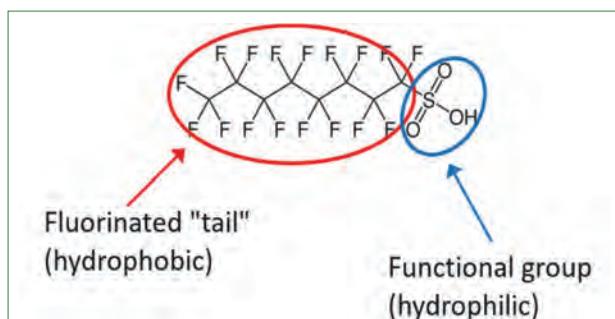


Figure 2: Components of PFAS (source: <https://www.ngi.no/eng/Projects/Reducing-negative-impact-of-PFAS/PFAS>)

can exist as solids, liquids, gases, and both polymers and non-polymers. According to USEPA [2009], PFAS can be classified into long-chain ($\geq 8C$) and short-chain ($\leq 7C$) substances in accordance with the number of carbon atoms in the molecular chain. According to Wang et al.; (2017) PFAS can be further classified into three subcategories; perfluoroalkyl acids (PFAAs), polyfluoroalkyl substances, and polymers. Moreover, PFAAs subcategories include perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), perfluoroalkyl phosphonic acids (PFPAAs), and perfluoroalkyl phosphinic acids (PFPIAs). PFAAs precursors are well-studied and include perfluoroalkane sulfonyl fluorides (PFASFs) such as FOSAs (perfluoroalkyl sulphonamides) and fluorotelomers. PFASFs' polymers include fluoropolymers and perfluoropolyether (PFPEs) (Figure 1).

As previously mentioned, polyfluoroalkyl substances (PFASs) are a class of fluorinated, organic, man-made compounds that do not naturally occur in the environment. PFASs are characterized by a special molecular structure containing both a hydrophobic fluoroalkyl chain and a hydrophilic functional group (Figure 2). [Sznajder-Katarzyn'ska et al., 2019; Wang et al., 2017]. Furthermore, the C-F bond is extremely strong (485 kJ/mol) in perfluoroalkyl compounds, due to the high electronegativity, electron affinity, and polarizability of fluorine as well as the overlap between the carbon's equivalent 2s and 2p orbitals and the fluorine's 2s and 2p orbitals (Sznajder-Katarzyn'ska et al., 2019, Krafft et al., 2015). The strength of the C-F bond makes PFASs very resistant to thermal, chemical, and biological degradations, thus, they remain stable in the presence of acids, bases, oxidants, and reductants. (Lyu 2022).

The two most prominent types of PFAAs that have attracted substantial scientific and regulatory interest are perfluoroalkyl sulfonic acids (PFSAs, such as PFOS) and perfluoroalkyl carboxylic acids (PFCAs, such as PFOA). All of the carbons in PFAAs are bound to fluorine atoms, moreover, they are low molecular weight surfactants and made up of homologous series of molecules with varying carbon chain lengths (Valschi 2017). PFAAs exhibit high persistence and water solubility, making them transport-

able from original locations by water currents and aerosols to far-off places. Additionally, PFAAs show strong resistance to microbial destruction as well as photolytic or metabolic activities, they also exhibit high polarity and stability characteristics (Parsons et al., 2008). Due to their toxicity and bioaccumulation characteristics, PFOS and PFOA have raised environmental and health concerns during the past years, which caused the US to stop producing PFOS in 2002 (Toure and Sadmani 2019). Besides, USEPA established a (USEPA, 2016) health advisory level of 70 parts per trillion (ppt) threshold value in drinking water.

Regulatory and policy measures addressing PFAS in the European Union (EU)

The European Union has taken several regulatory and policy measures to address PFAS contamination, including setting drinking water standards, restricting the use of certain PFAS in products, and conducting research to better understand the sources and effects of PFAS exposure.

Table 2 summarizes the main regulations addressing PFAS contamination in the EU (OECD (2021).

