Degree project in Chemical Engineering

Second cycle, 30 credits

Thermal degradation of PFAS in solid matter

The efficiency of thermal degradation of PFAS in solid matter and potential byproduct formation during thermal treatment

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Master's Programme in Molecular Science and Technology

Date: 2024-03-01

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School of Chemical Engineering

Host company: Stockholm Exergi AB

Swedish title: Termisk nedbrytning av PFAS i avfall

Swedish subtitle: Effektiviteten av den termiska nedbrytningen av PFAS i avfall och bildandet av potentiellt skadliga biprodukter under termisk behandling.

Abstract

Per- and polyfluoroalkyl substances (PFAS) are man-made organic compound widely used in consumer and industrial products. They exhibit attractive properties such as resistance to water, heat, and grease. Therefore, PFAS are used in fire foam, non-stick pans, water-resistant clothes, make-up, and furniture. Recent studies have revealed that PFAS substances can be harmful to humans, animals, and the environment. Some PFAS substances have, therefore, been classified as persistent, bioaccumulative, and toxic (PBT), and very persistent and very bioaccumulative (vPvB). This means that PFAS resists degradation, accumulates in living organisms and biota, and inherits toxic effects.

In previous and current research, the focus has been on the behavior of PFAS in different environmental settings. However, there is a gap in research on how these PFAS substances behave during thermal treatment processes in commercial facilities at temperatures of 850-950 °C and how effective the thermal degradation is. This project investigates the effectivity of thermal degradation via combustion and the fate of PFAS post-combustion, focusing on the formation of potentially hazardous by-products. Therefore, the combustion of PFAS-containing sewage sludge in a bench-scale bubbling fluidized bed (BFB) was to be conducted to fulfill the objective of this study. Due to hindrances, the experiments were performed in a conventional furnace furnace instead. Also, a literature study was conducted to investigate the fate of PFAS after combustion.

From this study, it was concluded that thermal treatment via combustion at temperatures 850 and 950 °C is an effective method to degrade PFAS in sewage sludge. Also, the literature study investigation revealed that persistent short-chain PFCAs were most abundant in the ash, liquid, and gaseous residues after thermal treatment. A few investigations indicate that thermal treatment of PFAS-containing matter possibly results in ozone-depleting compounds. Based on the conducted literature study, there is a lack of strong evidence that supports the claim of the formation of ozone-depleting compounds during combustion of PFAS.

Sammanfattning

Per- och Polyfluorerade alkylsubstanser (PFAS) är syntetiskt framställda organiska föreningar som har använts i stor utsträckning i konsument- och industriprodukter. PFAS-substanser besitter attraktiva egenskaper såsom resistans mot väta, fett, fläckar och är dessutom värmetåliga. De används i bland annat brandskum, smink, vattentäta kläder med "andas-funktion", möbler och non-stickstekpannor. Den senaste forskningen har dock visat att PFAS utgör en fara för levande organismer och miljön. Vissa PFAS-substanser har klassats som persistenta, bioackumulativa och toxisk (PBT), samt väldigt persistenta och väldigt bioaccumulativa (vPvB).

Existerande forskning har fokuserat på beteendet hos PFAS i olika miljöer. Dock finns det en kunskapslucka när det gäller hur dessa PFAS-substanser beter sig under termiska behandlingsprocesser, samt förbränningsgraden i kommersiella förbränningsanläggningar vid temperaturerna 850–950 ℃. I detta projekt undersöks därför nedbrytningsgraden av PFAS genom förbränning samt bildning av potentiellt farliga biprodukter efter förbränning. För att genomföra denna studie skulle förbränning av PFAS-haltigt avloppsslam i en pilotskalig bubblande fluidiserad bädd (BFB) genomföras. På grund av hinder utfördes experimenten i stället i en konventionell och simpel laboratorieugn. Dessutom genomfördes en litteraturstudie för att undersöka bildandet av potentiellt farliga biprodukter efter förbränning av PFAS. Denna studie har visat att termisk behandling genom förbränning är en effektiv metod för att behandla PFAS i avloppsslam med reduktion under kvantifieringsgränserna. Undersökning av potentiellt farliga biprodukter baserat på litteraturstudier har visat att kortkedjiga PFCAs var mest förekommande i aska, vätska och gasformiga rester efter termisk behandling. Några undersökningar tyder på att termisk behandling av PFAS-haltigt material möjligen resulterar i ozonnedbrytande ämnen. Utifrån den genomförde litteraturstudien i detta projekt saknas starka bevis för att kunna påstå att det bildas ozonnedbrytande ämnen under förbränning av PFAS

Nyckelord

PFAS, PFOS, PFOA, PFCAs, termisk nedbrytning, förbränning, avloppsslam

Acknowledgments

I would like to express my gratitude to my supervisor and examiner Klas Engvall, and supervisor at Stockholm Exergi Eva-Katrin Lindman for their continuous support and guidance throughout this project. I would also like to thank Erik Dahlén for giving me this opportunity to do my master's thesis project at Stockholm Exergi.

Last but not least, a big thank you to my fantastic family for your support during the past 6 years. I would not be able to do this without you.

Stockholm, January 2024
Tuqa Al-Badri

Table of contents

List of figures

List of tables

List of acronyms and abbreviations

PFAS	Perfluoroalkyl and polyfluoroalkyl Substances
PFOS	Perfluorooctane sulfonic acid
PFOA	Perfluorooctanoic acid
PFAAs	Perfluoroalkyl acids
PFCAs	Perfluoroalkyl carboxylic acids
PFSAs	Perfluoroalkane sulfonic acids
FTOH	Fluorotelomer alcohol
PBT	Persistent, bioaccumulative and toxic
vPvB	Very persistent very bioaccumulative
POP	Persistent organic pollutants
BFB	Bubbling fluidized bed
CFB	Circulating fluidized bed
OECD	The International Organization for Economic Cooperation and Development
LOQ	Limit of quantification
d.m.	Dry matter

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic organic chemicals developed in the 1950s for industrial application (Lindman, 2023).

PFAS are chemically stable due to their structure; therefore, they have high resistance to degradation. They possess distinct properties, such as resistance to water and oil, heat durability, and effective surfactant capacities. These qualities of PFAS have led to their widespread application in diverse fields, such as food packaging, cosmetics, household items, fire extinguishers, and industrial processes (Glüge et al., 2023). Recent studies have shown that PFAS poses a danger to humans, animals, and the environment. PFAS are classified as persistent, bioaccumulative, and toxic substances (PBT) (Kemikalieinspektionen, 2023).

Some individually studied PFAS substances are established to pose a higher risk than others PFAS substances and are regulated. For example, perfluorooctane sulfonic acid (PFOS) and its derivatives have since 2009 been restricted from being used for industrial purposes according to the Stockholm Convention and Persistent Organic Pollutants (POPs) Regulation. The substance Perfluorooctanoic acid (PFOA) and its derivatives were, on the other hand, included in Stockholm Convention 2019, to be completely prohibited since 2020 in accordance with POPs regulation (OECD, 2023). In February 2023, Denmark, Norway, Sweden, Germany, and the Netherlands proposed a restriction that includes furthermore PFAS substances, and this proposal is now under evaluation by ECHA's committee (OECD, 2023; ECHA, n.d.). Many PFAS substances are still unregulated, and they are still widely used in industries. The problem with the use of PFAS use in products is that these substances can be released during the products' entire life cycle, leading to continuous contamination of the surrounding environment (Naturvårdsverket, 2017). PFAS have been found everywhere in the society and the environment, including atmosphere, groundwater, drinking water, living organisms, and sewage sludge. Sewage sludge is residual product generated in wastewater treatment plants. One common method to treat sewage sludge is through anaerobic digestion, meaning degradation of the sewage sludge in an oxygen free environment (Stockholm Vatten & Avfall, n.d.). During the anaerobic digestion process, biogas is produced. The residual sludge is dewatered and then used as fertilizer in agriculture, due to high content of valuable nutrients in the sludge such as phosphorus (Lindman, 2023). However, the application of sewage sludge in agriculture has been proven to result in relatively elevated levels of PFAS in the soil (Johnson, 2022). Even if the sewage sludge applied in agriculture has low concentrations of PFAS, this would still be a challenge as persistent PFAS can accumulate in the soil over time (Baresel et al., 2023).

Stockholm Exergi is an energy company that produces electricity, district heating, and district cooling by utilizing thermal treatment of solid waste, such as municipal and industrial waste. In this project, Stockholm Exergi is interested in investigating thermal treatment, specifically via the combustion of PFAS in sewage sludge. The reason for this interest is that Stockholm Exergi aims to combust sewage sludge mixed with other biofuels and thereafter, the generated ash can be applied in the forests as a fertilizer due to the high content of phosphorus. Stockholm Exergi is also interested in investigating potential hazardous byproducts that can form during the combustion of PFAS-containing waste in general (Lindman, 2023).

In current studies that have been conducted so far, the major focus has been on the behavior of PFAS in various settings, such as soil, surface water, and sewage sludge. However, a comprehensive review of how PFAS behaves during thermal treatment processes in commercial combustion facilities remains absent. Details concerning their combustion efficiency, potential emissions, and the creation of incomplete and possibly harmful byproducts in thermal treatment are still relatively unexplored (Björklund et al., 2023).

1.1   Objective

The initial objective of this master thesis project was to study (i) the efficiency of thermal degradation of PFAS in sewage sludge at a temperature of 750, 850, and 950 ℃ in a bench-scale bubbling fluidized bed (BFB) at the Royal Institute of Technology (KTH) and (ii) potential harmful by-products that are formed during thermal treatment, by analyzing the thermally treated sewage sludge. The efficiency of the thermal degradation of PFAS can be calculated by establishing a mass balance for the PFAS concentrations in the system pre and post combustion for each temperature such as:

$$[PFAS]_{incoming\ sludge} = [PFAS]_{bottom\ ash} + [PFAS]_{fly\ ash} + [PFAS]_{condensate} + [PFAS]_{flue\ gases}$$

Due to delays in finishing the construction of the bench-scale BFB, an adjustment to the original objective had to be made. The interest of the project shifted into a similar objective, which is (i) the efficiency of thermal degradation of PFAS in sewage sludge at a temperature of 850 and 950 ℃ in a conventional lab furnace at KTH and (ii) potential harmful by-products that are formed and during thermal treatment based on existing literature and research. For measuring the efficiency of the thermal degradation, the mass balance had to be adjusted to the following:

$$[PFAS]_{incoming\ sludge} = [PFAS]_{generated\ ash} + [gases]_{PFAS,other\ etc}$$

The second term in the right side of the equation could not be considered, as there was no equipment available to measure the outgoing gases.
Even though the primary objective changed, this report will provide valuable insight into the project's original objective. Therefore, the report will contain a design of the bench-scale BFB setup and sample collection methodology. This may be beneficial for future research in this area.

