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Spring-Summer 2025

Environmental management, land use, biodiversity

THE EXPERIENCES OF CUSTOMERS REGARDING THE DEPOSIT REFUND SYSTEM OF BEVERAGE BOTTLES ■ BIOGAS POTENTIAL AND CALORIFIC VALUE OF DIFFERENT AGRICULTURAL MAIN AND BY-PRODUCT ■ PFASS IN COMPOSTS ■ PÁLINKA SPENT WASH COMPOSTING

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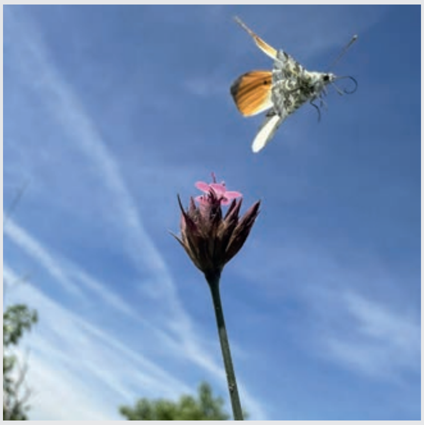

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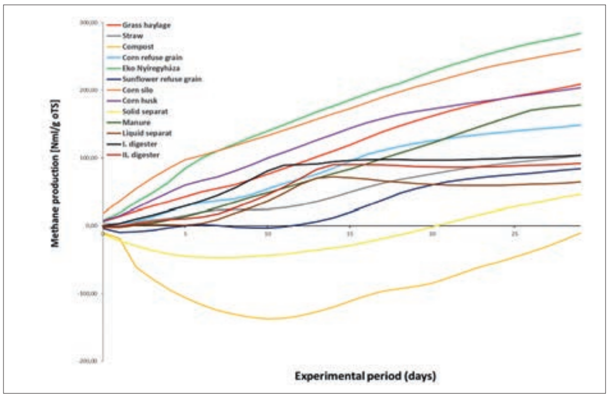

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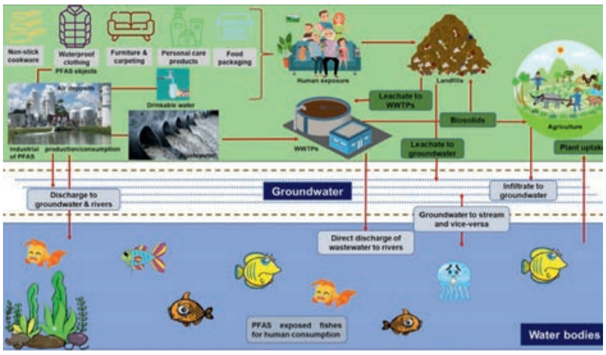

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THE EXPERIENCES OF CUSTOMERS REGARDING THE DEPOSIT REFUND SYSTEM OF BEVERAGE BOTTLES

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ABSTRACT

The goal of our research is to assess people's buying habits regarding the return of beverage bottles. Before the start of the system, we already carried out research that predicted certain expected customer reactions. In the course of our present research, we would also reflect on our previous results. We are mainly looking for an answer to how the purchase of products with a deposit is developing, and in addition, how the selective collection habits of people may have changed. At the same time, our aim is to re-examine customer attitudes related to the introduction of deposit fees, thereby supporting the work of decision-makers/legislators.

In order to achieve our goals, we conducted an open questionnaire survey using the Google Form application. We published the questionnaire on social media platforms, which was available to those who completed it for almost a month between October 18 and November 18, 2024.

Based on our results, the proportion of people participating in selective waste collection increased by almost 5% in almost a year. REpont's deposit refund system is used by people for the purpose of environmentally conscious behaviour, however, quite a few suggestions to be taken to heart were formulated in connection with the further practical development of the system.

Keywords: return, recycling, environmental protection, packaging material, REpont

INTRODUCTION

On the basis of the European Parliament and Council Directive (2019/904 of 5 June 2019) - on single-use plastics - which had regard to the reduction of the impact of individual plastic products on the environment, the European Parliament reached a resolution on the circular economy on 10 February 2021 in its new action plan (European Parliament 2021).Following this resolution, the Ministry of Technology and Industry issued a decree in Hungary entitled *"Detailed rules for the establishment and application of redemption fees and the distribution of redemption fee products"*.

Within the framework of this decree, by applying the REpoint redemption system, all plastic, metal and glass beverage packaging became subject to a mandatory deposit fee and redemption began on January 1, 2024. With the exception of milk and milk-based beverage products, all non-reusable or reusable packaging made of plastic, metal or glass, in the shape of a bottle or box, with a volume of 0.1–3 liters, participates in the redemption process (Government of Hungary 2022).

Redemption systems have a history dating back centuries. Deposit refund systems were originally introduced by the beverage industry itself in the 19th and 20th centuries. century to ensure the return of refillable beverage containers, typically glass bottles (Friedel R. 2014). As an example, I would cite the "Rinse and return" method used for milk bottles, which is widespread in England, where milk processors reused the glass bottles up to 40 times (Tom L. 2020). Not much changed in the following times, but this changed with the invention of plastic bottles in 1970 (and the invention of the PET - polyethylene terephthalate - bottle in 1973) (Belis M. 2023). In connection with this, we actually start talking about modern redemption systems, because the first large-scale reimbursement system is also connected to this date, which can be linked to the Canadian province of British Columbia (British Columbia 2018). The first European deposit return system, abbreviated DRS (Deposit-Return Scheme), was introduced fourteen years later in Sweden (Tosca B. 2021).

Since then, deposit-fee exchange systems have been implemented in 16 countries in Europe (in chronological order: Sweden, Iceland, Finland, Norway, Denmark, Germany, Estonia, the Netherlands, Croatia, Lithuania, Latvia, Slovakia, Malta, Romania, Ireland and, finally our country). In addition, 8 countries have adopted legislation on the topic and in another 8 countries this topic is currently debated (Sensoneo 2024).

The aim of our research is to reassess the population's attitude to the topic and how it changed after the introduction of the system. In connection with the redemption of beverage cans, has the perception of the measure changed, and what has been the attitude of customers towards redemption after its introduction. Also helping and supporting the work of decision-makers in making future decisions and modifying their currently active activities as necessary. This new regulatory system already has a significant impact on rural development in relation to waste management. Furthermore, it imposes significant tasks on the regional public administration (Rákóczi 2022) and has significant social effects (Rákóczi 2021). At the same time, prior to this research, we also carried out investigations regarding alternative waste management alternatives (Rákóczi A. – Duray B. 2014)

MATERIAL AND METHODS

We also dealt with the topic within the framework of our previous article. At that time, our research goal was to assess people's shopping habits in connection with their selective waste collection habits before the introduction. Based on the results of our research, it was possible to predict that in the event of the introduction of a deposit fee for PET bottles, a reduction of only around 40% in the consumption of pill bottles would be expected, but the proportion of bottles going to selective collectors would also increase by 10% in excess of the quantities above redemption (Zs. Vigh - Rákóczi A. 2024).

The data for our research was collected using the Internet. We used one method during data collection:

We created an anonymous questionnaire prepared in advance with questions (only the gender and age of the person filling it in are given, no other data, only their opinion) on the Google Forms interface, and after it was created, we posted it on various social media interfaces. The questionnaire was available for almost a month from October 18th of 2024 to November 18th of 2024. Anyone could fill it out between these two dates, who posessed the link we provided as an access point. The questionnaire contained a total of 11 questions, consisting of 10 open-ended questions and 1 open-answer option. In the case of 4 questions to be decided, the person filling in had the opportunity to provide further explanations should they wish to do so. The results of the questionnaire were collected in separate graphs using the software, and their data were collected in tables for better transparency. 105 people filled out the questionnaire in the specified time interval. The questionnaire was closed at the end of the deadline, no further completion was allowed, and all the data collected up to that point was recorded in the evaluation phase of our research.

Where it was possible, we compared the results with the results of the previous research, so that both positive and negative changes were presented.

RESULTS

Result of the survey - details of those who completed survey

Nearly 68% of the respondents were women and 32% were men. The distribution of the applicants by age group shows a varied picture. It was filled out to the greatest extent by people in the age groups 41-50 (~38%), 31-40 (~24%) and 51-60 (~17%). In addition, the remaining nearly one-third of the applicants belong to the 61-70 (~6%), 21-30 (~12%), 71-80 (~2%) and 18-20 (1%) age groups. Furthermore, it can be noted that no one from the age groups over 81 took part in filling out the questionnaire (Table 1, Table 2).

The breakdown of respondents by place of residence is also varied, although all respondents declared themselves to be living in Hungary, their distribution by county concerned eight counties (Bács-Kiskun, Békés, Borsod-Abaúj-Zemplén, Budapest, Csongrád-Csanád, Győr-Moson-Sopron, Nógrád , Pest). Of these, the three most

Table 1: Distribution of genders who filled out the questionare

Gender	Percentage based on all responses	Changes compared to the last survey
Female	67,6%	-4,2%
Male	32,4%	+4,2%
I do not wish to answer	0%	-

Table 2: Distribution of ages who filled out the questionare

Age	Percentage based on all responses	Changes compared to the last survey
18-20	1%	+0,1%
21-30	12,4%	+1,7%
31-40	23,8%	-2,1%
41-50	38,1%	+5,1%
51-60	17,1%	-1,7%
61-70	5,7%	-4,1%
71-80	1,9%	+1%
81-90	0%	-
91-100	0%	-

significant administrative areas were Békés (~71%), Pest (~13%) and Budapest (~11%). The percentage of respondents in the other 5 counties was 1-1% (Table 3).