PFAS precursor transformation

a) Chemical transformation of PFAS

Under ambient environmental circumstances, abiotic processes including hydrolysis, photolysis, and oxidation can transform precursors into PFAS. Some precursors can be hydrolyzed, then biotransformed to create PFCAs and PFSAs. While indirect photolysis of certain precursors, most notably fluorotelomer alcohols (FTOHs), does occur in the atmosphere and can contribute to PFCA depositions, direct photolysis of PFAS has not been detected. Additionally, perfluoroalkane sulfonyl fluorides can undergo abiotic degradation by oxidizing in the atmosphere to produce PFCAs in yields up to ten times higher than FTOHs (Martin et al., 2019). According to D'Eon et al., (2006), oxidation reactions involving hydroxyl radicals and sulfonyl fluoride derivatives can also result in the production of shorter-chain PFSAs like PFBS. Finally, although the ultimate synthesis of PFAAs may still be conceivable, in some circumstances, abiotic precursor reactions may not initially yield any PFAAs.

b) Biotransformation of PFAS

The biodegradation and biotransformation of perfluoroalkyl compounds are challenging due to the strong carbon-fluorine (C-F) bond and the significant electron-withdrawing properties of the hydrophilic head-group and hydrophobic perfluoroalkyl tail chemistries, thus it is often restricted to molecules or parts of molecules that are not entirely fluorinated (Choi et al., 2022). Some precursors may undergo biotransformation to become more recalcitrant PFAS, such as PFAAs. Recalcitrant PFAS are

Table 2: PFAS Regulations in Various European Countries - Soil and Water Guidelines

Regulation	Description	PFAS addressed
Restriction of Hazardous Substances (RoHS) directive	Restricts the use of several hazardous substances, including certain PFAS, in electrical and electronic equipment sold in the EU.	Perfluorooctanoic acid (PFOA), its salts, and related substances.
Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation	Requires the registration of substances produced or imported in quantities greater than one ton per year.	All PFAS
European Chemicals Agency (ECHA) evaluation	Ongoing evaluation of the risks posed by PFAS.	All PFAS
Drinking Water Directive (98/83/EC) (proposed amendment in 2020)	The proposed amendment would set a combined limit of 0.1 micrograms per liter for the sum of six PFAS compounds, including PFOS and PFOA. The amendment is currently under review by the European Parliament and the Council of the European Union.	Perfluorooctanoic acid (PFOA) Perfluorooctane sulfonic acid (PFOS) Perfluorohexane sulfonic acid (PFHxS) Perfluorononanoic acid (PFNA) Perfluorobutane sulfonic acid (PFBS) Perfluoroheptanoic acid (PFHpA)
Regulation on the Use of Recycled Nutrients in Fertilizers (2019/1009)	The regulation sets a limit of 100 micrograms of total PFAS per kilogram of organic material for compost and other organic fertilizers.	All PFAS
Temporary Soil Quality Decree, Netherlands (2019)	The THB sets guidelines for acceptable levels of PFAS in soil, water, and other environmental media, and provides procedures for handling and removing contaminated soil. The guidelines include a limit of 0.1 micrograms per kilogram for the sum of PFOS and PFOA in soil	PFOS and PFOA

more easily transmitted across groundwater and soil environments because they have reduced adsorption potential to geosorbents and better mobility in groundwater compared to their precursors. Biotransformation of PFAS occurs under both aerobic and anaerobic environments [Choi et al., 2022; Lyu et al., 2022]. Additionally, perfluorinated chemicals, such as PFAAs, are far more difficult to biodegrade than their precursors because they lack hydrogen atoms on their alkyl chain.

PFAS in biowastes

In several nations, large amounts of biowastes are generated and applied to soil to improve soil health and production. Some of these biowastes are thought to

be diffuse sources of PFAS in soil and groundwater, as well as the second most important source of PFAS after AFFF (Bolan et al., 2021). It is important to mention that data on the fate of PFASs in the terrestrial environment is scarce, furthermore, few research has been published on the uptake of PFASs by plants and earthworms from the soil, therefore, the exposure pathway of humans from biowastes composts is still not well understood nor well investigated (Zhu et al., 2018; Bolan et al., 2021; Choi et al., 2019).