1.2   Purpose

Despite of change of the objective, the purpose remains the same- to understand the efficiency of thermal degradation of PFAS and sort out potential harmful by-products generated from PFAS during thermal treatment.

1.3   Research questions

i.   How can a bench-scale facility reactor be designed to study thermal degradation of PFAS in sewage sludge?

ii.   How effective is thermal degradation of PFAS in sewage sludge in a conventional lab furnace?

iii.   Based on existing research and literature, which by-products are formed during thermal treatment of PFAS in sewage sludge?

1.4   Research Methodology

To be able to answer on the research questions suggested in chapter 1.3, the following was proceeded:

- Literature studies to get a better understanding of PFAS substances, recent technologies to treat PFAS-containing matter.
- Interviews with professors and experts from different universities

- Analysis of PFAS in incoming sewage sludge.

- Combustion of PFAS-containing sewage sludge at different temperatures.

- Analysis of the ashes to identify remaining PFAS after combustion.

- Research in existing literature, which potential fluorinated byproducts can form after incineration of PFAS-contaminated waste.

1.5 Project administration and coordination

This master thesis project has been led by the energy company Stockholm Exergi. In view of the objective, the work was divided into two parts. One part is the theoretical work which includes research of existing literature studies and interview with experts. The other part of the project is a practical part that includes experiments and sample collections conducted in a small scale at KTH under supervision of the professor Klas Engvall

2   Background

This chapter provides basic information about the chemistry of PFAS substances, their different forms and how PFAS substances are used in the industry. Additionally, this chapter describes the toxic effects PFAS in environment, ecosystem, and humans. Two important aspects that are explained in this chapter is how PFAS substances contaminate the environment, and how current and future legislation regulate the use of PFAS.

2.1   PFAS

PFAS is a collective name for thousands of synthetic organic compounds used in the industry since the 1950s. PFAS are characterized by their highly fluorinated alkyl chains and extremely stable C-F bonds (Lindman, 2023).

The chemical structure of PFAS depends on whether the substance is a perfluoroalkyl or a polyfluoroalkyl substance. Perfluoroalkyl substances have a carbon chain where all hydrogen atoms on the carbons are replaced by fluorine atoms, as shown in Figure 1. Polyfluoroalkyl substances, on the other hand, have a partially fluorinated carbon chain, meaning that some carbons in the chain may still be attached to hydrogen atoms. In contrast, other carbons are attached to fluorine, see Figure 1.
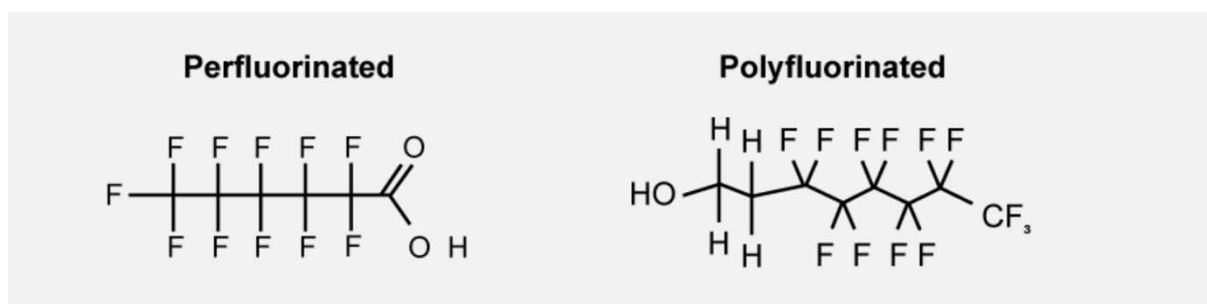
Figure 1. Structure of perfluorinated and polyfluorinated compounds (Kemikalieinspektionen, 2023)

There is still no internationally used definition for what PFAS is. According to the Swedish Chemicals Agency and the International Organization for Economic Cooperation and Development (OECD), PFAS is defined as "substances that contain at least one fully fluorinated methyl group (-CF_3) or fully fluorinated methylene group (-CF_2-) without any hydrogen, chlorine, bromine, or iodine atom attached to it" (Kemikalieinspektionen, 2023; OECD, 2021). This same definition is applied by the Swedish Chemicals Agency.

Perfluorinated substances, where all carbon atoms are completely fluorinated, exhibit remarkable stability and resistance to degradation. On the other hand, polyfluorinated substances with partially fluorinated carbon chains are less stable and more prone to degradation. Over time, these polyfluorinated substances degrade into relatively stable perfluorinated compounds. Polyfluorinated substances are, therefore, often referred to as precursor compounds (Göckener et al., 2021). According to the OECD, 4730 substances can be classified as PFAS substances. The Swedish Environmental Protection Agency and The Swedish Chemicals Agency have identified over 10,000 PFAS substances (Kemikalieinspektionen, 2023; Naturvårdsverket, n.d.). On the other hand, PubChem has listed more than 6 million PFAS substances. Due to technological limitations, it is vital to understand that PFAS substances are hard to identify and study. Although there are thousands of PFAS substances, there are 2 PFAS substances that have been identified and attracted a lot of attention in industry and research: PFOA and PFOS, as shown in Figure 2.
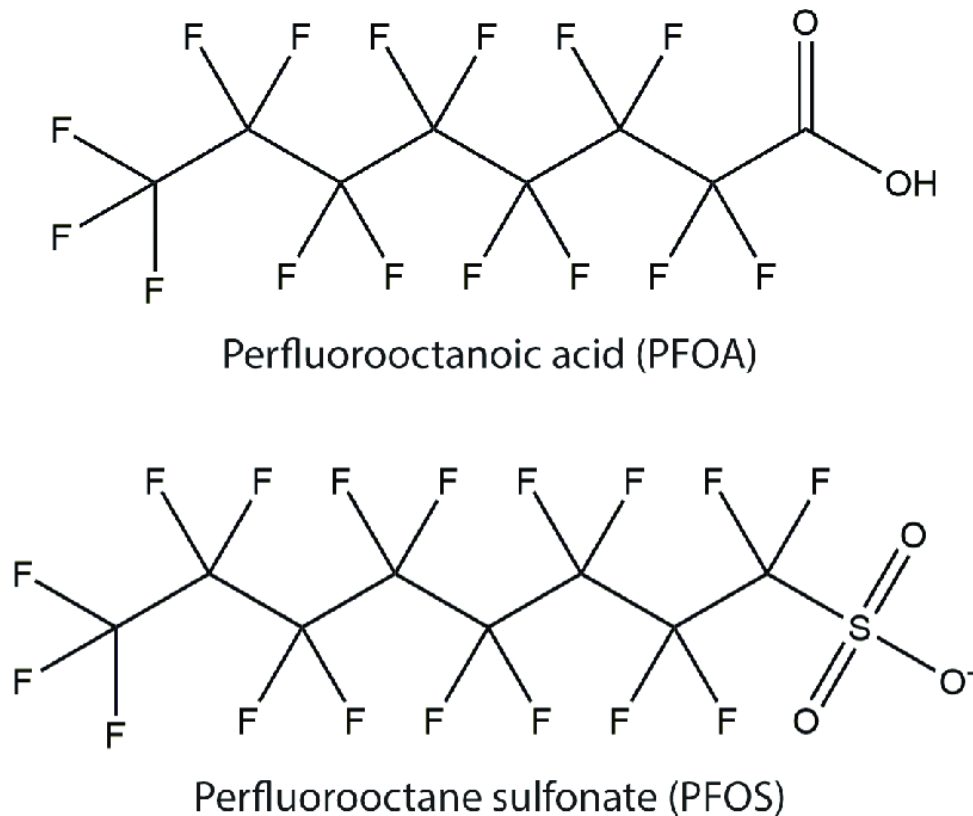
Figure 2. Molecular structure of PFOA and PFOS (Post et al., 2017)

PFOS and PFOA are the most used PFAS substances in the industry. They have been found in high concentrations in different environmental compartments such as soil, watercourses, air, and animals. A study has shown that increased PFOS and PFOA concentrations in the blood result in impaired immune systems. Also, increased concentrations of PFOA have been connected to impaired liver function and high cholesterol levels (Kemikalieinspektionen, 2023).

2.2 Polymeric and non-polymeric PFAS

PFAS substances are divided into polymeric PFAS and non-polymeric PFAS. The difference between polymeric and non-polymeric PFAS lies in their molecular structure. The non-polymeric PFAS are molecules with a linear carbon-fluorine chain with a simple structure. The non-polymeric PFAS usually have a tail bound to a functional group, such as hydroxyl groups (R-OH) or carboxyl groups (R-COOH)(Kemikalieinspektionen, 2023); see PFOS and PFOA in Figure 2.

The polymeric PFAS, on the other hand, has a more complex fluorinated carbon chain with a lot of branches on the carbon-fluorine chain. Polymeric PFAS substances are not as studied and researched as the non-polymeric PFAS. The reason is that polymeric PFAS are less chemically stable and persistent than non-polymeric PFAS and are therefore used to a lesser extent in industries than the non-polymeric PFAS. Therefore, they are not a high priority (Glüge et al., 2023; Lohmann et al., 2023). Figure 3 illustrates a clear division of the polymeric and non-polymeric PFAS. The Figure shows that the polymeric PFAS is divided into three subclasses: Fluoropolymers (for example, PTFE used in non-stick pans), perfluoropolyethers and side-chain fluorinated polymers.