Table 3: The distribution of those who completed the questionnaire by county

County	Percentage based on all responses
Bács-Kiskun	1%
Békés	70,5%
Borsod-Abaúj-Zemplén	1%
Budapest	11,4%
Csongrád-Csanád	1%
Győr-Moson-Sopron	1%
Nógrád	1%
Pest	13,3%

Result of the survey - Shopping habits

Table 4: Do you regularly carry a reusable shopping bag, basket, or other reusable storage device with you?

Opinion	Percentage based on all responses	Changes compared to the last survey
Yes	76,2%	-11,3%
No	23,8%	+11,3%

Table 5: Do you currently collect waste selectively in your home?

Opinion	Percentage based on all responses	Changes compared to the last survey
Yes	83,8%	+5%
No	16,2%	-5%

Based on Table 4, it can be seen that nearly two-thirds (~76%) of the respondents pay attention to environmental awareness and regularly take reusable shopping bags, baskets, and other recyclable storage devices with them during their purchases.

Examining Table 5 - which shows the selective waste collection trends - observations confirm a positive increase, nearly 84% of the respondents have environmentally conscious homes. Since there was also an option for justification after this question, it is worth analyzing as well.

Of the 105 respondents, 94 gave reasons for their answers, only 11 refrained from doing so, of which 78 answered the question ***"If yes, why?"*** and 16 ***"If not, why?"***. These data points can be classified into further subcategories, and examples can also be shown during these categorizations. Participants who provide positive reasons can be classified into four subcategories:

- To protect the environment (42 individuals)
- Recycling and sustainability (18 individuals)
- Ethical (8 individuals)
- Provided a detailed answer (10 individuals)

I would like to highlight a few of them:

"Because less waste is produced in the mixed bin, and more waste can be recycled. I consider waste a valuable raw material, and I think there is a very small proportion of it that could not be reused."

"Because of the environmental aspect, and I lived in Germany before, and I found this system very good there."

"We have been returning the glass since I was a child, and I have always put the plastic in the selective collectors.

"I think it is important to protect our environment and it serves as an example for children, for whom selective waste collection will become natural during their later adult lives."

"Because the woman bought nice selective bins at IKEA.

"Because it feels good"

"Important to me"

We can also classify the reasons given by the respondents who gave a negative motivation into three subcategories:

- Is indifferent to sustainability (5 individuals)
- Can't be enviromentally friendly due to outside factors (9 individuals)
- Provided a detailed answer (2 individuals)

I would like to highlight a few responses:

"Because this does not contribute as much to environmental protection as it does the amount of inconvenience and extra attention it requires"

"It's unnecessary, because it goes into the pit among the others in the Gödöllő landfill."

"Because in Hungary, they put both the selective and plain trash in the same car."

"There aren't enough bins"

"I don't have time for selective waste collection"

Table 6: Did the introduction of the deposit refund system affect your shopping habits?

Opinion	Percentage based on all responses
Yes	57,1%
No	42,9%

Table 7: Do you buy fewer products with a deposit fee compared to before?

Opinion	Percentage based on all responses	Changes compared to the last survey
Yes	21,9%	-20,6%
No	78,1%	+20,6%

After further analysis of purchasing habits, it can be seen by looking at the data in Table 6 that more than half of the respondents (~58%) were influenced after the introduction of the deposit refund system. They have changed their habits, tendencies, and what products they buy in their everyday life.

In this regard, the results of Table 7 serve as an additional interesting data point, as more than two-thirds of the respondents (~78%) admit that they did not buy less of the products with a deposit fee even after the introduction of the fee. Since there was also a justification option for this question, it is worth analyzing the answers here as well. Out of 105 respondents, only 23 justified their answer *"If you buy less - Will you replace it with something, or will you not buy it at all?"* These data points can also be classified into additional subcategories, and examples can also be shown during the categorization.

- Won't even purchase it (11 individuals)
- Replaced it with something else(10 individuals)
- Provided a detailed answer (5 individuals)

I would highlight a few of them once more:

"It makes me busy to buy less of these products (e.g. mineral water) and I'm thinking about purchasing bottled water, for example."

"We have rarely bought soft drinks until now, we drink water/syrup, but now we hardly ever buy such products"

"I don't always buy a few products."

"We always bought fortified mineral water, but we now use a soda machine."

"Mineral water can be replaced with well water, but I also buy bottled water"

Results of the survey - opinions regarding the deposit refund system

Table 8: Storage of empty bottles with a deposit fee participating in the deposit refund:

Opinion	Percentage based on all responses
Causes discomfort	62,9%
Does not cause discomfort	37,1%

Table 9: Since the introduction of deposit refund system, has there been a change in the amount of selectively collected waste in your home?

Opinion	Percentage based on all responses
The amount increased	13,3%
The amount decreased	48,6%
There was no change	38,1%

Table 10: Would you change the value of the deposit based on experience so far?

Opinion	Percentage based on all responses	Changes compared to the last survey
The current 50 HUF is sufficent	75,2%	~ +35,3%
A price between 50 and 100 HUF would be better	9,5%	~ -14,4%%
Only above 100 HUF would the fee be worth it	6,7%	**~ +0,5%**
Other (I'd like to share my own opinion)	8,6%	**~ -21,5%**

In relation to the data in Table 8, which deals with deposit-fee bottles participating in the exchange program - compared to the results of the previous answers - we can notice that new challenges have appeared for the public due to the introduction of the deposit refund system. More than half (~63%) of those who completed the questionnaire encountered difficulties in storing bottles with a deposit fee. Since it was also possible to express one's own opinion here, 88 people were willing to justify their decision - and 30 of them also gave detailed reasons - I would like to highlight some of these answers:

"Until now, I have selectively collected it in the selective bin, now I have to store it, moreover, it is very difficult and a lot of inconvenience to return it. All return places are dirty and smelly, and take a lot of time, because on the one hand, they work clumsily, and on the other hand, a lot of people bring them back with bags and it's terrible because of that to stand in line to wait for more bags to be exchanged in front of me."

"I take it back to the store about once a week, where there is always a delay in front of the machine, so I don't want to waste time on it more than once."

"You can't drop them off in every store, and it's not worth going to a bigger store with a few items just to exchange them, so we store them and then exchange them when we go shopping."

"I collect it in a garbage bag and then store it outside in the yard or in the garage, but it takes up space everywhere, and if there's more, it's impossible to fit."

"It's not difficult to collect and later exchange the bottles with a deposit fee, but there are situations when you have to throw them away because I can't store them with me."

"It's better not to cause problems than to cause problems, but only because there is plenty of space in the big house, the situation would be different in an apartment because it can still be annoying"

"They cannot be compressed, so they take up a lot of space in the apartment or in the car. For those who do not have a car, it is difficult to solve the exhcange."
"In a family house with a garden, there is plenty of space to solve the storage problem. Upstairs would definitely cause problems."
The data in Table 9 also deal with this, only nearly 13% of those filling in said that the amount of waste participating in selective waste collection in their homes has increased. Nearly 38% of respondents say that there has been no change, and almost half of respondents (~48%) say that the amount of such waste in their homes has decreased.
This is favorable, since CLXXXV. of 2012. law on waste, § 3 point one, the basic principles are based on the principle of preventing waste generation *"The best waste is that which is not even generated"*.
"Section 3 (1) The following basic principles must be enforced during the activities resulting in waste, as well as during waste management - in accordance with the following:
a) the principle of waste prevention:
aa) it must be promoted that prevention, as the highest level of the waste hierarchy, results in the development of resource efficiency and the reduction of the impact of waste on the environment,
ab) promote innovative production, business and consumption models that reduce the presence of hazardous substances in materials and products, encourage longer product life and promote reuse, through the creation and support of reuse and repair networks such as social networks operated by businesses, deposit-fee or recharge systems, measures to encourage the re-production and renovation of products and, where applicable, the modification of their purpose, or through sharing platforms,
ac) the attention of consumers must be drawn to the importance of waste prevention, consumers must be encouraged to actively cooperate in improving resource efficiency, and as part of this, consumers must be provided with continuous communication and training opportunities related to the issues surrounding waste prevention and waste disposal to increase awareness, as well as
ad) if necessary, measures must be taken to use deposit fee systems and set quantitative target values, as well as to introduce economic incentives that determine the behavior of manufacturers;..."
In connection with the assessment of the deposit refund system, we sought answers to two additional questions. In the first case, we sought the answer to the single open-ended question of the questionnaire: "What suggestions would you have regarding the deposit refund sytem, based on your experiences so far?" to those filling out the questionnaire. All 105 people who completed the questionnaire answered this. These data can also be classified into further subcategories, and examples can also be shown after this categorization:

- Has no recommendation (23 individuals)
- Has recommendation (57 individuals)
- Provided a detailed answer (25 individuals)