a) PFAS in biowaste composts

The main human exposure pathway is PFAS ingestion, which includes drinking polluted water, eating contaminated land-based food and shellfish, and eating

Table 3: A selection of published concentrations (ng/g) of PFAS in various solid materials (Moodie 2021)

Product/material	PFAS type	Reported PFAS concentration	Reference
Cosmetics (foundation, eye shadow, face colour)	Total PFAS	10700	Danish EPA 2018
	Total PFAS	5900	Fujii et al 2013
Sunscreen	PFHxA	180-6500	Fujii et al 2013
	PFOA	5700	Fujii et al 2013
Paper	diPAP	34-2200	D'Eon et al 2009
Detergents/cleaning products	PFOS	1.6	Kotthoff et al 2015
	PFOA	1.1	
	8/2 FTOH	547100	
Household dust	ΣdiPAPs	7637	De Silva et al 2012
	PFOS	71	
	PFOA	30	
Food packaging	<LOD – 275.84	PFBA	Microwave bags, Zafeiraki et al 2014 Trier, Granby and Christensen 2011
	Range 200 - 700	diPAPS+SdiPAPS	

Table 4: Organic chemical contamination of PFAS (µg/kg) in biowaste composts

Feedstock	country	PFASs	Concentrations (µg/kg dm ³)	Reference
Composts FOGO (n = 13, collected from 32 composting facilities)	Switzerland	6:2FTS/FT(U)CA*	1.20	Krupper et al., 2006
		PES*		
		PFCA	4.30	
		FOSA/FOSE*	3.50 0.10	
MSW composts	Switzerland	6:2 FTS	1.40-1.50	Brandli et al., 2007
		PFHxS	0.07-039	
		PFOS	1.00-3.60	
		PFDCS	0.31	
		PFHxA	0.24-2.10	
		PFHpA	0.36-0.81	
		PFOA	0.67-3.60	
		PFNA	0.23-0.91	
		PFDCA	0.50-1.70	
		PFUnA	0.26-0.31	
		PFDoA	0.20-0.37	
		PFOSA	0.20-0.34	
FOGO	Australia	PFDA	<5	NSW EPA (2019)
		PFDoA	<5	
		PFHpA	<5	
		PFHxA	<5	
		PFNA	<5	
		PFOA	5.49	
		PFOS	<5	
		PFPeA	<20	
PFTeDA	<5			
OFMSW (n = 10, collected from 9 commercial facilities and 1 backyard compost)	US	PFBA	0.15-12.04	Choi et al., 2019
		PFPeA	0.80-8.59	
		PFBS	0-7.63	
		PFHxA	0.38-49.84	
		PFHpA	0-2.56	
		PFHxS	0.07-0.25	
		PFOA	0.04-10.31	
		PFNA	0-1.05	
		PFOS	0.35-1.69	
		PFDA	0-4.43	
		PFDS	0.12-0.49	
		PFUdA	0	
		PFDoA	0-1.71	
		PFTTrDA	0-0.24	
		PFTeDA	0-0.65	
PFHxDA	0			
PFODA	0-0.14			
FOGO	Canada	PFBA	0.8	
		PFBS	<LOQ	
		PFHxA	8.4	
		PFHpA	2.3	
		PFHxS	<LOQ	
		PFOA	4.1	
		PFNA	<LOQ	
		PFOS	<LOQ	
		PFDA	1.7	
		PFDS	<LOQ	
		PFUdA	<LOQ	
		PFDoA	0.9	
		PFTTrDA	<LOQ	
		PFTeDA	0.4	
PFHxDA	<LOQ			
Commercially available com- posts	Australia	PFBA	2.36-3.52	Sivaram et al., 2022
		PFOA	0.04-0.22	
		PFOS	0.21-0.60	
		PFDA	0.09-0.12	
		PFPeA	1.19-1.89	
		PFHxA	1.06-1.39	
		PFHpA	0.03-1.14	
		PFDS	0.06-0.47	
		PFNA	0.03-0.06	
		PFPeS	0.02-0.10	
		PFHxS	0.02-0.59	
		L-PFBS	0.01-0.19	

food packed in PFAS-containing materials (Poothang et al., 2020). PFAS are contained in various daily-life compostable products such as food wrapping materials, drink can lining materials, nonstick cookware, water-resistant textiles and apparel, grease/oil resistant papers and surfaces, and firefighting foam. As mentioned above, Some PFASs (precursors) breakdown in the environment into persistent PFAAs, which include PFCAs and PFSAs. As a result, biological degradation processes during composting procedures frequently result in an increase in PFAA concentrations (Choi et al., 2019). Table 3 represents a selection of published concentrations (ng/g) of PFAS in various solid materials.