The non-polymeric PFAS is further divided into two subclasses: Perfluoroalkyl substances and polyfluoroalkyl substances. The polyfluoroalkyl substances are divided into perfluoroalkane pulfonamido and fluorotelomer substances.

Perfluoroalkyl substances are divided into further five groups. The first group is perfluoroalkyl acids (PFAAs). PFAAs are divided into two subgroups: Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs). PFOA belongs to PFCAs, while PFOS belongs to PFSAs. Both of PFCAs and PFSAs, especially PFOS and PFOA, have received a lot of attention. Therefore, the major research focus has been on PFCAs and PFSAs since these are classified as PBT. One problem with these harmful PFCAs and PFSAs is that they were widely manufactured and used in consumer and industrial products. The other problem is that it has been proven that other PFAS substances from other subclasses and groups can be potential precursors to PFCAs and PFSAs, meaning that PFCAs and PFSAs can form due to degradation from other PFAS substances (Meegoda et al., 2020; Buck et al., 2011; Kemikalieinspektionen, n.d)
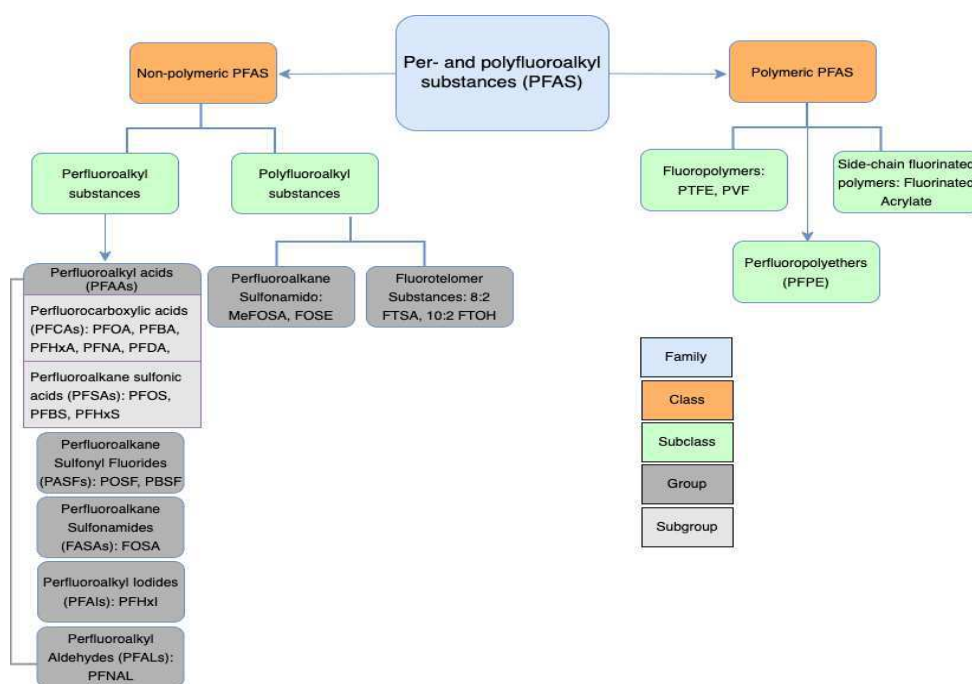
Figure 3. Schematic division of polymeric and non-polymeric PFAS (Based on Ahrens et al., 2011; Meegoda et al., 2020)

2.3   Chemistry and properties of PFAS

PFAS are man-made organic compounds that do not occur naturally. The C-F bond is a very strong covalent bond due to the high electronegativity, low polarizability, and the small size of the fluorine atom. A large amount of energy is required to break the C-F bond, a property that makes the PFAS substances highly resistant to chemical, biological, and thermal degradation. Some PFAS do not degrade at all, and some degrade into other even more persistent PFAS substances, and are therefore called precursor compounds. PFAS substances are chemicals that last forever in the environment. Therefore, they are also called Forever Chemicals (Meegoda, et al., 2020).

Another property of PFAS to consider is that PFAS are hydrophilic and hydrophobic simultaneously. The carbon-flour chain is hydrophobic, while the functional group attached to the carbon-flour chain is a hydrophilic part. PFAS being hydrophilic and hydrophobic simultaneously means that a PFAS molecule is happy to settle between a water-based and organic layer, see Figure 4. Even though all PFAS substances contain C-F bonds, the length of the carbon chain significantly

influences the properties of these compounds. The chain length of PFAS affects the substance's behavior in their environment. The longer carbon-chain PFAS have, the more bioaccumulative the substance is (Kemikalieinspektionen, n.d.)

Functional groups also affect the properties of PFAS. For instance, two PFAS compounds with identical chain lengths can exhibit varying degrees of resistance to degradation if they have different functional groups. A PFAS substance with sulfonates is harder to degrade than a PFAS with a carboxylic group. Therefore, PFCAs with carboxylic groups are more prone to degradation than PFSAs with sulfonates (Meegoda et al., 2020).
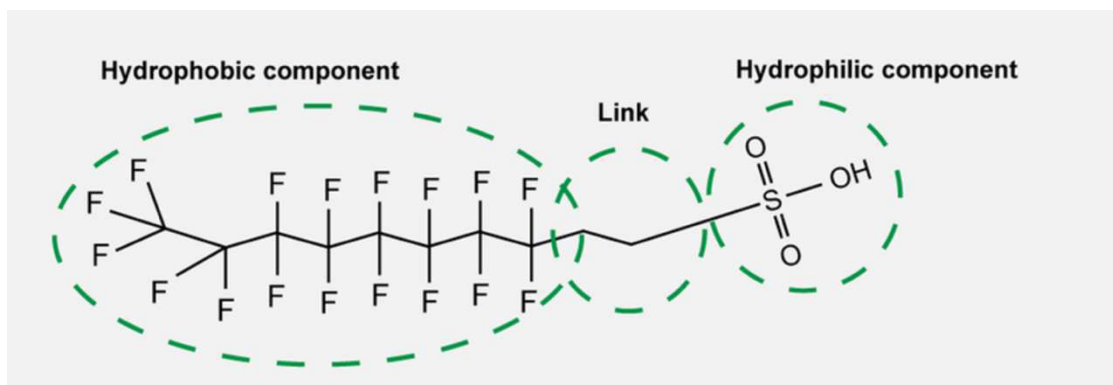
Figure 4. Hydrophilip and hydrophobic components in PFAS (Kemikalieinspektionen, 2023)

Functional groups in PFAS can undergo dissociation into ionic forms under specific conditions. The dissociation can result in an anion, cation, or zwitterion, with anion being the more commonly observed in the surrounding environment. Different ions exhibit different behaviors in different environmental settings. For example, cationic PFAS are prone to adsorption onto soil particles (sand, clay, organic matter), as soil particles carry a net negative charge. Anionic PFAS exhibits lower adsorption onto soil particles. Even pH can play a role in the ionic forms of PFAS. Higher pH values of electrostatic repulsion from deprotonated oxides may hinder the sorption of anions onto soil surfaces (Meegoda et al., 2020). PFOA and PFOS, which are extensively detected in the environment, both have hydrophobic and hydrophilic parts in their molecules. They are inert, water-soluble, and abundant in their anionic form across a broad range of pH values. PFOS exhibits higher adsorption onto soil and solid particles in the environment. Therefore, PFOS has been chiefly detected in solid environmental settings. PFOA, on the other hand, has mostly been detected in aqueous environments. PFOS has been observed to be more prone to bioaccumulation because of its longer perfluoroalkyl chain length in comparison to PFOA. PFOS has eight fluorinated carbons (Meegoda et al., 2020), while PFOA has seven fluorinated carbons, as shown in Figure 2.

2.4   PFAS in industry

Due to properties, such as water- and grease repellency, stability, and heat resistance, PFAS is widely used in many industrial applications (Gülge et al., 2020; Engzell, 2019). They are used in, for example, electronics, textiles, ski wax, Gore-Tex clothing, fire foam, cosmetics, popcorn packages, etc. They are found all around in the environment. Their property to withstand chemicals and high temperatures makes them very attractive on the market but very negative for the environment as they are chemically, biologically, and thermally stable. This means that they are long-lived and, therefore, persistent in the environment (Engzell, 2019).

A well-known example where most people encounter PFAS-containing products in everyday life is through non-stick Teflon pans. Those pans are made of a PFAS substance called PTFE. Those pans

are coated with PTFE to repel grease and water. Non-stick pans have been under debate, whether they are dangerous or not. According to different studies, non-stick pans are safe if they are not overheated in temperatures above 260 ℃ and if the PTFE-coating is not damaged. PTFE coating on non-stick cookware can get damaged if metallic tools scratch the surface (Teflon.com, n.d.).

When PFAS substances are coated on products, e.g., fabrics, the emissions of PFAS should be minimal and negligible as the PFAS substances should stay in the fabrics. However, during wear time and usage, when the fabric is, for example, exposed to wet conditions, some PFAS residues will be emitted. In 2013, a study revealed that in sports/outdoor shops, increased levels of Fluorotelomer alcohol (FTOH) in the interior air have been detected compared to other indoor air environments (Schlummer et al., 2013). This suggests the presence of PFAS residues in the products being emitted to the atmosphere in the shops, which leads to potential human exposure through inhalation.

According to a report by Svenskt Vatten, the annual use of only PFOS in Sweden has been estimated to be around 190 kg. As of now, it is difficult to track and map every PFAS substance in every product. Interestingly, despite the regulation and restriction of PFOS and PFOA in the EU, those two chemicals are still manufactured and used outside the EU. Due to global trade, these PFAS-containing products are still imported to the Swedish market, making PFOS and PFOA a continued large problem (Baresel et al., 2023).