"We need more and better functioning automatic machines (it's very slow), but if the whole system could be deleted, that would be the best. Since I buy mineral water for home in large quantities, when I change it back it takes about half an hour. By then, it's already behind me it's the turn and everyone wants to move forward."
"Designing machines that take back products with a deposit fee in bulk, placing bins at the return points, requiring households to request large containers free of charge, in which the products can be stored separately until the return.
the machine crumples the thrown bottles and breaks the bottles, so why does it only accept the undamaged ones? It should also be possible to exchange face creams and other bottles/bottles."
"There should be a quantity limit for the redeemers in the store, those who carry them with bags, they should have another exchange option. Also, they should put more emphasis on the cleanliness of these machines and their environment. They are not hygienic at all."
"Don't be... It's horrible, the vending machines almost never work, there are snaking lines, which you either wait patiently or take home again and if you have time, take an even bigger portion again. Plus, the bins are constantly being taken apart, in case they find a few hundred HUF worth of plastic."
"It can be exchanged everywhere, as there are many catering establishments that charge the fee even though the consumption takes place locally and the bottle remains there, and thus they unilaterally charge the cost to the consumer."
"Operation of several return points outside the store, non-returnable products accumulate inside the store, dirty environment as a result of the drinks coming out of the bottles! We need informational campaigns to raise environmental awareness!"
"More return points should be operated than at present and more space should be provided for the machines at the designated return points. Collection containers should be placed next to the machines to store non-returnable bottles. With improvements, it could become possible for the machine to recognize the bar code by inserting several bottles at the same time, wherever it's on the bottle, you don't have to rotate and dose it one by one - this slows down the process terribly at the moment. In a system similar to the 1% offer of the tax, I would further increase the targeted transfer of the amount from the deposit fee to the organization of my choice, either in the form of a QR code or in the form of an application (this is currently available, but in a very limited circle and many people do not know about it). should be made

interested in the matter, because at the moment neither the staff nor the local resources can cope with this task. On the street, on the beaches, in sports facilities I would put out collection boxes so that those who don't want to bother with the exhcange don't throw the bottles away, and the homeless, who could have some money from the deposit refund, are not punished by "stealing" from the garbage! With further recycling development and processing, I would impose a deposit fee on all TetraPak and other milk and soda cartons and make them redeemable!"

"I don't think they thought that the machine could even fail. We need a more professional service network"

"It should be collapsible due to the use of space, a very small microchip could be placed in the neck of the bottles, which identifies it during the exchange, in my opinion, this would only cost a few pennies, but it would be very beneficial due to the space saving"

Lastly, we would analyse the data in Table 10, where we examined whether opinions regarding the preferred deposit fee amount have changed. The number of groups who think that a higher amount of currency would be necessary, even more than100 HUF, reached a value of around 16% overall, from which it can be predicted that a significant number of people are satisfied with the 50 HUF deposit fee. This question was the last opportunity for free expression. Unlike the others it was not possible to divide the results into several subgroups, since nearly 9% of the respondents indicated in a different wording, but uniformly, that they would abolish the deposit fee in its entirety.

Comparison of results with previous research data

The results of Table 4 would be considered positive in their lonesome, but in the previous research this value was higher (~88%). Because of this, a negative change can be filtered out from this perspective.

In contrast, the results of Table 5 show a positive change, as they indicate an increase of almost 5% compared to the period before the introduction of deposit refund processes, in a time interval of almost 1 year after implementation.

Comparing the data in Table 7 with the previous data, it can be highlighted that before the introduction of the deposit refund system, nearly 58% of those who completed the previous questionnaire stated that they would not change their shopping habits after the introduction. Examining this, nearly 21% of the population changed their opinion after the introduction of this system.

Looking back at the results of Table 10, it can be noticed that compared to the total of those who preferred the deposit fee between 41-50 HUF and 51-60 HUF (~40%), the proportion of those who chose this amount showed an increase of almost 35% (Vigh Zs. - Rákóczi A. 2024).

Based on the responses to our research, it can be predicted that after the introduction of the PET bottle deposit fee, the number of people participating in selective waste collection increased by 5% in almost a year, and nearly 49% of respondents noticed a decrease in the amount of waste in their homes. Furthermore, it can be predicted that most people continue to support this institution of exchange, but find problems with the current system, mainly with the condition of the REpont machines, the expectations of their operation, and the storage of products with a deposit fee at home.

CONCLUSION

The purpose of our research was to reassess the population's attitude to the topic and how it changed after the introduction of the system. In connection with the deposit refund system of beverage cans, has the perception of the people changed regarding it, and what has been the attitude of customers towards the exchange after its introduction. People's environmentally conscious behaviour can be measured. Based on the results of our research, it can be predicted that the number of people participating in selective waste collection increased by 5% in one year, and nearly 49% of respondents noticed a decrease in the amount of waste in their homes. Furthermore, it can also be predicted that most of them will continue to support the institution of REpont's deposit refund, but based on their demonstrated results, they would further develop the service.

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11. Tosca Ballerini (2021); Making Empties Count: Deposit Return Schemes Across the World; Renewable Matter - Materia Rinnovabile article; 21 Jan 2021 00:00
12. Vigh Zsolt József – Rákóczi Attila (2024): A tisztább vidékért: a PET-palack visszaváltás hajnalán, vásárlói attitűdök vizsgálata; - "A Falu" negyedévente megjelenő lektorált szakmai folyóirat 2024/Nyár kiadása

APPLICABLE LAWS

1. CLXXXV of 2012. law on waste
2. Decree of the Government on the amendment of the government decrees related to the environmental protection product fee - 1. LXXXV of 2011 on the environmental protection product fee. 343/2011 on the implementation of the law (XII. 29.) Govt. amendment of the decree

BIOGAS POTENTIAL AND CALORIFIC VALUE OF DIFFERENT AGRICULTURAL MAIN AND BY-PRODUCT

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ABSTRACT

This study assessed the biogas potential and calorific values of the different agricultural main and by-product. Adequate management of different agricultural biomass, residues and by-products can reduce their negative impacts on the environment. An alternative way to use for agricultural wastes, biomass to produce biogas or agripellets to heating. Our work is depending on an ongoing project where the aim is to increase the biogas production, increase the capacity of the biogas plant and reassemble the mixture if it is needed. We investigated the methane potential of 14 sample with the Automatic Methane Potential Test System (AMPTS II) (NaWaRo Ltd) and 9 sample calorific values with Elementar CHNS. system. The significance of our research is that due to the measurements we can exactly determine the possible methane production from the local agricultural wastes, biomass. Our results have shown that the retention time is currently is too long, and the feeding frequency of the digester is also too wide. The calorific values of the samples are parallel with the literature. The pelletized product calorific value similar like the dry wood or straw.

Keywords: biogas potential, calorific value, agricultural residues

INTRODUCTION

The use of biomass, including biogas, for energy purposes is possible mainly in counties with favourable conditions for agricultural production. The technology can be used to reduce fallow land, provide an alternative source of income for local agri-businesses and recover waste from livestock farms and food processing plants. It is necessary to determine the theoretical potential of the county in order to have a comprehensive picture of the amount of biogas that can be extracted in the area. The theoretical potential is the total amount of energy that can be physically extracted. It is important to note that there can be large variations in the specific biogas yield depending on certain factors (feedstock composition, technology used, etc.). The biogas potential of landfills and wastewater treatment plants and the biogas potential of waste materials from the food industry have not been taken into account in our calculations.

Large-scale livestock farming with livestock housing is best suited to the requirements of biogas production. The production of cattle, pigs, sheep, chickens and turkeys produces concentrated manure and causes environmental problems. To calculate the potential, the livestock population of the county was aggregated using the 2021 KSH data, and then the population of the different livestock species per livestock was determined from the KSH data series based on the following:

Based on literature data, the gross average gas yields for each species were calculated. Animal species produce manure with different properties, so the gas yield can be further differentiated by species In Hungary and Western Europe, “wet process” biogas plants based on slurry containing 5-15% dry matter are the most common.

Calculations show that more than 100 million m^3 of biogas can be recovered from livestock production, with an energy content of 2.21 PJ/year. The calculations do not include the biogas potential from manure from other poultry and other animal species.

The main and by-products from the crop production sector can also be considered as a source of biogas. There are changes in agricultural production in Europe today, where industrial and energy (non-food) crops are increasingly being produced, with food production being reduced.

This process foresees the emergence of a new industrial-energy crop production sector, requiring new agrotechnical, mechanisation and logistical applications. The crops most suitable for biogas production must meet a number of conditions. The characteristics of plants that can be easily integrated into the process must include excellent cultivability, storability, smooth harvesting, high dry matter yield, resistance to pests and, last but not least, excellent digestibility.

MATERIAL AND METHODS

Locally available biogas plant input materials

Organic matter load is an important consideration in sizing, which determines how much organic matter (on a dry matter basis) can be loaded per unit time for a given volume.

The aim of the methane potential test is to investigate the digestibility of the samples under mesophilic conditions (39°C) and the amount of biogas potential that can be produced from the samples.