When composts are amended to soils, their environmental fate is determined by a number of processes. It was shown in some studies that PFAAs' precursors travel along the soil profile, may be transmitted from polluted soil to plants, and accumulate in organisms (including humans) via the food chain (Sepulvado et al., 2011). However, most of the reported studies in the literature are conducted in culture pots, thus they may not completely replicate field circumstances, such as temperature and moisture fluctuations, as well as interactions with other edaphic, biotic, and climatic elements, thus more field studies are required (Zhu et al., 2018; Xiang et al., 2018; Stalh et al., 2009).

Table 4 showcases studies related to the concentration of PFASs in biowaste composts conducted mainly in developed countries. As Table 2 demonstrates, only few research was conducted on the topic.

LOQ = Values below the quantification limit; 6:2FTS/FT(U)CA=6:2 fluorotelomer sulfonate and saturated/unsaturated fluorotelomer carboxylates; PFS = perfluorinated sulfonates; FOSA/FOSE = fluorooctane sulfonamides and -sulfonamidoethanols; FOGO= food organics and garden organics; dm=dry mass

Choi et al., (2019) analyzed the loads and leachability of 17 PFAAs in nine organic fractions of municipal solid waste (MSW) commercial composts and one backyard compost via total oxidizable precursor assay (TOP). TOP indirect approach for semi quantifying PFAA precursors that involves oxidizing and converting the precursors to quantifiable PFAA. Choi and his team weighed and extracted air-dried composts, then combined supernatants and dried them under N₂ flow to near dryness. Followed by a treatment of each tube's residues with a 3 mL combination of 50 mM K₂S₂O₈ and 100 mM NaOH. Afterward, Vortexed tubes were put in a temperature-controlled water bath at 85 °C for 6 hours. Following centrifugation, a 500 L aliquot was combined in a 1:1 volume ratio with methanol containing an internal standard and processed using ENVI-Carb. The supernatant was centrifuged and transferred to a high-performance liquid chromatography vial for liquid chromatography (LC)MS/MS analysis. Their results showed that PFAA loading varied from 28.7

to 75.9 µg/kg in MSW composts including food packaging and from 2.38 to 7.60 µg/kg in composts containing no food packaging. Furthermore, All composts included perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS); however, MSW composts were dominated by short-chain PFAAs (>64%) and perfluoroalkyl carboxylates (PFCAs, >68%), notably the C6 PFCA. Moreover, the TOP assay indicated the presence of PFAS precursors in three MSW composts for which 6:2 fluorotelomer sulfonate and 6:2 dipolyfluoroalkyl phosphate ester were identified.

A more recent study conducted by Sivaram et al.; (2022) investigated the presence of 38 PFAS in 19 different commercially available composts, garden soils, and potting mixes by means of compost extraction followed by TOP assay. Results indicated that PFAS loads were 1.26 to 11.84 µg/kg, where the total concentration of PFCAs surpassed that of PFSAs in all 19 composts. The TOP assay revealed an increase in short-chain PFCAs which ranged between 0.48 to 7.63 µg/kg suggesting that PFCAs precursors were transformed into short-chain PFCAs.