2.5   Short-chain and long-chain PFAS

PFAS can also be categorized into short-chain and long-chain PFAS substances, based on the length of the carbon-chain for the PFAS substance. Above all, it is a way to categorize PFCA and PFSA. According to OECD is the chain length of PFCAs and PFSAs is defined as following (OECD, 2013):

Short-chain PFCA/PFSA:

PFCA with ≤ 7carbon atoms

PFSA with ≤ 5carbon atoms

Long-chain PFCA/PFSA:

PFCA with ≥ 8 carbon atoms

PFSA with ≥ 6 carbon atoms

2.6   PFAS precursors

PFAS precursors are PFAS substances that degrade to other more PBT PFAS substances than the original PFAS substances. PFAS precursors can undergo degradation under certain conditions and processes, such as thermal, chemical, and/or biological processes (Forsberg, 2022). The research on PFAS precursors is still new, but researchers have observed interesting findings when it comes to potential PFAS precursors. Treated textile in car seat covers, when exposed to UV radiation, was found to increase the concentrations of the persistent PFAS substances PFOA and PFHxA (Wu et al., 2021).

One environment in which PFAS degradation has evidently been observed is wastewater treatment plants (WWTPs). In the biological step during wastewater treatment, precursor compounds such as FOSA, FTOH, FOSAA, FTS and FTSA have been observed to degrade to the PBT substances: PFOA, PFHxA and PFOS. The PFAS compounds 6:2 FTS and 6:2 FTOH have also been found to degrade to PFHxA and PFPeA (Moneta et al., 2023). Only 6:2 FTOH on its own has been proven to transform into PFBA, PFPeA, PFHxA, and 5:3 Fluorotelomer carboxylic acid (FTCA) in the sewage sludge in

WWTPs. This one example shows how one PFAS substance can transform and degrade into multiple harmful substances that endanger the environment (Forsberg, 2022).

In a study by Eriksson et al., potential PFAS precursors were investigated in sewage sludge from three municipal WWTPs in Sweden. From this investigation, it was found that the concentration of PFAS precursors was higher than the concentration of PFCAs and PFSAs. This suggests potential transformation to harmful PFCAs and PFSAs is possible (Eriksson et al., 2017). In this study, it was found that the concentration of the persistent PFCAs and PFSAs such as PFOS, PFOA, perfluorohexanoic acid (PFHxA), and perfluorohexanesulphonic acid (PFHxS) has an increase of 58%, 28%, 83%, and 37% respectively in the effluents (Eriksson et al., 2017).

In another study of WWTPs in the USA, the mass flow of PFOS, PFOA, perfuorononanoate (PFNA), fluorodecanoate (PFDA), and fluoroundecanoate (PFUnDA) showed an increase in the effluent after the secondary water treatment step, the biological step (Zhang et al., 2023; Sinclair & Kannan, 2006). This supports that degradation of precursors is a significant factor contributing to the presence of PBT PFAS in the effluent discharged from WWTPs.

2.7   Pathway of contamination of PFAS

As mentioned previously, PFAS is widely used in many consumer and industrial products. PFAS can contaminate the surrounding environment throughout a product's entire life cycle. PFAS-containing products can contaminate the surrounding environment during production, use, and post-use as waste (Naturvårdsverket, 2017). There are two types of PFAS contamination: direct and indirect contamination. Direct contamination of PFAS substances can be referred to as "point source" contamination, which includes PFAS factories, firefighting foam, airports, and WWTPs (Engzell, 2019; Kurwadkar, 2022). Point sources are often stationary, and the contamination is from the same place (Kurwadkar, 2022).

The other way of contamination is indirect, referred to as "non-point source" contamination. Non-point sources are often diffuse and of unspecific and multiple origins (Kurwadkar, 2022). Non-point source contamination includes, for example, the degradation of PFAS precursors to stable, persistent PFAS substances that contaminate air and water. Another example of non-point source contamination is PFAS-containing products used in homes and industries, such as non-stick cookware, waterproof textiles, and food packaging. During their use, especially when these products are heated or come in contact with water, PFAS can leach out from the products and enter the surrounding environment immediately. For example, when non-stick cookware is heated, PFAS may be released into the air. PFAS can contaminate water when PFAS-treated products are exposed to wet conditions. According to researchers, there is strong evidence that outdoor textiles with PFAS surface treatments degrade over time, resulting in PFAS contamination in water (Van der Veen et al., 2020). Where the contamination of PFAS substances takes place, e.g., if the contamination is in soil, air, or water, depends therefore on the type of product that PFAS is used in, and it depends also on the chemistry of the PFAS substance in question. Perfluorinated compounds (PFCs), mainly short-chain PFSAs and PFCAs are extensively used in consumer and industrial products. PFCs are water-soluble and can therefore contaminate water and spread through the water from a local to a global level. Long-chain PFSAs and PFCAs do not seem to be as soluble in water as short-chain PFSAs and PFCAs. A possible reason is that the hydrophile part in short-chained PFSAs and PFCAs is more dominating and, hence, requires less energy to dissolve in water than what long-chained PFSAs and PFCAs do. Long-chain PFSA and PFCA are mainly hydrophobic. Due to their hydrophobicity, they instead bind to particles such as soil, vegetation, and forest (Ahrens et al., 2014).

Recent correlations have also found that some PFAS substances also can contaminate the atmosphere, both indoors and outdoors. A study investigating inter alia carpeted kindergartens and

outdoor clothing stores found that FTOHs were ubiquitous in indoor air. Indoor air and dust are vital uptake pathways for human PFAS exposure as we humans spend 90% of our time indoors (Morales-McDevit, 2021). Several studies have in fact found that FTOHs, perfluoroalkane sulfonamides (FOSAs), PFAAs, and perfluoroalkane sulfonamidos (FOSEs) are often found to be volatile in the atmosphere (Engzell, 2019; Morales-McDevit, 2021), more about that in chapter 2.7.3

It is important to point out that PFAS contamination is a complex process. Ecosystems are connected to each other, and the spread of PFAS forms a vicious circle. In a report done by Svenskt Vatten, a flowchart for how PFOS transportation can look in the Swedish Society is illustrated in Figure 5. First of all, PFAS substances are not manufactured in Sweden. Therefore, all PFAS-containing products are imported through consumer and industrial products. It has been estimated that approximately 190 kg of PFOS-containing products enter the country every year. These products will eventually end up as solid waste that either will be incinerated in waste treatment plants or put in landfills. From waste treatment plants and landfills, PFOS will be emitted via water, soil, and air. As shown in Figure 5, atmospheric deposition represents a major factor in PFOS contamination, with circa 310 kg of PFOS per year that will contaminate water, biota, and soil in Sweden. Sewage sludge is estimated to contaminate soil with 2 kg PFOS per year (Baresel et al., 2023).

This is a very simplified view of reality. Quantifying the incoming PFOS and other PFAS substances in society and the environment is nearly impossible. Figure 5 should, therefore, be used only as a potential scenario that does not reflect all contamination sources and transport pathways (Baresel et al., 2023).
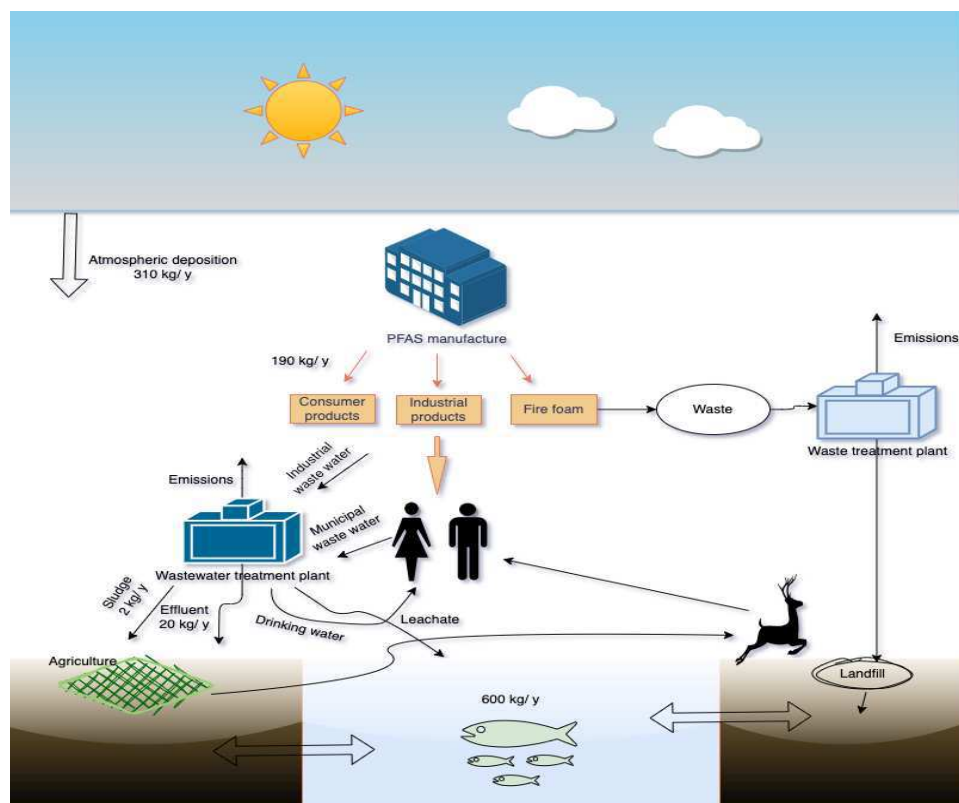

Figure 5. PFAS contamination in different environmental seetings (Based on Baresel et al., 2023)

2.7.1   Wastewater treatment plants (WWTPs) contamination

WWTPs are a known PFAS-contamination source. From WWTPs, PBT PFAS substances can spread into liquid effluent, in air, and in sewage sludge, creating global contamination (Fredriksson et al., 2022; Hamid & Li, 2016). As shown in Figure 5, PFAS substances spread from WWTPs into the atmosphere, as some PFAS substances are more volatile than the others. These volatile PFAS substances evaporate during wastewater treatment, and they end up travelling long-range in the atmosphere. PFAS can also end up in effluents and sewage sludge after wastewater treatment, which eventually contaminate water, soil, and agriculture (Ahrens et al., 2009; Hamid & Li, 2016). Another factor that is important to consider is discussed in Chapter 2.6, which is the high degradation of PFAS precursor compounds to even more harmful PFAS compounds such as PFOS and PFOA in the wastewater treatment processes.