Determine the formulation leading to the maximum methane yield

FOS/TAC analyses provide guidance on the optimal conditions for methane formation. The FOS/TAC analysis was developed to determine the ratio of acid concentration to buffer capacity in the digestion mixture. FOS is an abbreviation for volatile organic acids, measured in mg acetic acid equivalent/ dm^3, while TAC is an abbreviation for total inorganic carbon (the basic buffer capacity), measured in mg $CaCO_3$ /dm^3. Methane production slows down below pH 6.0 and stops above pH 8.0. The pH can vary greatly if the system is not adequately buffered.

In practice, a FOS/TAC ratio of between 0.3 and 0.4 is normal, but each plant has its own optimum ratio, which can be determined by long-term monitoring and system control, whereas a wider optimum (0.15 - 0.45) has been established.

The pH in the digestors of the plant varied between 7.1 and 8.0, indicating that the buffer capacity of the system is about adequate, with only a few cases of significant pH fluctuations.

The basis for pelletisation of potentially available local agricultural by-products

CHNS elemental analysers, used for the calorific value determination of various agricultural products, offer the possibility of rapid determination of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) in organic matrices and other types of materials.

The calorific value is the amount of heat that is released when a unit mass of fuel is burnt perfectly, if the temperature of the fuel before combustion and the temperature of the combustion products after combustion are both 20°C, the carbon content of the fuel is present in the combustion products in the form of carbon dioxide, and the initial moisture content of the fuel and the water produced during combustion is in the form of vapour after combustion, i.e. it does not give off any heat of vaporisation when the combustion products are cooled. The calorific value is therefore less than or equal to the heat of combustion.

The advantage of burning agricultural biomass, pelleting, briquetting is that the calorific value is similar to domestic brown coal (15 500 – 17 200 kJ/kg), but cleaner. It has a lower ash and sulphur content than coal.

RESULTS

Locally available biogas plant input materials

In Figure 1, methane production is plotted as a function of time. The length of the digestion time was 30 days, which is considered as an average time. Since there was no significant increase in the overall gas production curve from day 25, it is likely that a longer experiment would not have yielded better results.

The Corn Silo (4 993 Nml) and EKO Nyíregyháza (4 882 Nml) samples gave the highest total biomethane yields.

Lower gas production was recorded in five samples compared to the control sample: Compost, Solid Separat, Liquid Separat, I. Digester, II. Digester.

Table 1: Test material characteristics

Sample name	Dry matter content [m/m %]	Organic dry matter content [m/m %]
Liquid separat	5,49	65,40
I. digester	8,51	74,75
II. digester	5,91	70,79
Pre-tank	0,89	63,86
Solid separat	21,05	84,98
Manure	16,04	82,14
Grass haylage	36,86	91,49
Straw	81,42	92,28
Compost	50,71	76,38
Corn refuse grain	83,94	96,79
EKO Nyíregyháza	14,59	97,03
Sunflower refuse grain	82,21	85,88
Corn husk	44,66	93,87
Corn silo	25,1	96,37

Figure 1 shows the specific biological methane production in terms of dry organic matter content of the sam-

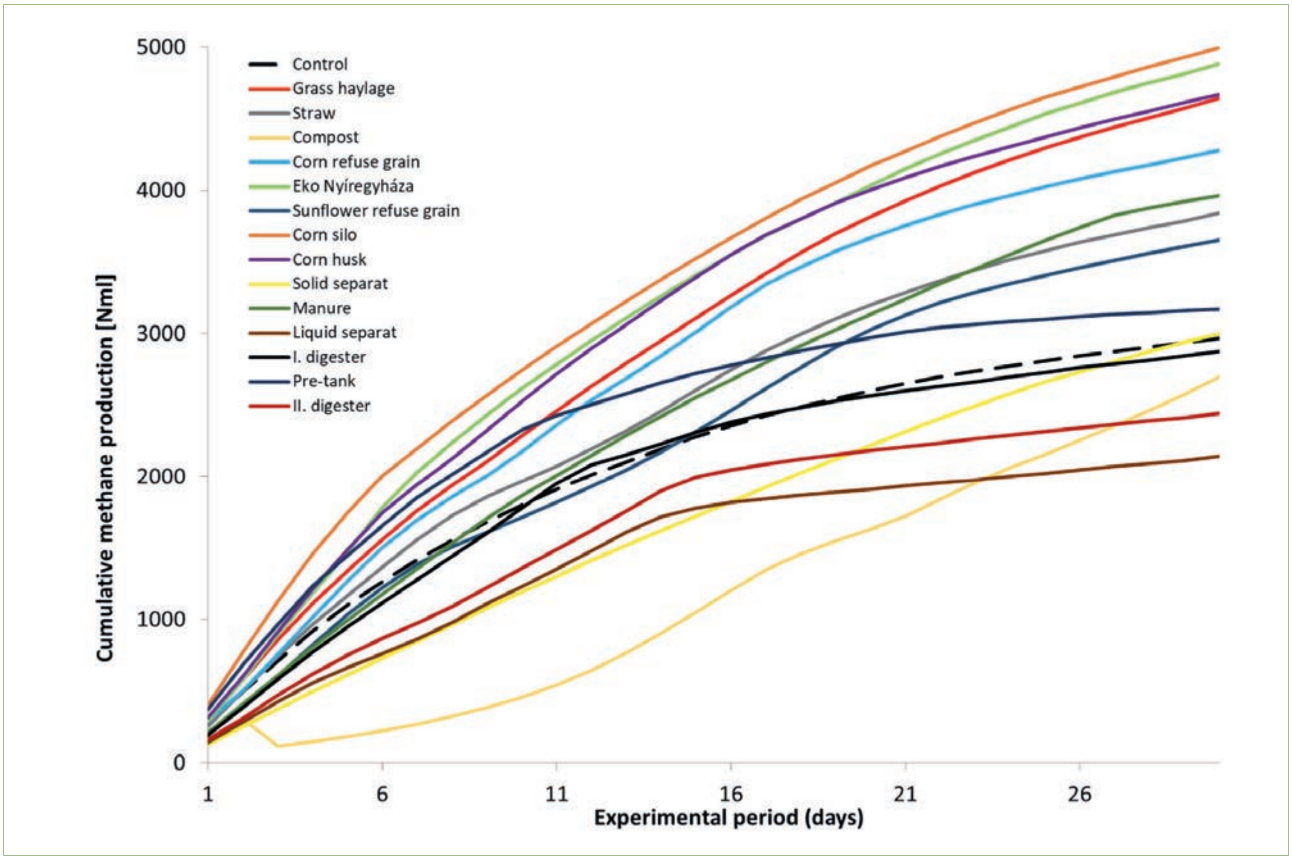

Figure 1: Total methane gas production over the period

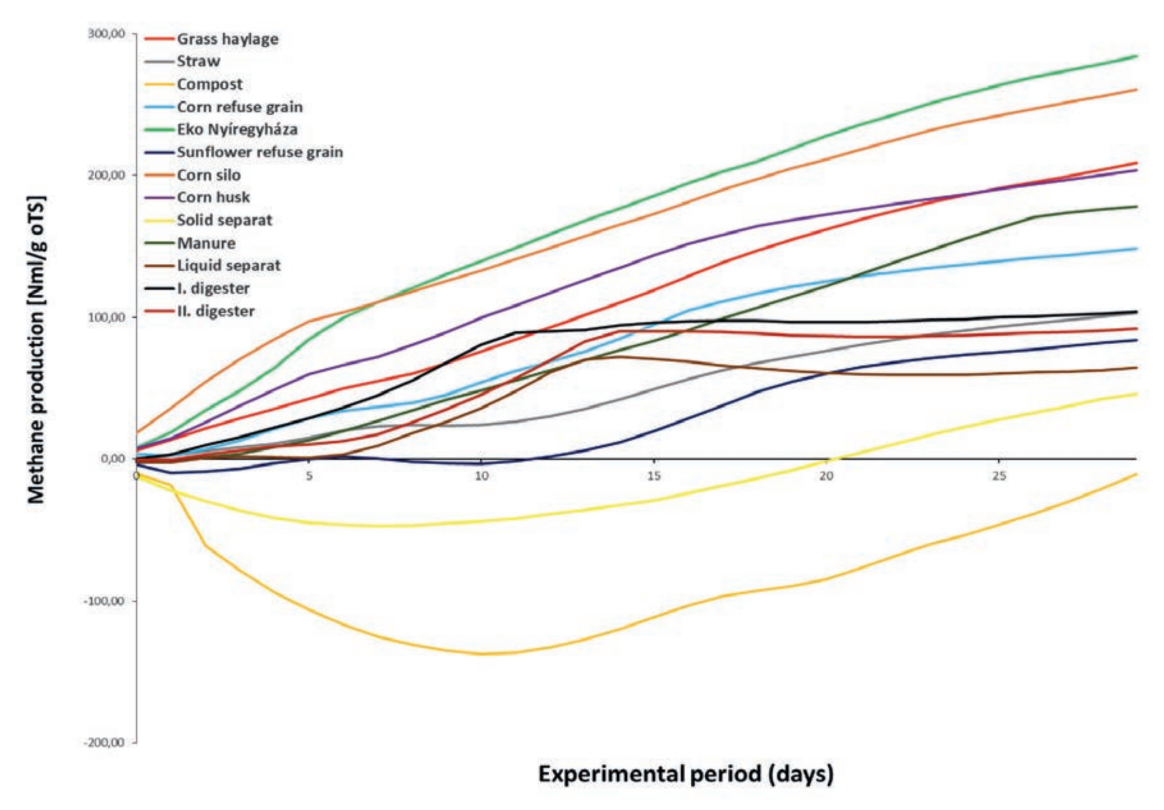

Figure 2: Specific methane production per organic matter corrected for negative control (inoculum)

ples (Nml/g oTS) without the amount of gas produced by the inoculum.