Rohler et al (2019) investigated the longevity of PFASs agricultural sources in a 12-year-long study in Germany and compared standardized column percolation tests to long-term leaching of PFAS from contaminated sites. Based on soil campaign data, 1802 ha of farmland in the studied site were likely contaminated with 420 kg PFASs, where leaching of these substances into a nearby river was observed. Furthermore, the PFASs identified at the site are largely concentrated in the top 0.6 m of soil, and the maximum PFAS concentration detected within the soil was approximately 6,300 g PFOS+PFOA/kg, resulting in an estimated 390 kg PFOS+PFOA being applied to 90,000 tons of soil. Column percolation tests used in this study, analyze the inorganic and organic target compounds' release behavior from solid materials. Under saturated conditions, the material is packed into a column and percolated with water in the up-flow mode. Leachate was collected and analyzed for PFOAs and PFOSs using an LC system coupled to a triple quadrupole instrument. Primary results at the beginning of the experiment showed initial concentrations of 700 µg/kg and 6,600 µg/kg of topsoil PFOAs and PFOSs respectively, whereas subsoil PFOA and PFOS initial concentrations were 400 µg/kg and 1,500 µg/kg, respectively. Results showed that column leaching studies with PFOS and PFOA-contaminated soil mimicked the initial quick drop but did not anticipate the long-term behavior (tailing) seen at the field site over 12 years. Trend analysis of PFAS field data from the studied site revealed that concentrations had stabilized and that individual PFAS displayed different seasonal changes; the latter is likely owing to the continuous transformation of precursors and a seasonal effect on mobile PFAS production rates. An important conclusion suggested by Rohler and his team states that while biodegradation is

one of the key transformation mechanisms for precursors, the increased half-life for long-chain PFAA precursors has been associated with lower solubility, resulting in decreased bioavailability.

Results vary from one study to another, however, a common observation in most of the studied composts is that the majority of the PFAS identified were shorter-chain PFAAs, which have shorter half-lives in humans; nevertheless, shorter-chain PFAAs are more mobile and had preferential absorption in plants. Furthermore, there is currently a dearth of accurate understanding of PFAS toxicity, exposure pathways from composts, and the threshold values at which PFAS might cause serious health problems. Hence, more study is required before detailed risk evaluations for PFASs can be done.

b) PFASs in biosolids, influents, and effluents from wastewater treatment plants (WWTPs)

WWTPs primarily transfer PFAS into the environment via four primary routes: i.) effluent discharge to water, ii.) biosolids land application and residual disposal, iii.) inadvertent leakage from surface impoundments, iv.) air emissions (Garg et al., 2023). The several industrial sources via which PFAS enter the sewage system in WWTPs

include fluoropolymer and AFFF manufacturing sites (Prevedouros et al., 2006). The inability of PFAS resistant compounds to be destroyed or removed during treatment using traditional WWTP systems leads in PFAS buildup in sewage sludge (Garg et al., 2023). In fact, degradation of PFAS precursors and fluoride compounds in water treatment processes results in the production of PFAAs due to the oxidation of polyfluorinated precursors, hence the treatment process may result in higher levels of PFCA and PFSA in biosolids. If not disposed of properly, these biosolids can introduce PFAS in both surface and groundwater, Figure 3 represents the human exposure pathways to PFAS.

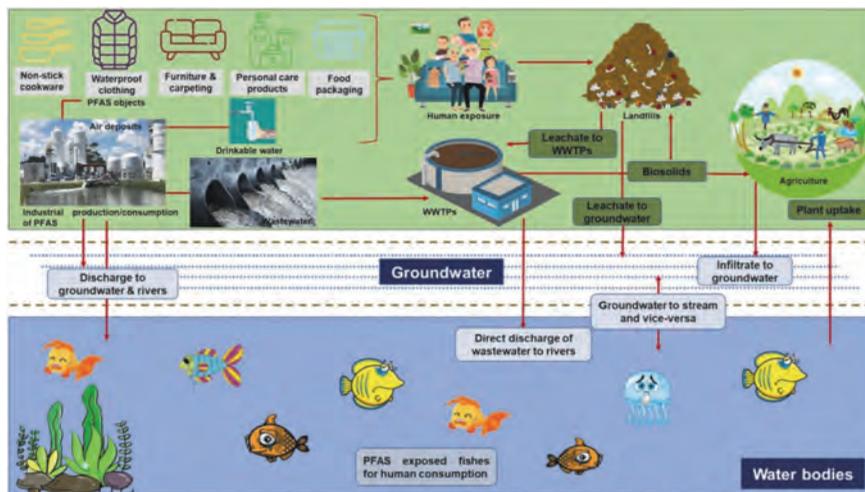


Figure 3: Exposure pathways to PFAS (Garg et al.; 2023)