As indicated in Figure 5, the concentration of PFOS in the effluent and the sewage sludge is approximately 22 kg/year in Sweden, which is relatively small. Even though the PFAS contamination from atmospheric deposition and contaminated land areas may be considered a priority, effluent from WWTPs and sewage sludge still constitute significant sources that can be controlled. In this way, a part of the PFAS-contamination that arise in WWTPs can be eliminated by treating the PFAS in the sewage sludge, with e.g., thermal treatment.

PFAS in municipal WWTPs predominantly originate from domestic and industrial wastewater sources, with occasional contributions from tap water sources (Hamid & Li, 2016). According to studies, municipal WWTPs that treat both domestic and industrial water will have higher PFAS concentrations than WWTPs treating only domestic wastewater (Forsberg, 2022). The main reason for PFAS-contamination in water in Sweden, according to the Swedish Chemicals Agency, is by Aqueous Film Forming Foams (AFFF) (Kemikalieinspektionen, 2023).

WWTPs have different water treatment techniques, but normally, all WWTPs have mechanical, biological, and chemical treatment steps, see Figure 6 (VA-ingenjörerna, n.d.; Eriksson, 2023). The mechanical step removes debris and particles from wastewater. Some PFAS contaminants, such as microscopic particles pass through the mechanical step and can be carried in wastewater to the next step, which is biological treatment step. In the biological treatment, organic matter in the water is intended to be removed by utilizing microorganisms, but these microorganisms can degrade PFAS substances to precursor compounds as mentioned in chapter 2.6. The biological treatment step has a vital role in the context of PFAS. On the one hand, it can be a source of degradation of PFAS precursors, and on the other hand, the biological step also acts as a sink for PFAS as these compounds can be sorbed by the secondary sludge generated from the biological step (Forsberg, 2022). In the next step, the chemical treatment step is intended to reduce phosphorus from water. In this step, chemicals such as iron sulfate are used to precipitate and coagulate phosphorus. These flocks sediment to the ground, and sewage sludge is then formed. In the chemical step, when the phosphorus coagulates, some PFAS substances bind to the coagulants, which result in detectable PFAS concentrations in the sewage sludge (VA-ingenjörerna, n.d.). However, the majority of the PFAS substances in WWTPs are carried out in the effluent, and a minor part of PFAS ends up in the sewage sludge as shown in Figure 5 (Baresel et al., 2023). In this report, the investigated sewage sludge is from Bromma WWTPs. See Chapter 2.9 for more information about Bromma WWTP.
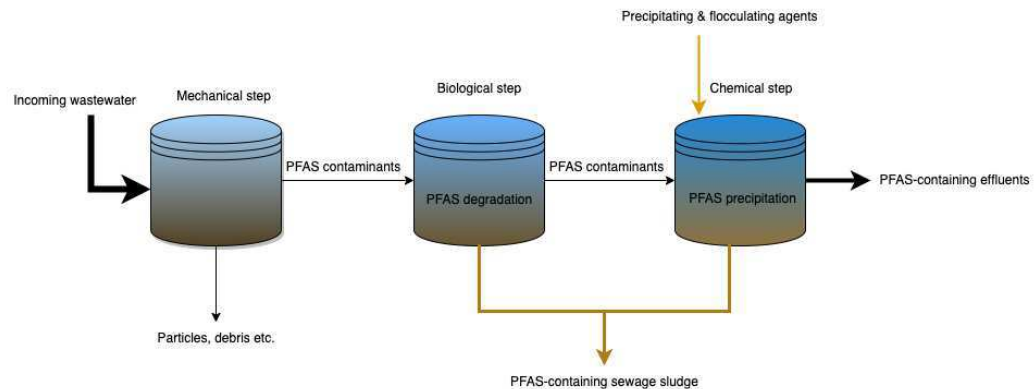
Figure 6. Treatment steps in WWTPs (Based on Helsinge Vatten AB, 2022)

Sewage sludge is a semi-solid or semi-liquid byproduct that is generated during wastewater treatment in WWTPs as shown in Figure 6. The composition of sewage sludge depends on the source of the sludge and the treatment technology of wastewater. Generally, sewage sludge contains mainly water, dissolved materials, and 0,5-12% of suspended solids (Microbiologynote, 2022). The sludge generated during the mechanical step, carries settleable solids from the untreated wastewater. Secondary sludge, from the biological step, consists of biological material along with extra settleable solids. The sludge generated in advanced wastewater treatment may consist of trace elements and low levels of PFAS and may contain microorganisms, such as salmonella. Sewage sludge contains also valuable nutrients such as phosphorus, potassium, and nitrogen (Fytili et al., 2006; Werther et al., 1999), therefore sewage sludge is valuable as fertilizer in agricultural and other forestry applications (European Commission, n.d.). Sewage sludge that is used as fertilizer in agriculture is hygienized and composted for at least six months, in purpose to neutralize any microorganisms (Lindman, 2024). In this project, 26 metal, phosphorus, nitrogen, potassium as well as PFAS, have been analyzed to understand the composition of the sewage sludge in question.

2.7.2   PFAS in sewage sludge

As sewage sludge contains a high amount of minerals and other valuable substances, it can be utilized as fertilizer in agriculture and forests. According to statistics, 37% of sewage sludge is being used in agriculture, 40% is landfilled, 11% incinerated, and the remaining 12% of sewage sludge is used in other areas (Fytili et al., 2006). From these statistics, the most common method of sewage sludge disposal on a global scale is via landfill, followed by agriculture.

Recycling of sewage sludge contributes to a sustainable development objective and implementing a circular economy. However, applying sewage sludge on soil raises concerns as the PFAS in the sewage sludge contaminates what is planted in that soil, and animals that graze on that land can also be contaminated with PFAS. The Ph.D. student Skirfors at the Swedish University of Agricultural Sciences (SLU) indicates that PFAS substances can transfer into plants from soil and sludge, creating an exposure risk to animals, humans, and the surrounding environment. In fact, most of the PFAS that is found in the human body originates from ingesting plant-based food (Skirfors, 2023).

A study by Fredriksson et al. investigated 81 different PFAS substances, including two relatively less studied perfluoroalkyl sulfonamide-based (FASA) copolymers in sewage sludge samples. A total of 28 sludge samples were collected from four WWTPs in Sweden within the time interval 2004-2017. The result from the study is illustrated in Figure 6, showing that precursors to PFCAs were dominating in the sludge, with a concentration of 71%. PFSAs and PFCAs were present in a concentration of 9%, respectively (Fredriksson et al., 2022).
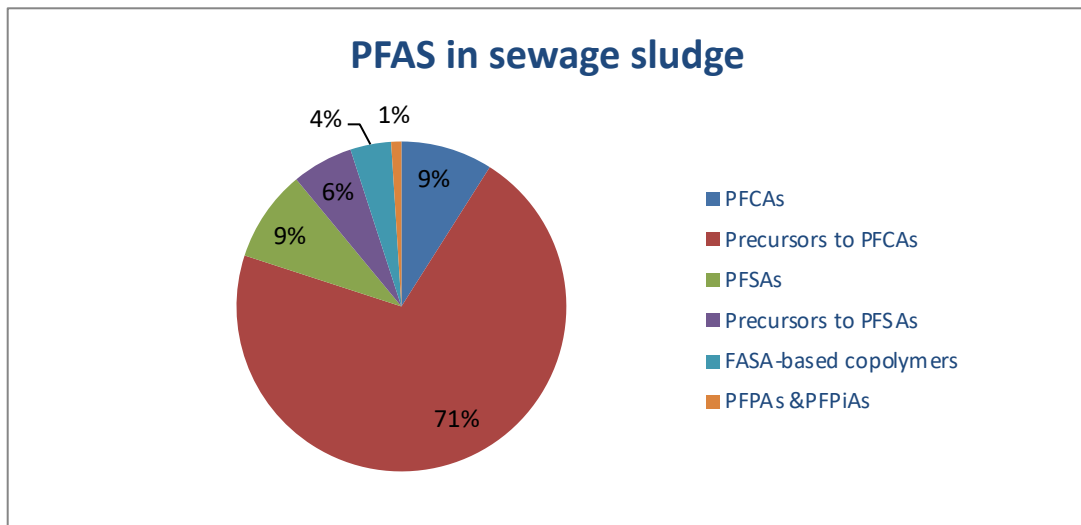
Figure 7. Distribution of different PFAS in sewage sludge (Based on Fredriksson et al., 2022)

2.7.2.1 *Sewage sludge in agriculture and landfill disposal*

Applying sewage sludge on agricultural land has increased from 30% to 50% in 2017-2022 (Naturvårdsverket, n.d.). To utilize sewage sludge in agriculture, there is the so-called Sludge Directive, also known as Directive 86/278/EEC and SNFS 1994:2 och 20 § I SFS 1998:944, to regulate utilizing sludge as fertilizer in agriculture (Fytili et al., 2006; Naturvårdsverket n.d.). The key provisions for utilizing sludge as fertilizer are the following:

1. Establishing quality standards for sewage sludge, particularly for heavy metal content, for example Zn, Cu, Hg etc.

2. Setting limits for heavy metal concentrations in sewage sludge used in agriculture.

3. Requiring treatment to reduce pathogens in sewage sludge.

4. Mandating monitoring and reporting by member states.

5. Placing restrictions on specific uses of sewage sludge to protect soil and water quality.

Although the directive aims to ensure the safe and environmentally responsible utilization of sewage sludge in agriculture, there is a gap regarding PFAS substances present in sewage sludge.

From 2023, Sweden has the goal to annually gather and provide data on the annual production of sewage sludge in the country, the portion of this sludge used as fertilizer in agricultural areas, the average levels of certain heavy metals present in the utilized sludge, and the specific locations where the sludge was applied on agricultural land. Based on statistics from 2022, Sweden produced 203,799 tons of sewage sludge and applied 106,737 tons of sewage sludge on farmland. Table 1 illustrates the concentrations of the seven heavy metals: Cadmium, copper, nickel, lead, zinc, mercury, and chromium that were applied on agricultural land through sewage sludge in 2022 (Naturvårdsverket, n.d.)