Of the test materials, the EKO Nyíregyháza and the Corn Silo samples had the highest specific methane production capacity. By the 15th day of the digestion process, the specific biomethane production potential of the EKO Nyíregyháza sample was 176.56 [Nml/g oTS], while the Corn Silo sample had a specific biomethane production potential of 165.21 [Nml/g oTS]. After further incubation, their values measured on day 30 of the study increased to 284.06 [Nml/g oTS] and 260.79 [Nml/g oTS], respectively.

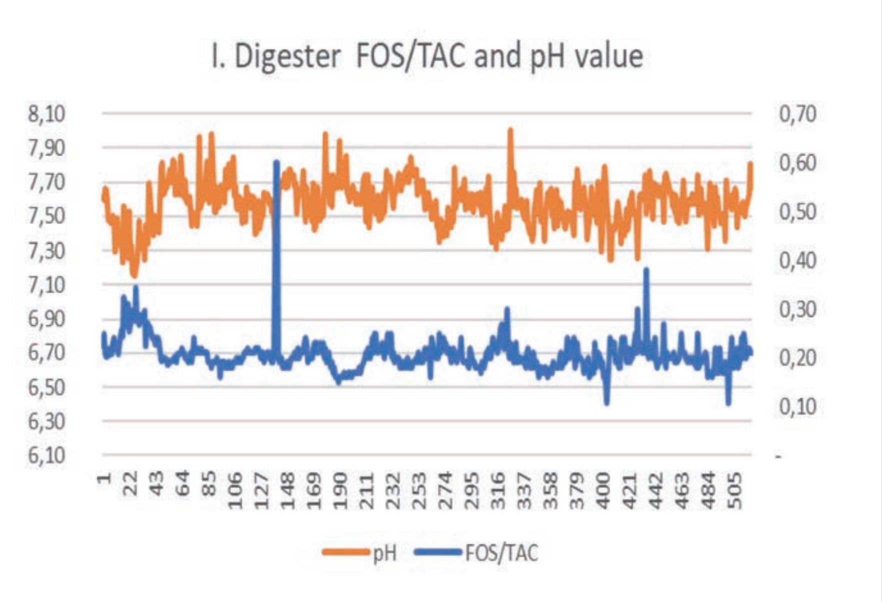

Figure 3: Evolution of the FOS/TAC and pH ratio in digester I

Straw, Sunflower refuse grain, Manure, Liqiud Separate and Digester II samples showed reduced gas production at the beginning of the measurement compared to the control, which can be attributed to the characteristics and composition of these feedstocks. After the initial phase, their gas production was in line with expectations.

Table 2: FOS/TAC ratio assessment based on literature data (Mézes et.al.; 2011)

Evaluation of FOS/TAC ratios according to empirical experience

FOS/TAC ratios	Background	Suggestion/Counter Action
>0,6	Highly excessive biomass input	Stop adding biomass
0,5-0,6	Excessive biomass input	Add less biomass
0,4-0,5	Plant is overflowing	Monitor the plant more closely
0,3-0,4	**Biogas production at the maximum**	**Keep biomass input constant**
0,2-0,3	Biomass input is too low	Slowly increase the biomass input
<0,2	Biomass input is far too low	Rapidly increase the biomass input

Table 3: C/N ratio of samples on dry weight

Sample name	C%	N%	C/N ratio	S%
Liquid separate	45.54	2.14	21.28	0.42
Manure	43.36	1.75	24.78	0.34
Grass haylage	46.51	1.14	40.80	<0.13
Straw	46.06	0.70	65.80	<0.13
Compost	40.64	4.02	10.11	0.71
Corn refuse grain	47.22	1.41	33.49	<0.13
Sunflower refuse grain	47.26	2.49	18.98	0.20
Corn husk	47.13	1.36	34.65	<0.13
Corn silo	39.96	0.80	46.20	<0.13

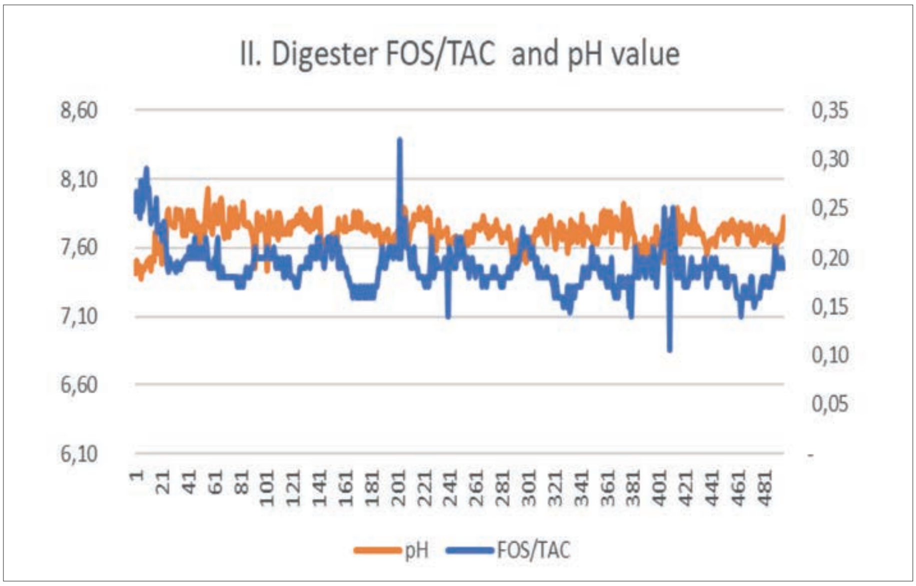

Figure 4.: Evolution of FOS/TAC and pH ratio in digester II

Determine the formulation leading to the maximum methane yield

The data in the diagram 3 and 4 show that the plant is on average characterised by a slightly alkaline chemistry and low FOS/TAC (Figures 5, 6). Overall, although the values obtained are lower than those reported in the literature, this does not mean that the plant is out of balance. However, based on this and on the biogas potential measurements, it is worth reconsidering the frequency of feeding and the hydraulic retention time (HRT).

According to the data of the consortium leader Zrt., in 2021 the number of animals was 2,612, and the total amount of manure produced in livestock farming was 3,962,560 kg, including solid and slurry manure.

For the calculations, only the amount of material that could potentially be taken into account was taken into account, which in 2021 was 2000 t of Corn silo, 2.3 t of Corn straw, 2893.32 t of Corn husk and 83.5 t of sunflower straw.

Calorific value calculation results

The samples with high nitrogen content were solid separation, manure, compost and sunflower straw. Higher sulphur content was also measured in these samples, which may cause corrosion of the combustion equipment in the long term.

As in the literature, calorific values between 16 and 18 MJ/kg were measured, except in two cases, compost and manure.

The moisture content of the samples fell within their typical range, and in order to pelletize or briquette them, pretreatment is required to achieve the right moisture content. The ash content was well below the ash content of lignite. Compost and manure only showed higher values. Based on the results of the sample analysis, the most suitable feedstocks for pelleting can be clearly selected from the locally available biomass raw materials.

CONCLUSIONS

These researches were completed within a project whose aim was to take a good practice for the implantation of an innovative biomass based renewable energy production and use. At least the final output of the system will be renewable energy and energy carriers, which are and will continue to be of key importance from both an environmental and energy security perspective.

Table 4: Calorific value of samples on a dry matter

Sample name	Calorificvalue MJ/kg
Liquid separate	16.830
Manure	15.784
Grass haylage	16.792
Straw	16.769
Compost	14.161
Corn refuse grain	17.333
Sunflower refuse grain	17.961
Corn husk	17.218
Corn silo	18.200

Table 5: Moisture and ash content of samples

Sample name	Moisture content % moisture	Ash content %
Liquid separate	21.05	15.26
Manure	16.04	18.47
Grass haylage	36.86	8.62
Straw	10.55	8.36
Compost	50.71	25.50
Corn refuse grain	83.94	3.30
Sunflower refuse grain	82.21	14.27
Corn husk	44.66	6.32
Corn silo	25.10	3.68

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PFASS IN COMPOSTS – NEW CONCERNS IN COMPOST APPLICATION

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ABSTRACT

Per-and polyfluoroalkyl substances (PFASs, C_nF_{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 (≥8C) and short-chain (≤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 instigated 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_nF_{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)

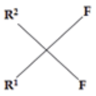
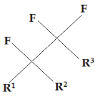
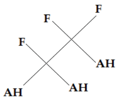
Furthermore, the transformation of precursor compounds in designed and environmental systems can contribute to the presence of PFAS in subsurface habitats, hence indirect sources of PFAS include municipal sludge from wastewater treatment facilities, biosolids applied to the soils, MSW composts, potting mixtures, AFF 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 threshold 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:

Table 1: Regulatory and nonregulatory definitons of PFASs

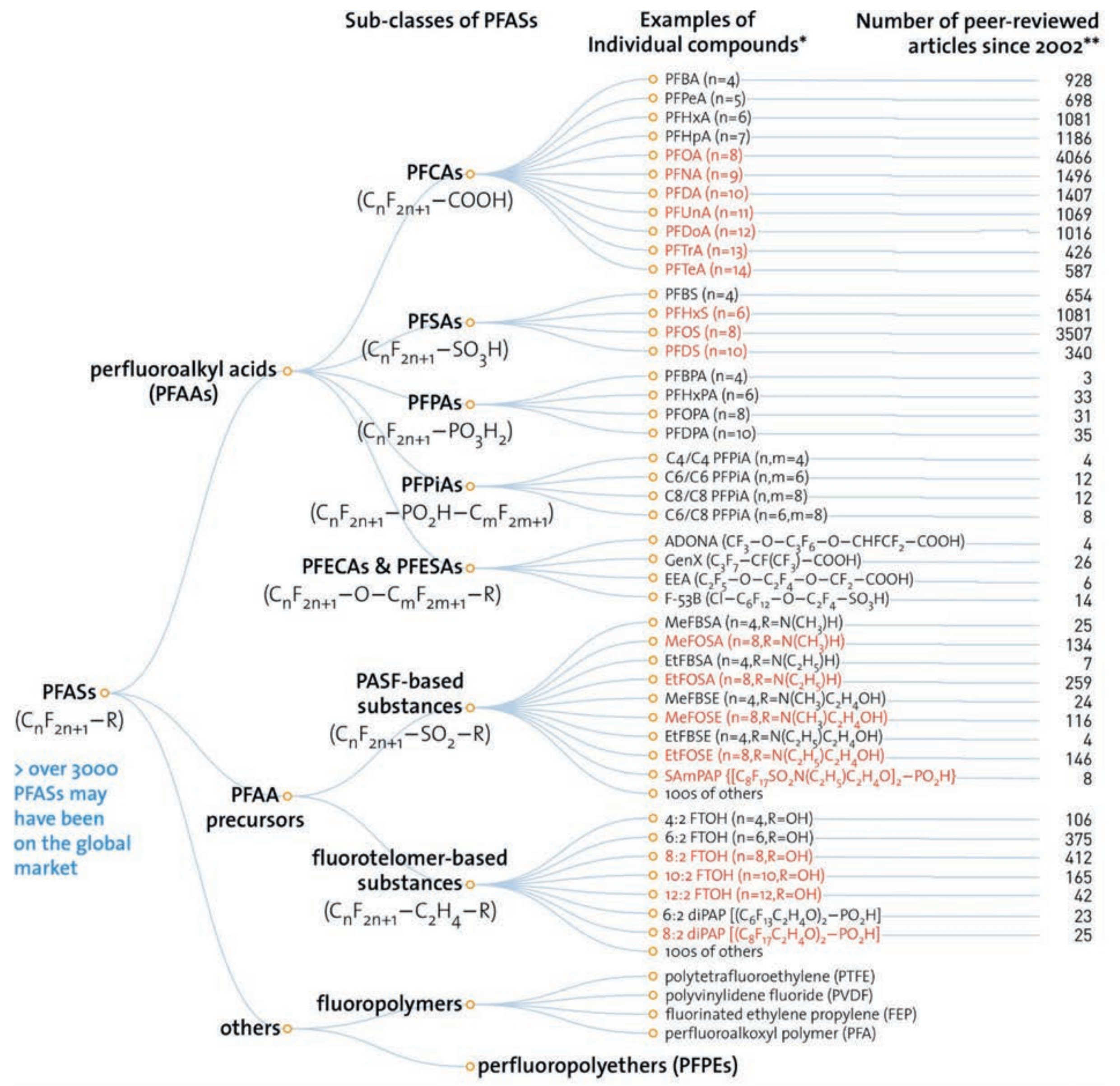
Entity	Paper/Report/Act	Definition	Schematic representation of the PFAS definitions
Buck et al., (2011)	Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins.	"Aliphatic compounds comprising one or more C atoms on which all of the H substituents present 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}
OECED, 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 (–CF3) or a perfluorinated methylene group (–CF2–) is a PFA"	
EPA, 2021	Safe drinking water act	"PFAS is a structure that contains the unit R-CF2-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-nmnnd-v3.	"Each compound that contains an (AH)(AH)(F)C–C(AH)F2 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."	

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 other 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 can exist as solids, liquids, gases, and both polymers and non-polymers. According to USEPA [2009], PFAS can be classified into long-chain (≥8C) and short-chain (≤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 sub-categories; perfluoroalkyl acids (PFAAs), polyfluoroalkyl substances, and polymers. Moreover, PFAAs subcategories include perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl sulfonic acids (PFSAs), perfluoroalkyl phosphonic acids (PFPAs), and perfluoroalkyl phosphinic acids (PFPiAs). PFAAs precursors are well-studied and include perfluoroalkane sulfonyl fluorides (PFASFs) such as FOSAs (perfluoroalkyl sulphonamides) and fluorotelomers. PFASs' polymers include fluoropolymers and perfluoropolyether (PFPEs) (Figure 1).



* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

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

PFAS physicochemical properties

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 transportable 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.

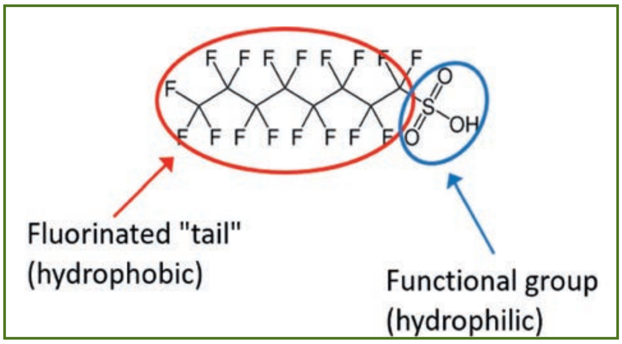


Figure 2: Components of PFAS (source: https://www.ngi.no/eng/Projects/Reducing-negative-impact-of-PFAS/PFAS)

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).

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

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 sulfonamides 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 sulfonamido 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 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 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.

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

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

Feedstock	country	PFASs	Concentrations (µg/kg dm*)	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	
		PFTrDA	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	
		PFTrDA	<LOQ	
		PFTeDA	0.4	
		PFHxDA	<LOQ	
Commercially available composts	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	

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 PFOASs 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 halflives in humans; neverthe-

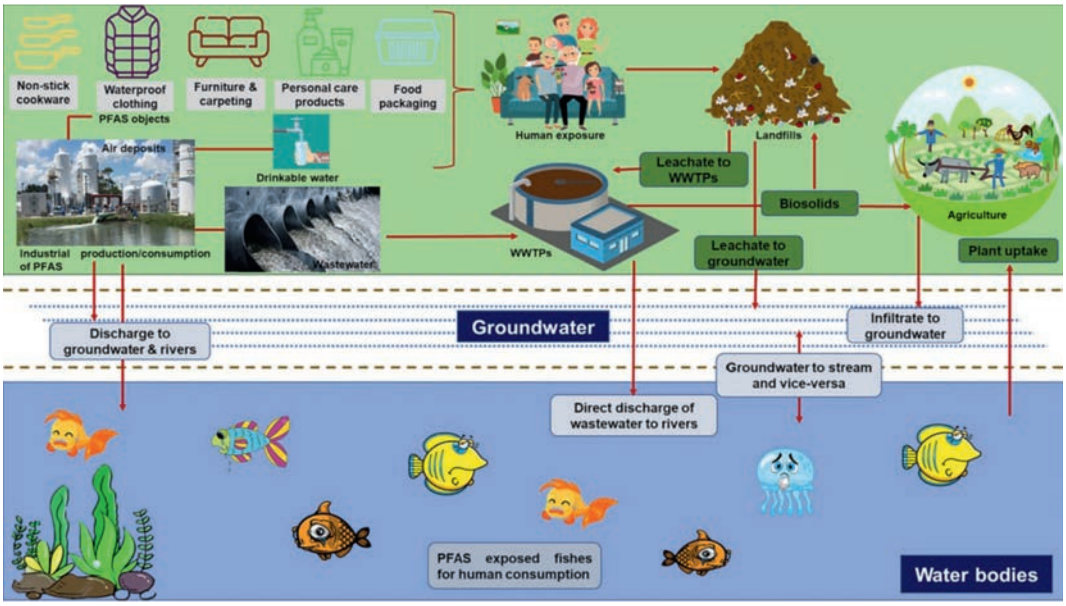


Figure 3: Exposure pathways to PFAS (Garg et al.; 2023)

less, 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.

a) 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. 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%) (Sharma 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, PFASswere 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.

a) 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.

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)	Refrences
Biosolids	Australia	Perfluoroctanesulfonate (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	Sindiku 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	
		PFTrDA	2.3	
		PFTeDA	1.2	
		PFHxDA	0.	
Composted biosolids with municipal solid waste		PFBA	3.2	
		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	
		PFTrDA	0.6	
		PFTeDA	0.7	
		PFHxDA	0.6	
Composted biosolids with residential yard trimmings		PFBA	5.2	
		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	
		PFTrDA	2.5	
		PFTeDA	2.7	
		PFHxDA	1.3	
Composted biosolids with plant materials		PFBA	3.9	
		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	
		PFTrDA	1.3	
		PFTeDA	1.2	
		PFHxDA	0.5	

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.