Table 5: Concentrations of PFAS from different WWTPs plants reported in studies around the world in given in µg/kg dry mass

Source	country	PFAS concentrations (µg/kg dm)	References
Biosolids	Australia	Perfluorooctanesulfonate (PFOS) (<LOD 380)	Gallen et al.; 2016
Sewage sludge	Canada	[PBDE]= 530–8800	Kim et al.; 2019
Treated biosolids		[PBDE]= 420–6000	
Influent	China	[Total PFAS]= 0.0196 – 0.232	Pan et al.; 2016
Effluent		[Total PFAS]= 0.0155 – 0.234	
Sewage sludge		[Total PFAS]= 31.5 – 49.1	
Sludge	Nigeria	[Perfluoroalkyl carboxylates]= 0.010–0.597 [Perfluoroalkyl sulfonates]= 0.014–0.540	Sindikou et al.; 2013
Biosolids	USA	PFOS: 80–219	Sepulvado et al.; 2011
Sludge	Greece	PFOS: 6.7	Arvaniti et al.; 2012
Influent	17 provinces in China	Total PFAS was highest in Shanghai (12) and lowest in Kunming (0.220)	Wang et al.; 2020
Effluent		Total PFAS was highest in Qingdao (9.100) and lowest in Kunming (0.250)	

Table 6: PFAS from different biosolids composting plants reported in studies around the world

Feedstock	Country	PFAS	PFAS concentration (µg/kg dm*)	Reference
Composted biosolids with woodchips	Canada	PFBA	3.4	Lakshminarasimman et al.; 2020
		PFBS	19.7	
		PFHxA	17.3	
		PFHpA	5.3	
		PFHxS	0.45	
		PFOA	19.1	
		PFNA	8.1	
		PFOS	10.4	
		PFDA	11.7	
		PFDS	2.	
		PFUdA	8.0	
		PFDoA	4.6	
		PFTriDA	2.3	
PFTeDA	1.2			
PFHxDA	0.			
Composted biosolids with municipal solid waste		PFBA	3.2	Lakshminarasimman et al.; 2020
		PFBS	3.8	
		PFHxA	6.4	
		PFHpA	<LOQ	
		PFHxS	0.8	
		PFOA	8.6	
		PFNA	0.7	
		PFOS	3.5	
		PFDA	2.2	
		PFDS	0.6	
		PFUdA	1.0	
		PFDoA	1.0	
		PFTriDA	0.6	
	PFTeDA	0.7		
	PFHxDA	0.6		
Composted biosolids with residential yard trimmings		PFBA	5.2	Lakshminarasimman et al.; 2020
		PFBS	38.1	
		PFHxA	21.5	
		PFHpA	4.4	
		PFHxS	<LOQ	
		PFOA	19.0	
		PFNA	3.6	
		PFOS	5.9	
		PFDA	9.6	
		PFDS	0.2	
		PFUdA	4.2	
		PFDoA	6.3	
		PFTriDA	2.5	
	PFTeDA	2.7		
	PFHxDA	1.3		
Composted biosolids with plant materials		PFBA	3.9	Lakshminarasimman et al.; 2020
		PFBS	33.2	
		PFHxA	11.6	
		PFHpA	4.1	
		PFHxS	0.47	
		PFOA	21.5	
		PFNA	4.9	
		PFOS	10.1	
		PFDA	11.5	
		PFDS	<LOQ	
		PFUdA	4.0	
		PFDoA	4.8	
		PFTriDA	1.3	
	PFTeDA	1.2		
	PFHxDA	0.5		

PFAS have been detected in biosolids, influents, and effluents from WWTPs all around the world. Table 5 summarizes different studies' concentrations of PFASs in WWTPs plant biosolids, sludges, influents and effluents.