Current regulations cover only the above-mentioned heavy metals. The Swedish Environmental Protection Agency's regulations cover these seven heavy metals for utilizing sewage sludge on agricultural land. The limit values are illustrated in Table 1 (Thuresson et al., 2005; Jordbruksverket, 2021).

Table 1. Concentration of 7 heavy metals applied on agricultural land via sewage sludge versus current limit values.

Substance	Concentration (mg/kg d.m) year 2022	Limit value (mg/kg d.m)
Cadmium	0.606	2
Cupper	334	600
Nickel	16.8	50
Lead	13.72	100
Zinc	470	800
Mercury	0.341	2.5
Chromium	19.78	100
$\sum Nitrogen$	49 510	-
$\sum Phosphorus$	28 672	-

2.7.2.2 Thermal treatment of PFAS-containing solid matter

Thermal treatment has begun to attract interest from various energy actors. There are several advantages of combustion of solid waste. With thermal treatment, there is a possibility to recover and recycle energy while eliminating and destroying hazardous material in the waste in question. Compared to landfilling, thermal treatment does not need large areas, nor does thermal treatment produce methane or leachate. For the combustion of sewage sludge, a vital advantage is eliminating hazardous material such as PFAS and, at the same time, utilizing the nutrient-rich ash as fertilizer in forestry, which Stockholm Exergi plans to conduct.

However, there is a need for additional research regarding byproduct formation during the combustion of PFAS-containing material, especially in commercial combustion facilities. According to Björklund et al., differences in combustion conditions and the overall complexity of combustion chemistry are two factors that contribute to this gap. In general, we have a better understanding of byproduct formation in ashes but less knowledge of byproduct formation in liquid and gaseous residues. Ideally, the fate of PFAS in a combustion treatment plan should be studied by setting a complete mass balance to estimate the destruction and release of PFAS after combustion. Mass balance involves accounting for the inputs, outputs, and potential accumulations of these substances within the system (Björklund et al., 2023). The mass balances for combustion in the BFB reactor versus the lab furnace are showed in Chapter 1.1

2.7.3 Atmospheric PFAS contamination

As shown in Figure 5, atmospheric deposition is a big contributor to PFOS contamination. The root cause of this contamination lies predominantly with human activities. Had PFAS not been produced initially, there would be no atmospheric deposition at all. Several factors contribute to atmospheric contamination with PFAS. Emissions of PFAS from industry, landfills, and WWTPs are a few examples of how PFAS can be dispersed into the air from other media (Pfotenhauer et al., 2022). WWTPs have been proven to be a significant point source of many PFAS volatilizing into the atmosphere (Ahrens et al., 2011)

Volatile PFAS can travel long-range in the atmosphere from any point source, making those substances a global problem even though they are imitated to the atmosphere locally (Kemikalieinspektionen, n.d.). The mechanism for long-range PFAS contamination in the

atmosphere is through sorption to aerosol particles in the atmosphere. In aquatic environments, for example, in the sea, when waves break on the water's surface, PFAS-containing bubbles burst and release tiny droplets into the atmosphere; this process is called sea spray. This is how PFAS can transfer from aquatic environments to atmospheric environments (Faust J, 2023). A recent investigation suggests that aquatic environments can contribute significantly to PFOA to the atmosphere. However, there are very few field measurements of how much PFOA is dispersed into the atmosphere (Ahrens et al., 2011)

2.7.3.1   *PFAS contamination through dry and wet deposition*

PFAS contamination is a vicious cycle. PFAS can transfer from the atmosphere into aquatic and terrestrial ecosystems and vice versa. Transfer from the atmosphere into aquatic and terrestrial ecosystems occurs through dry and wet deposition (Pfotenhauer et al., 2022). Dry deposition of PFAS means that the volatile PFAS substances fall to the earth directly from the atmosphere in their dry state together with other gases and particular matter. Dry deposition PFAS can attach to solid particles such as soil, forest, and vegetation (Ahrens et al., 2014). In this way, PFAS can bioaccumulate for a long time in the biota.

Wet deposition of PFAS means that PFAS substances fall to the earth in a wet state through rain, snow, or other water droplets. Similar to dry deposition, wet deposition PFAS can bioaccumulate for an extended period of time. They can attach to aquatic systems such as rivers, seas, and other watercourses. The rate of dry deposition is believed to be slower than wet deposition, meaning that wet deposition is the dominant vehicle of transfer from the atmosphere to the earth. The rate of dry versus wet deposition is influenced by water solubility, volatility, air concentrations, and potential for transformation in the atmosphere (Pfotenhauer et al., 2022)

2.8   Regulations of PFAS

Despite PFAS posing a high risk to the environment, ecosystems, and humans, regulations are still inadequate. Many PFAS substances are still not covered by any regulations at all, while other specific PFAS substances are regulated.

The new EU drinking water directive that will be executed starting January 2026 has set a limit value of 4 ng/L for four PFAS substances: PFOS, PFOA, PFNA, and PFHxS. The directive includes a limit value of 100 ng/L for 21 PFAS substances, listed in Table 2. From January 2023, according to the EU regulation 2023/915, limit values for the same four PFAS substances were introduced to apply even in food like eggs, meat, fish, crustaceans, and mussels (Livsmedelsverket, 2023).

Five PFAS substances (PFOS, PFOA, PFNA, PFDA, and APFOA) are regulated by CLP (Kemikalieinspektionen, n.d.). CLP stands for Classification, Labelling, and Packaging, and this regulation implies that products that contain the PFAS mentioned above substances must be clearly communicated and marked with consumers and workers. Also, harmonized classification should apply to all products containing the PFAS mentioned above (Echa, n.d.)

PFOS and its precursors, as well as PFOA, its salts, and related substances, have been included in the Stockholm Convention. This inclusion means that these substances are subject to international restrictions and regulations with the aim to reduce their production, use, and release to protect human health and the environment. Additionally, since 2020, PFHxS and its derivatives have been included in the Stockholm Convention to be regulated. On the 28th of August 2023, the ban on PFHxS and its derivatives entered into force under the POPs Regulation (Tüv Süd, n.d.).

Another regulation that applies is Registration, Evaluation, Authorisation and Restriction (REACH of Chemicals. REACH applies for several PFAS, and these PFAS substances are included on the

Candidate List of Substances of Very High Concern (SVHC). Table 2 lists these PFAS on the SVHC with a description of their effects.

Table 2. A list of PFAS substances that are classified as SVHC susbtances (Based on OECD, 2023)

PFAS substance	CAS-no	Effects on health and environment
HFPO-DA (GenX)	-	Pose serious risks for human health and the environment
PFBS (C4)	-	Pose serious risks for human health and the environment
PFHxS (C6)	-	vPvB
PFHpA (C7)	108-78-1	Reproductive toxic, PBT, Pose serious risks for human health and the environment
PFOA (C8)	335-67-1	Reproductive toxic % PBT
PFNA (C9)	-	Reproductive toxic & PBT
PFDA (C10)	335-76-2	Reproductive toxic & PBT
PFUnDA (C11)	2058-94-8	vPvB
PFDoDA (C12)	307-55-1	vPvB
PFTrDA (C13)	72629-94-8	vPvB
PFTeDA (C14)	376-06-7	vPvB
Reaction mass of 2,2,3,3,5,5,6,6-octafluoro-4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)morpholine and 2,2,3,3,5,5,6,6-octafluoro-4-(heptafluoropropyl)morpholine	-	vPvB

In February 2023, thanks to a Swedish initiative, EU have prohibited 200 PFAS substances that are rarely used but are very resistant to degradation (Kemikalieinspektionen, 2021). Another proposed restriction regarding PFAS substances that is currently under evaluation is to ban all PFAS substances altogether. This proposal was submitted on behalf of Denmark, Germany, the Netherlands, Norway, and Sweden to ECHA in January 2023. If this proposal is approved, the ban will come into force in 2025 (Echa, 2023).

The European Food Safety (EFSA) has recommended a guideline of a tolerable weekly intake of PFOA, PFNA PFHxS, and PFOS to be 4,4 ng/kg bodyweight per week. This guideline covers only 20% of the overall PFAS intake (EFSA, 2020)

Certain restrictions and regulations of PFAS depend on what matrix the PFAS substances are present in. Table 3 shows how regulations of PFAS are depending on the matrix (Baresel et al., 2023).

Table 3. PFAS regulations in different matrices (Based on Baresel et al., 2023)

Matrix	Limit value	Comment
Drinking water	Minimum limit value according to 2020/2184 in EU: $\sum PFAS21: 100\frac{ng}{L}$ $\sum PFAS4: 4\frac{ng}{L}$ $\sum PFAS\ (total): 500\frac{ng}{L}$	Suggestion to new stricter regulations in accordance to 2022/01733, by including even 6:3 FTSA in PFAS21, meaning that 22 PFAS substances will be regulated in drinking water
Ground water	Reference value: $\sum PFAS11: 90\frac{ng}{L}$ Preliminary reference value: $PFOS: 45\frac{ng}{L}$ Suggested reference value: $\sum PFAS4: 2\frac{ng}{L}$	-
Sewage sludge	No regulations of PFAS in sewage sludge in Sweden. In Denmark the following regulations apply: $\sum PFAS4: 0,01\frac{mg}{kg}\ d.m.$ $\sum PFAS22: 0,4\frac{mg}{kg}\ d.m.$	Revision of PFAS in sewage sludge directive is expected to be evaluated 2024

2.9 Bromma wastewater treatment plant

Bromma WWTP is located in Stockholm, near Bromma airport. In this WWTP, water from ca 290 000 residents is daily treated (Stockholm Vatten & Avfall, n.d.), which equals approximately 133 151 m3/day of water (Eriksson, 2023). The water is treated through 3 steps: mechanical, chemical, and biological treatment steps. In Bromma WWTPs, primarily Iron Sulfate Heptahydrate is used as the precipitation chemical, along with polymers such as starch/acrylamide-based polymer. Additionally, during the winter months, Pix 111 (iron chloride) is employed for additional enhancement (Stockholm Vatten & Avfall, 2022).