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

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.

RESULTS AND DISCUSSIONS

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

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.)

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

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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MITIGATING ENVIRONMENTAL RISK FACTORS AND PROMOTING SUSTAINABLE AGRICULTURE THROUGH PÁLINKA SPENT WASH COMPOSTING

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ABSTRACT

This paper addresses environmental challenges in Hungary's Pálinka distillery industry and advocates for sustainable agriculture through Pálinka spent wash composting. Pálinka production generates substantial organic waste known as spent wash, posing environmental issues due to its high organic content, low pH and complex composition. Composting provides an eco-friendly solution by transforming this waste into humus-rich material and reducing phytotoxic substances. The study focuses on environmental concerns, especially copper in Pálinka spent wash. It explores the potential of Pálinka spent wash compost to mitigate these issues and enhance soil quality for sustainable agriculture. The investigation tracks copper reduction through co-composting with garden compost, diatomaceous earth and wood ash. Various analyses, including physicochemical assessments and germination tests, evaluate the compost's suitability for seed growth. This research highlights the importance of addressing environmental and health risks linked to Pálinka spent wash while emphasizing its potential as a valuable soil enhancer to improve soil health and fertility.

Keywords: composting, Pálinka spent wash, co-composting, copper, Bokashi Organico.

INTRODUCTION

Pálinka, a celebrated Hungarian hard liquor, yields around 300,000 tons of mash residue annually referred to as Pálinka spent wash (PSW). This organic byproduct is a blend of organic and inorganic components and constitutes a significant portion, about 85%, of the input material (Borges et al. 2022) With a low pH (3-4), substantial organic load, polyphenols and macro and micronutrients content, improper disposal of PSW can lead to water pollution, eutrophication and oxygen depletion (Borges et al. 2021).

The Pálinka production in Hungary employs two main distillation methods: traditional Pot-Still Double Distillation (PSDD) and Rectification Column Distillation Systems (RCDS) (Géczi et al. 2018; Korzenszky et al. 2020). Understanding these methods is essential for grasping the composition of PSW, including metals content, e.g., copper, moisture content, nutrients and polyphenols. Furthermore, the broader food industry is shifting towards sustainability, focusing on waste reduction and alternative energy sources (Géczi et al. 2016; Borges et al. 2015) Harnessing PSW for composting offers a solution to these environmental issues. Composting, whether aerobic or anaerobic, is a sustainable and effective approach for handling organic waste, alleviating odor and nutrient concern and enhancing various soil parameters, such as soil organic matter, nutrient availability and microbial activity, ultimately enhancing soil health and fertility. PSW compost further enhances soil structure, water-holding capacity and organic matter sequestration, stabilizing soil organic matter (SOM) (Marhuenda et al 2007; Bustamante et al. 2010). However, PSW has characteristics unsuitable for traditional composting due to its low pH and high moisture content. To optimize composting, mash residue can be combined with additives like diatomaceous earth, wood ash and garden compost, creating an ideal environment for microbial activity. These additives primarily serve as water-retaining materials and pH buffers. Moreover, alternative anaerobic composting, such as *Bokashi Organico*, offers a unique approach to food waste fermentation. It involves sealing food waste in a container known as a *Bokashi Organico* bin, preventing air contact and facilitating natural waste fermentation with the help of a bran-based starter material containing natural ingredients and effective microorganisms (Borges et al. 2022).

Successful PSW composting follows best practices, including balanced material selection, appropriate system design and critical parameter monitoring (e.g., moisture, temperature and odor) (Borges et al. 2022). These practices ensure high-quality compost, enriching the soil, promoting nutrient cycling and enhancing soil structure and water-holding capacity. Composting PSW and exploring innovative methods like *Bokashi Organico* align with the discussion on food chain risk factors and offer an eco-friendly approach to environmental conservation and sustainable agriculture.

MATERIALS AND METHODS

In this research, we explore two distinct composting techniques for managing PSW:

1. Anaerobic Composting with Bokashi compost (BC): *Bokashi Organico* bin-produced compost was mixed with varying proportions of Pálinka spent wash (PSW) in 150 ml Mason Jars over a 4-week period. The study involved different BC and PSW ratios: 100% BC + 0% PSW, 75% BC + 25% PSW, 50% BC + 50% PSW, 25% BC + 75% PSW and 0% BC + 100% PSW, with each combination replicated three times, totaling 15 samples. Germination tests were conducted using lettuce, wheat, corn and mustard seeds, both before and after anaerobic composting. After the 4-week period, we collected samples, mixed them with distilled water, centrifuged them and filtered them to obtain an aqueous extract at a 1:10 ratio (w/v). For control treatments, drinking water was used, while Bokashi compost and the other treatments utilized the aqueous extract.

2. Aerobic Composting with Additives: We conducted a comprehensive 12-week composting experiment in controlled laboratory conditions. Perforated plastic boxes were used as incubation vessels for PSW composting. The initial conditions of the mash residue included a pH of approximately 3.5, a moisture content of 93.82% and an organic matter content of 99.60%. The treatments involved control (C), garden compost (GC), diatomaceous earth (DE), wood ash (WA) and combined treatments (CT). The diatomaceous earth, derived from Miocene-aged organic sedimentary rock, enhanced soil structure and moisture balance due to its water-retention properties, primarily consisting of silt-sized particles and containing amorphous silica (76–78%), calcite (15–17%) and montmorillonite (6–7%). Wood ash, known for its high potassium content, helped neutralize the acidic mash residue while improving water retention. The experiment also included wood ash-treated mash residue, revealing its potential as an organic fertilizer for acidic soils. Details of the composting treatments and additive quantities are presented in Table 1.

For both composting methods, we assessed a range of physicochemical parameters, including pH, electrical conductivity, total dissolved salts, nitrogen forms, phosphate, copper, sodium, potassium and organic matter.

Table 1: Treatments and additive weights used in the PSW aerobic composting experiment (Unit: grams)

Treatments and additives	PSW	GC	DE	WA
Control	5000	-	-	-
GC+PSW	2500	2500	-	-
DE+PSW	5000	-	2500	-
WA+PSW	3750	-	-	2500
CT	4000	1000	1000	1000

RESULTS AND DISCUSSION

The chemical properties of PSW, Bokashi compost (BC) and their mixtures were analyzed (Table 2). Mixing Bokashi compost with PSW raised pH slightly, which remained acidic. Total dissolved salts were noticeable, especially in treatments with higher Bokashi compost ratios. PSW featured significant potassium content.

Table 2: Parameters of PSW, Bokashi compost and the different treatments with Bokashi compost and spent wash.

Treatments and Parameters	pH (H_2O)/ pH (KCl)	EC (mS/cm)	Total Dissolved Salts (mg/L)
Pálinka Spent Wash (PSW)	3.5/3.44	3.59	1976.73
Bokashi Compost (BC)	4.27/4.27	3.27	1633
0% BC + 100% PSW	3.47/3.41	1.32	658.33
25% BC + 75% PSW	3.69/3.63	1.71	853.00
50% BC + 50% PSW	3.83/3.78	2.31	1155.33
75% BC + 25% PSW	4.01/3.93	2.78	1387.00
100% BC + 0% PSW	4.29/4.19	3.77	1886.33

Germination tests revealed that PSW, before anaerobic composting, did not support seed growth. After 4 weeks of anaerobic composting, improved germination occurred, particularly for wheat (Table 3).

Table 3: Seed germination percentages of anaerobic composting treatments and Bokashi compost after 4 weeks; control with only drinking water

Treatments	Lettuce	Wheat	Corn	Mustard
Control	41%	95%	67%	59%
Bokashi compost (BC)	0%	60%	61%	3%
100% BC + 0% PSW	0%	71%	45%	7%
75% BC + 25% PSW	3%	76%	52%	33%
50% BC + 50% PSW	3%	84%	52%	48%
25% BC + 75% PSW	1%	75%	30%	49%
0% BC + 100% PSW	0%	80%	45%	21%

Table 4: Chemical characteristics of the additives used for PSW aerobic composting

Chemical Parameters	Garden compost	Diatomaceous earth	Wood ash
$pH_{(H2O)}$/ $pH_{(KCl)}$	7.7/7.28	7.93/7.35	13.65/13.79
Total Dissolved Salts (mg/kg)	1480	356.5	104 500
NO_{2-}, NO_{3-}, NH_{4+} (mg/kg) of dry matter	42.3	6.15	5.5
P_2O_5 (mg/kg) of dry matter	2232.35	587.49	576.24
K_2O (mg/kg) of dry matter	3666	331	66 400
Cu (mg/kg) of dry matter	Under detectability	-	-
Organic material (%)	92.43	15.19	60.78

For the second composting method, the mash residue underwent controlled fermentation before distillation. The process involved enzymatic apple pectin extraction and the introduction of special yeast with pH adjustment to 3.69 using phosphoric acid. The suspension had low total dissolved salts (1331 mg/l), with significant potassium (K_2O) (37,440 mg/kg) and phosphorus (P_2O_5) (1,231.2 mg/kg) in dry matter. Nitrite (NO^{2-}) and nitrate (NO^{3-}) were undetectable and ammonium (NH^{4+}) was minimal at 2 mg/kg. The suspension had 3.5% dry matter content, primarily composed of 93.2% organic matter. Treatment materials' physicochemical characteristics are summarized in Table 4.