c) PFAS in biosolids composts

A massive number of biosolids are generated from WWTPs worldwide. Typically, biosolids are rich in nutrients such as N (~3.2%), P (~2.3%), and K (~0.3%) (Shar-

ma et al., 2017), and organic matter content. Hence, their incorporation into soils can increase soil's organic matter content, water holding capacity, and air circulation, etc. However, if not handled properly, may cause a nutritional imbalance in soils, harmful pathogens introduction, surface, and groundwater pollution, and increase greenhouse gases (GHG) emissions, hence adequate pre-processing and pre-treatment is required for safe disposal and amendment (e.g ., alkaline stabilization of biosolids, anaerobic digestion (AD), composting, etc.). Furthermore, PFASs were detected in biosolids and in biosolids' composts (Coggan et al., 2019, Lakshminarasimman et al., 2020, Lazcano et al., 2020). Different studies on biosolids compost content in PFAS are summarized in Table 6.

d) PFAS in plants residues

Moreover, plant residues (e.g. straw, stems, leaves, seed pods, etc.) contain a considerable amount of nutrients and when used as soil supplements, can be beneficial nutrient sources for plants. However, some studies detected PFASs in various plants types and parts. For instance; a study conducted by Wang et al., (2020) demonstrated the presence of PFASs in vegetables (87 mg kg⁻¹), wheat grains (480 mg kg⁻¹), and maize grains (59 mg kg⁻¹) growing near fluorochemical industrial parks.

Techniques for PFAS analysis

a) Chromatography technique for analysis of PFAS

Some chromatographic analysis techniques include liquid chromatography (LC) such as high-performance liquid chromatography (HPLC), gas chromatography (GC), ultra-high-performance liquid chromatography/or ultraperformance liquid chromatography (UHPLC/UPLC), and capillary liquid chromatography (CLC) (Taniyasu et al.; 2008). HPLC has generally been used to examine ionic PFAS, but gas chromatography has been used for both semi-volatile and volatile surveys of PFAS such as perfluorinated sulfonamido ethanols and fluorotelomer alcohols. LC is a complicated method in general since it necessitates extensive apparatus and a time-consuming approach (Garg et al.; 2023).

b) PFAS analysis via total oxidizable precursor assay (TOPA) and total organic fluorine (TOF)

TOPA is an in-lab approach that oxidatively transforms poly- and perfluoroalkyl substances (PFASs) precursor chemicals into detectable perfluorinated alkyl acids (PFAAs). The approach is a powerful tool for semi-quantifying PFASs that would otherwise go undetected in traditional targeted analysis employing liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Larsson 2020).

PFCAs are challenging to investigate due to their sporadic prevalence in nature. As a result, innovative technologies such as TF organic and inorganic analysis, which includes absorbable organic fluorine (AOF), particle-induced gamma-ray emission (PIGE), and combustion ion chromatography, have been developed (CIC) (Garg et al.; 2020).

PFAS analysis experiment at Profikomp Inc.

The purpose of our preliminary study was to investigate the PFAS concentrations in different compost types in Hungary as according to our knowledge, it was not done before in Hungary.

MATERIALS AND METHODS

Three grab samples were taken from three different composts. Table 7 summarizes the details regarding each sample.

Before PFAS analysis each compost sample was screened with a 2 mm sieve. 500 g of under sieved compost were collected from each samples and sent to the laboratory for analysis.

PFAS instigation was carried out at a specialized laboratory (Eurofins Scientific Group, Budapest, Hungary). The implemented technique was high-performance liquid chromatography (HPLC) using a 6495C triple quadrupole LC/MS system (Agilent Technologies Inc., Santa Clara, United states). The analytical method characterized the concentrations of five PFAS that consisted of Perfluorononanoic acid (PFNA), Perfluorooctanoic Acid (PFOA), Perfluorooctyl Sulfonate (PFOS), Perfluorohexanesulfonic acid (PFHxS), and Perfluorobutane sulfonic acid (PFBS). The measuring unit was in milligrams of PFAS per 1 kilogram of dried compost.