In the year 2022, 19,661 tons of digested sewage sludge and 5, 603 tons of dewater sewage sludge were produced by Bromma WWTP. 14,874 tons of the produced sewage sludge was allowed to be used as fertilizer. 4,787 tons did not pass the REVAQ certification and was therefore not allowed to be used as fertilizer. The sludge that will be examined in this study is originated from Bromma WWTP.

2.10 Combustion treatment technologies

There are several technologies to treat PFAS depending on the contaminated matrix. For PFAS-contaminated drinking water, technologies such as granular activated carbon, ion exchange resins, and high-pressure membrane systems are used to filtrate from PFAS (EPA, 2023). On the other

hand, sewage sludge is not covered by any regulations regarding PFAS. Therefore, it is not treated from PFAS. Most PFAS-contaminated sewage sludge is disposed of through landfilling or applied on agricultural land, as mentioned in chapter 2.7.2. Stockholm Exergi's goal to investigate PFAS degradation in sewage sludge through thermal treatment is fundamental. It is important due to new limit values and directives constantly being introduced. In addition to that, it is essential to ensure a safe and toxic-free future for our and future generations.

There are several combustion technologies. Grate firing and fluidized bed combustion are Sweden's two most common technologies (Lindman, 2023). Fluidized bed combustion technologies enable homogeneous and even fuel combustion due to efficient thermal distribution through fluidization.

There are two types of fluidized bed technologies: circulating fluidized bed (CFB) and bubbling fluidized bed (BFB). Both techniques enable fluidization, CFB via circulation, and BFB via bubbling.

Fluidized bed technologies offer distinct advantages over conventional furnaces in various industrial applications. Their key advantages are high heat and mass transfer rates and efficient mixing. Fluidized beds are flexible, accommodating a wide range of solid fuels, making them ideal for diverse feedstocks such as biomass, coal, sewage sludge, or waste. Different fuels can also be mixed as a feedstock. Economically, fluidized offer higher thermal capacities, often in the range of several megawatts, and are easily scalable to meet varying industrial needs. They excel in emission control, mitigating pollutants, and complying with environmental regulations. The extended residence time of fuel particles in the fluidized bed enhances combustion efficiency, while uniform temperature distribution and efficient heat transfer contribute to higher energy conversion efficiency compared to conventional furnaces (Kaltschmit et al., 2022)

In general, BFB reactors have the disadvantage of sintering the bed, which leads to aggregate formation in the bed, and the heat transfer is then disturbed, leading to poor combustion. Sintering problems can be avoided by choosing an appropriate bed material that fits the combustion conditions. High concentrations of alkali metals in the fuel used, sewage sludge in this context, contribute to sintering at low temperatures (Engvall, 2023; Rosén 2023; Lindman, 2023).

In the case of this project, a sample of sewage sludge was sent to Eurofins for analysis of sintering problems to understand what conditions are appropriate for the combustion of sewage sludge in BFB combustion.

This project's initial objective was to conduct combustion trials of sewage sludge in a bench-scale BFB. To achieve the project's purpose, combustion trials with sewage sludge in a conventional furnace, irrespective of the combustion technology used. The trials and results of the conventional furnace can be a benchmark for future investigations with other combustion technologies.

3   Chemical analysis of PFAS

Chemical analysis of PFAS substances is a challenge because there are thousands of PFAS substances, and one analytical method to target all of these substances does not exist today. Today's technology offers strategies to analyze certain and specific PFAS substances (Baresel et al., 2023). Eurofins is a leading company that has been analyzing PFAS in several matrices, such as solid matter, water, food, and biota, since 2015. They offer many analysis packages for PFAS. Their smallest package is PFAS4, which includes the following 4 PFAS substances: PFOA, PFOS, PFHxS, and PFNA (Eurofins, n.d.). As mentioned in Chapter 2.8, these four specific PFAS are covered by limit values that may not exceed four ng/L in drinking water and food (Livsmedelsverket, 2023)

There are other analysis packages, such as PFAS11, PFAS 21, and PFAS35, that include more PFAS substances. PFA35 is the largest analysis package of PFAS in solid material. In Table 4, PFAS substances that are included in each analysis package (PFAS4, PFAS11, PFAS 21, and PFAS35) are compiled. Every analysis package has been highlighted with a specific color. The first four PFAS substances are marked in blue. PFAS11 is the first four substances in blue, plus the green rows. PFAS21 is the PFAS substance in blue, green, and yellow; this continues until PFAS35. These PFAS packages do not target the total content of PFAS in a sample but only the individual PFAS substances in Table 4. PFAS is analyzed with the analytical method LC-MS/MS, and each analysis has an uncertainty of ±36%.

Table 4. Compilation of PFAS4, PFAS11, PFAS21 and PFAS

Analytical method	LC-MS/MS
Uncertainty	±36
Analysis	LOQ* $\mu g/kg\ d.m.$
PFOA	0.03
PFNA	0.03
PFOS	0.03
PFHxS	0.03
PFBS	0.03
PFHxA	0.03
PFHpA	0.03
PFDA	0.1
PFBA	0.10
PFPeA	0.03
6:2 FTS	0.03
PFUdA	0.1
PFDoA	0.1
PFHpS	0.03
PFDS	0.03
PFTrDA	0.1

PFPeS	0.1
PFNS	0.2
PFDoS	1.0
PFUnDS	1.0
PFTrDS	1.0
PFOSA	0.1
PFTeDA	0.03
P37DMOA	0.5
HPFHpA	0.1
8:2 FTS	0.1
PFHxDA	0.03
4:2 FTS	0.03
EtFOSAA	0.1
MeFOSA	0.03
EtFOSA	0.2
MeFOSE	0.03
EtFOSE	0.1
MeFOSAA	0.03
FOSAA	0.1

Table 4. Compilation of PFAS4, PFAS11, PFAS21 and PFAS

LOQ* is the lowest PFAS concentration that can be quantitatively detected.

3.1   Other screening methods

In addition to those individual packages, there are other screening methods that aim to analyze specific parameters. Total oxidizable precursors (TOP), extricable organic fluor (EOF), and total organic fluor (TOF) are three examples of analytical tools that can be utilized to get a more comprehensive picture of how PFAS substances can behave when certain conditions apply (Eurofins, n.d.). Figure 8 shows the different screening methods and their ability to target PFAS in relationship to each other. The screening methods TF and TOF could be valuable for the project, as the amount organic and non-organic fluor can be detected. Due to analytical limitations, they cannot be applied for the analysis of sewage sludge in this project.

TF(Total Fluor) /TOF (PFAS) + non-organic Fluor

PFAS + non-organic Fluor= TF

EOF (Extractable organofluorine)

TOP (Total oxidizable precursors)

targeted PFAS analysis
(PFOS, PFOSA, PFAS11, PFAS21)
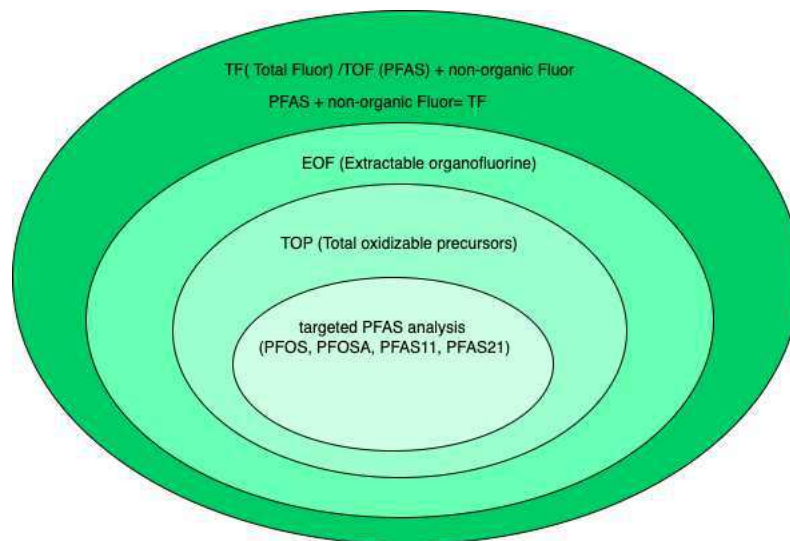
Figure 8. Schematic overview of PFAS screening methods (Based on Baresel et al., 2023)

3.1.1   Total Fluor (TF)

Total Fluorine, TF is a non-selective screening method used to determine the total concentration of fluorine in a specific matrix such as soil, liquids, and powders. With TF, organic fluorine (which PFAS is) can be detected as well as non-organic Fluorine, such as toothpaste, but the analysis does not say what type and form of fluorine is measured. It does not indicate the type of fluorinated substance in the sample or if it is organic or non-organic. TF can be combined with Total Organic Fluor (TOF) to detect the organic fluorinated substance, thus PFAS. See Figure 8.

Through an e-mail contact with the professor Hees at Eurofins, a requirement to be able to conduct TF analysis is that the sample can undergo combustion. Matrices such as ashes and condensate cannot be analyzed with TF (Hees, 2023). This means that TF analysis can be conducted only for the sewage sludge, not remaining residues. Based on this limitation of TF, mass balance cannot be established to keep track of material flow in the system/process, the PFAS in this case.

3.1.2   Total organic Fluor (TOF)

Total Organic Fluor (TOF) is similar to TF, but it is developed to target organic fluorinated compounds, thus PFAS substances. TOF can be combined with targeted PFAS analysis (PFAS4, PFAS21, PFAS35, etc.) to demonstrate to what extent the PFAS in the targeted analysis comprise the total organic fluorine content. This provides an estimation of our knowledge about the utilization of PFAS in the surroundings. For example, TOF analysis in sewage sludge provides an approximate idea of PFAS content in water from WWTPs and the management of PFAS in WWTPs. The high value of TOF means that PFAS is not considerably reduced during wastewater treatment.