Tests on compost samples highlighted Bokashi compost's buffering capacity. All treatments maintained a near-neutral pH range, crucial for microbiota. Garden compost exhibited the highest mineralized nitrogen levels, while wood ash excelled in nitrogen supply and water retention (Figure 1).

The high copper content in PSW was a concern. The analysis revealed substantial variation and a decrease over time (Figure 2). Diatomaceous earth exhibited the lowest copper concentration but combining it with PSW increased it. Wood ash also showed an increase over time due to the blending of substances.

The analysis of organic matter content indicated the potential for humus formation. Humus formation was central to soil fertility and the addition of compost-mash residue significantly increased humus content. Garden compost excelled in humus content, as observed with diatomaceous earth and wood ash (Figure 3). Humus qual-

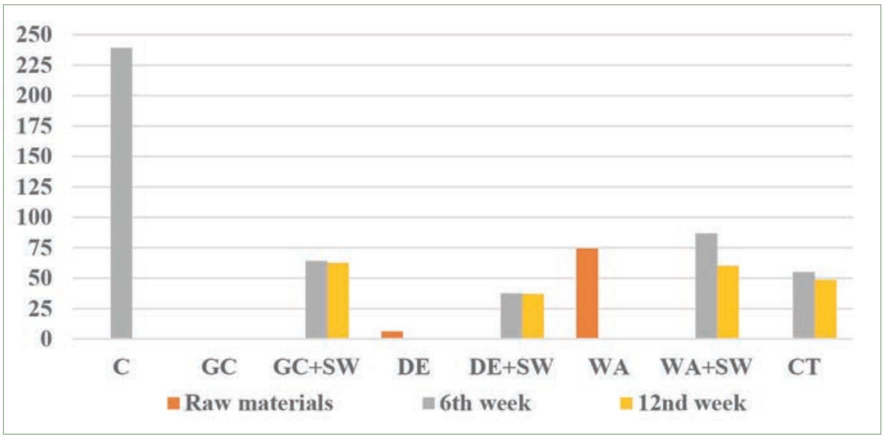

Figure 2: Effective reduction of higher copper content in mash residue by organic and mineral substances. (Unit: mg/kg)

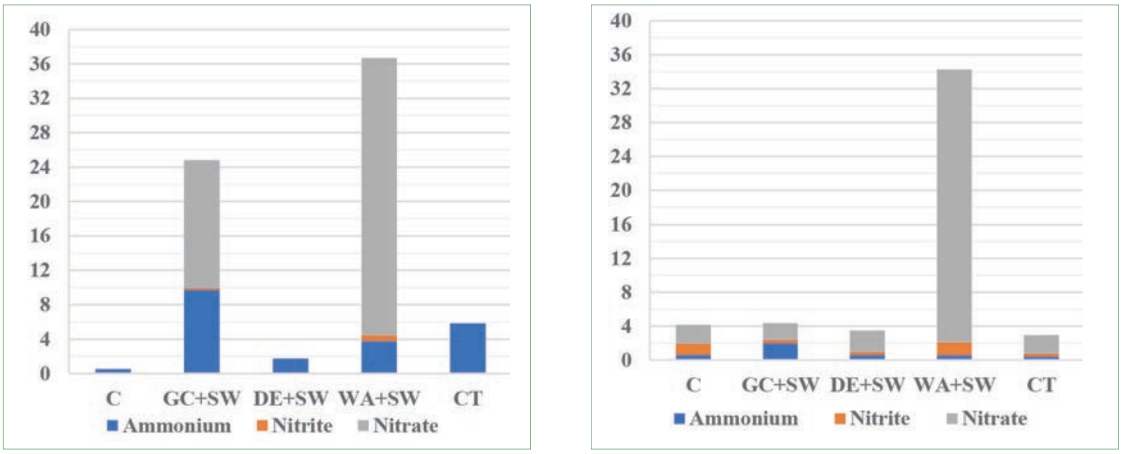

Figure 1: Nitrogen forms available to plants as a result of the treatments. Results from different times of the composting system, 6th week (left) and 12nd week (right). (Unit: mg/kg)

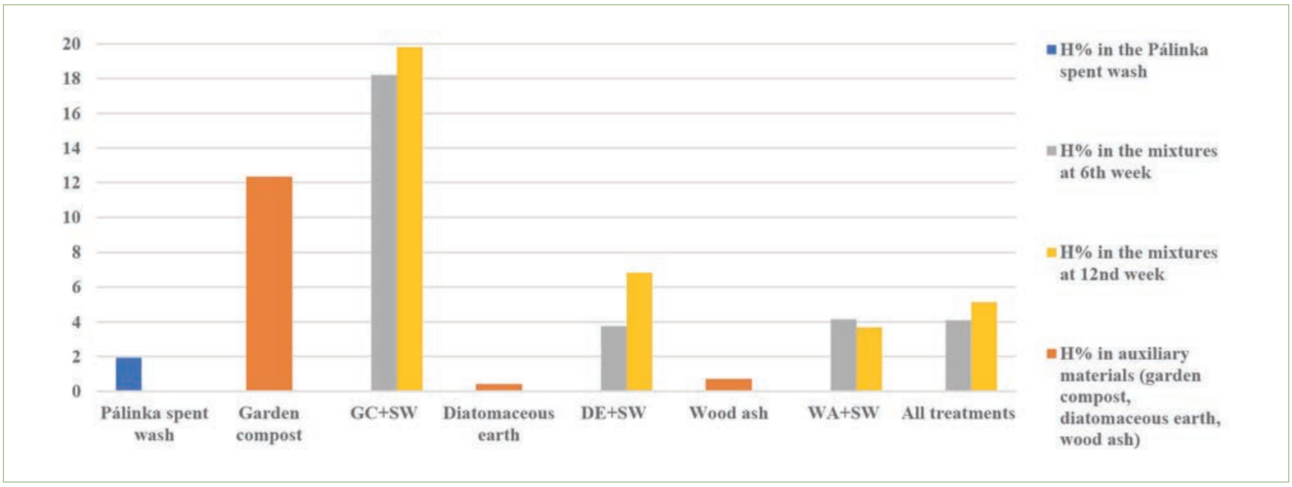

Figure 3: Humus quantity, in percentage, in Pálinka spent wash and additives, also in the treatments. (Unit: %)

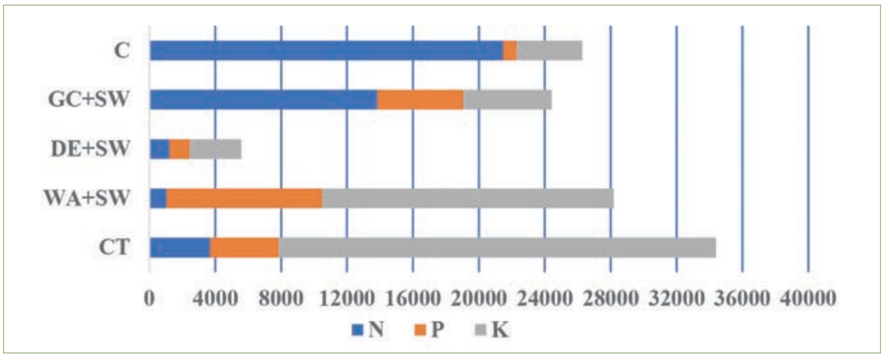

Figure 4: The ratio of macro elements (Nitrogen - N, Phosphorus – P and Potassium – K) in each treatment. (Unit: mg/kg)

ity and stability were indicated by fulvic and humic acids. Furthermore, PSW compost plays a vital role in enhancing microbial activity and diversity in the soil, thereby promoting a healthy soil ecosystem. Composting PSW enriches the soil with organic matter, creating a nutrient-rich environment that supports the growth and function of beneficial soil microorganisms (Martinez-Sabater et al. 2009). Bacterial activity prevailed, especially with diatomaceous earth treatment, leading to improved soil mineralization. Wood ash-mash residue provided remarkable nitrogen provision with a suitable N:P:K ratio (Figure 4).

In summary, the diverse treatments offer promising options for sustainable PSW management, improving soil health and agricultural practices while mitigating heavy metal risks.

CONCLUSION

Composting PSW emerges as a potent strategy for environmental risk mitigation and the promotion of sustainable agriculture. This study confirms that composting effectively reduces copper levels in the mash and enhances humus and nutrient content in the resulting compost, ultimately improving soil fertility, structure and overall ecosystem functionality. Ongoing semi-industrial experiments, exploring various additives in mash residue composting, represent a forward-looking and ecologically sound approach, offering the prospect of scaling up composting technology for substantial quantities of mash residue. This marks a significant stride toward sustainable waste management and soil enrichment, highlighting the potential to enhance soil fertility and reduce environmental hazards through composting Pálinka mash residue. These findings offer support for environmental preservation and the advancement of enhanced agricultural practices. Composting PSW provides a practical path to greener, more productive and environmentally responsible agricultural systems.

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