Table 7: Sampling details

Sample number	Processed raw materials	Composting technology	Treatment duration (weeks)
1	Biosolids	Aerated static composting pile	6
2	Biopolymers mixed with fresh manure	Aerated static composting pile system covered with a semipermeable membrane	12
3	Manure	Sidewall windrow system covered with semipermeable membrane cover	6

RESULTS AND DISCUSSIONS

The concentrations of the investigated PFAS from the 3 samples are represented in Table 8:

Table 8: Results of the PFAS analysis

PFAS	Unit	Samples		
		1	2	3
PFNA	mg/kg dm ¹	<0,005	<0,005	<0,005
PFOS	mg/kg dm ¹	<0,005	<0,005	<0,005
PFOA	mg/kg dm ¹	<0,005	<0,005	<0,005
PFHxS	mg/kg dm ¹	<0,005	<0,005	<0,005
PFBS	mg/kg dm ¹	<0,005	<0,005	<0,005

¹ dm=dry mass

The results of our study indicate that the investigated PFAS were not detectable (<5 ppb) in all three compost samples tested, suggesting that the concentration of PFAS in various compost types in Hungary is likely below 5 ppb; however, to provide a more robust scientific understanding of PFAS concentration, further analysis is needed to detect these chemicals at lower detection levels (e.g. ppt), and our research team at Profikomp Inc. is in the process of developing a comprehensive methodology to measure PFAS concentrations in compost samples, including lower detection levels (e.g. ppq), with measurements and results to be published in the near future. (See Table 3 for more details.)

CONCLUSIONS

PFAS has received global attention due to their toxicity, persistence, and potential for bioaccumulation which is linked to various adverse human health effects. PFASs are so prevalent in the environment that they may be detected in almost every home worldwide as they are present in grease-proofing agents used in packaging, stain repellent used in textiles and carpets, nonstick coating used in cookware, aqueous film-forming foams used in firefighting foams and various ingredient used in cosmetics, etc.

Moreover, the transformation of precursor compounds in designated environmental systems can contribute to the presence of PFAS in different environments and compounds including in composts. Nevertheless, there are no studies indicating the increase in human exposure to PFAS through composting. However, only a few studies have investigated the presence and concentration of PFAS in different compost types. Therefore, further experiments and investigations are required to establish maximum levels of PFAS in composts.

In Hungary, there has been no previous investigation into PFAS concentrations in composts, so our research team at Profikomp Inc. conducted a preliminary study on five different types of composts, which revealed that the PFAS concentrations in these composts were below 5 ppb, indicating that PFAS are not a major concern in Hungarian composts; however, more thorough analysis is needed to measure PFAS concentrations in ppt and develop a scientifically reliable database for PFAS in Hungarian composts, and our team is currently developing a comprehensive methodology to measure PFAS concentrations in various compost types at lower detection levels (e.g. ppq), with the results of our measurements to be published in the near future.

Due to their toxic and bioaccumulative nature, PFOS and PFOA have been identified as significant environmental and health concerns in recent years, prompting the US to cease production of PFOS in 2002. In response, the US Environmental Protection Agency (USEPA) has set a health advisory level of 70 parts per trillion (ppt) for PFOS and PFOA in drinking water. Furthermore, efforts are being made to regulate and ban PFASs in food packaging and other products to minimize their migration into various compartments, including composts. The European Union (EU) has established various regulations regarding PFASs, including a 6 ppt limit for drinking water, and restrictions on PFAS use in food contact materials, textiles, and firefighting foams. In addition, the EU is evaluating the need for regulations on PFASs in other compartments such as soil and sediments. In the US, various states have established their own regulations regarding PFAS contamination, including setting maximum contaminant levels for drinking water, restricting the use of PFAS-containing products, and implementing cleanup efforts for contaminated sites. Overall, there are ongoing efforts at both the US and EU levels to regulate PFAS contamination in various compartments, with a focus on minimizing the potential health and environmental risks associated with these chemicals.

In the future, there may be a continued effort to regulate and reduce the use of PFAS-containing products and materials, which has the potential to lead to lower levels of PFASs in composts. Furthermore, the development of more comprehensive testing methods for PFASs in composts could help to improve the accuracy and reliability of PFAS concentration measurements, which is a key objective of the ongoing research being conducted at ProfiKomp Inc. This research aims to provide a more robust and scientifically sound database on PFAS concentrations in composts, which may inform future regulatory efforts aimed at mitigating the potential risks associated with PFAS contamination.

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