TOF can also be combined with TF to understand the relationship between organic and non-organic fluoride and how this relationship changes when sewage sludge is exposed for combustion. If the non-organic fluor increases after treating sewage sludge through combustion, then there is a risk that organic fluor (PFAS) will decompose into other harmful by-products.
TOF has developed only one type of matrix, paper, cardboard, and paper-based material, as a collaboration between Eurofins and the Ministry of Food, Agriculture and Fisheries of Denmark

(Borg & Ivarsson, 2017). TOF cannot be used to analyze organic fluor in sewage sludge, ashes, condensate, or any other matrix that is not paper-based (Borg & Ivarsson, 2017; Hees, 2023).

In a study by the Swedish chemical agency, TOF was measured in different consumer products found in supermarkets. The intended products to be investigated were different brands of Microwave Popcorn bags, muffin forms, rinse aids, waterproof textile and shoe treatments, shoe wax, floor polish, and car wax. Due to methodological problems, TOF was not conducted on non-paper products (shoe wax, floor polish, car wax, etc). TOF could, though, be conducted in Microwave Popcorn bags, muffin forms, and rinse aid (Borg & Ivarsson, 2017).

3.1.3 Total Oxidizable Precursors (TOP)

Total Oxidizable Precursors (TOP) can be used to measure the total amount of PFAS precursor compounds that can potentially degrade to more harmful PFAS, such as PFOS and PFOA. This technique utilizes chemical oxidation with hot persulphate in an alkaline solution, leading to the formation of hydroxyl radicals ($OH^{\cdot}$), that target telomers and sulfonamide precursors while preserving initially present PFCAs and PFSAs. This process is a representation of how natural biodegradation occurs (Eurofins, n.d.).

4 Method

In this section, the methodology of what was conducted in order to answer the research questions given in Chapter 1.3.

4.1 Experimental set-up: Bench-scale BFB reactor

To address the research question "How can a bench-scale facility reactor be designed to study the thermal destruction of PFAS in sewage sludge?" an investigation was conducted using a bench-scale BFB reactor located at KTH, Teknikringen 42. This reactor, depicted in Figure 9, can be used for combustion trials with PFAS-containing sewage sludge.
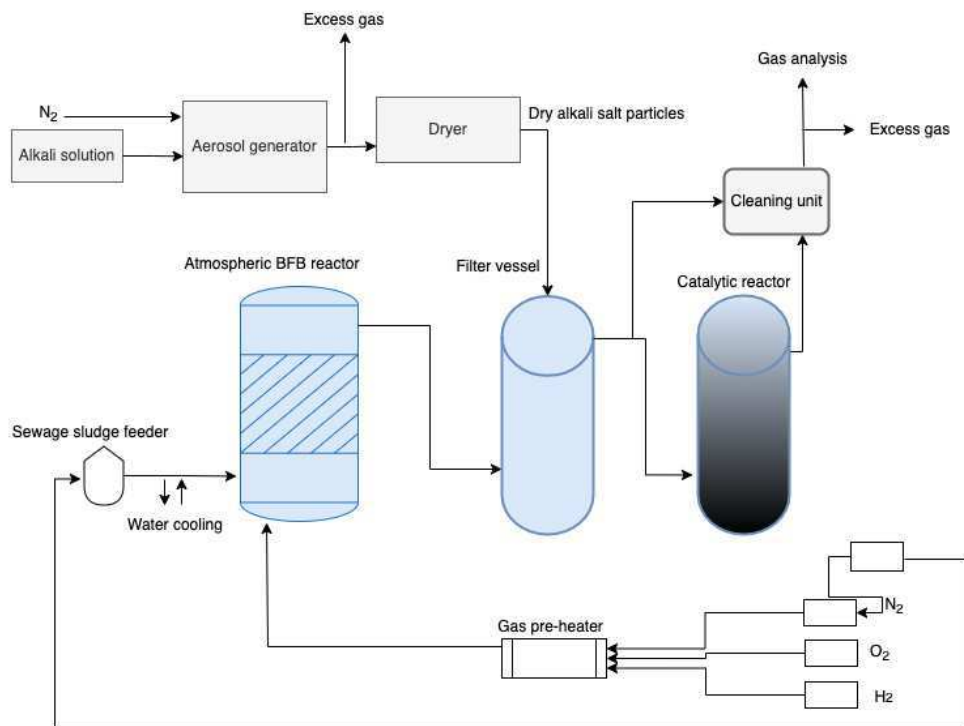
Figure 9. Schematic drawing for the overall bench-scale BFB

First, before delving into the combustion trials, it was crucial to define the parameters for measurement aligning with the project objective: investigating the efficiency of combustion treatment of PFAS in sewage sludge. Three temperatures- 750, 850, and 950 °C, were selected with a residence time of two seconds. These temperatures were chosen to establish a pattern or a trend line illustrating how the combustion efficiency of PFAS increases with temperature. If it would.

Prior to the three sharp combustion trials, 2-3 preliminary trials should be conducted to identify and address potential operational issues and refine the overall method.

It was identified that investigate efficiency of PFAS combustion, PFAS should be measured in these streams:

- Incoming sewage sludge (pre-combustion)
- Bottom ash
- Fly ash

- Condensate water

It is noteworthy that PFAS in flue gases are hard to measure due to limitations of analytical tools developed for such analysis.

Second, an evaluation of the bench-scale BFB reactor was undertaken. Through discussions with the supervisor and examiner, Klas Engvall, and a thorough literature review, certain components in the BFB reactor were identified to be irrelevant to the study and consequently excluded. A detailed plan was developed, outlining how the combustion trials would be conducted, specifying the parameters to be adjusted. This plan also included specifications for the equipment used and instructions for conducting the experiments, the results of which are presented in Chapter 5.1.

4.2 PFAS in incoming sewage sludge

It is important to take safety precautions when managing sewage sludge due to potential hazardous substances. The following equipment was used to avoid contamination:

- Lab coat (chemical-resistant)
- Gloves (nitrile)
- Goggles
- Fume hood
- A vaccination for Hepatitis A+B was taken two weeks before managing sewage sludge.

On November 8, 2023, one plastic container (pre-ordered from Eurofins) was sent to Eurofins for analysis of PFAS35 (analysis code: PLWN0). The container was marked with "KE200X-torkat slam-PFAS." The sewage sludge sent to Eurofins was air-dried in a fume hood at a room temperature of maximum 25°C for a week, reducing the water content from 75% to 18%. The sewage sludge had therefore dry matter (d.m.) of 82%. To speed up the drying process, the sewage sludge can be dried in a furnace. However, in this case, as the goal was to analyze the concentration of PFAS in incoming sewage sludge, air-drying was a better alternative to prevent any eventual PFAS from evaporating.

4.3 Measuring other Parameters in the Sewage Sludge

Same safety precautions were taken as described in chapter 4.2

On November 8, 2023, one plastic container was filled with sewage sludge, 15% d.m., and sent to Eurofins for analysis of energy content (analysis code: PSLBV), sintering problems (analysis code: PSLT1), and metals (analysis code: PYB51) in sewage sludge. The analysis codes PSLT1 and PYB51 were chosen to ensure that sewage sludge can be combusted in the BFB reactor without causing sintering problems. The analysis PSLBV was conducted to ensure that sewage sludge has enough energy to be combusted on its own without the addition of other fuels.

4.4 Treatment of PFAS in sewage sludge in conventional furnace

The PFAS-containing sewage sludge was combusted in a conventional lab furnace in two temperatures respectively: 850 and 950 °C, see Figure 10. Prior to combustion, some preparations had to be done, these are described below.
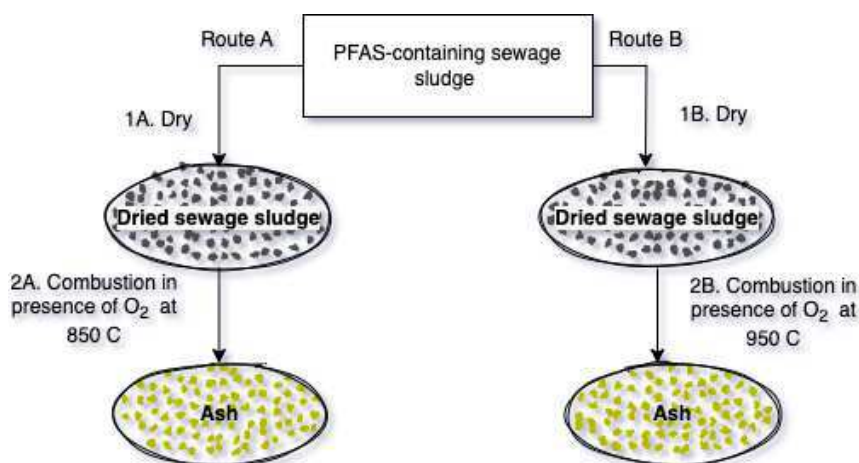
Figure 10. Pathways for sewage sludge combustion in a conventional ovan

4.4.1 Pre-experiment: preparation procedure

Before commencing with the sewage sludge thermal treatment, it is crucial to properly clean the graphite crucibles. The following steps were conducted:

- Three graphite crucibles were selected.

- The crucibles were washed thoroughly with dish soap, followed by acetone.

- The furnace was pre-heated to 200 °C

- The crucibles were placed in the furnace for one hour, to dispose any impurities.

- After one hour, the temperature was lowered to 25 C, and the crucibles were to cool down to 25°C.

- The crucibles were taken out with crucible tongs.

- Weight each crucible and note the weight.

- This procedure was done for route A and B

4.4.2 Drying of sewage sludge

In both route A and B, drying the sewage sludge was necessary to get rid of the access water. Each graphite crucible was filled with sewage sludge and the weight of each filled crucible was noted, see Table 10 and 11 in the Appendix for raw data. The graphite crucibles were placed in the lab furnace as shown in Figure 10, with a temperature of 30 °C for 24h.

The drying procedure was done two times separately, to ensure enough amounts available for analysis sent externally to Eurofins. The amount of ash must be ≥ 25 g for each temperature in route 2A and 2B.

Figure 11. Illustration of how crucibles were placed in the lab furnace.

4.4.3 Route 1A: combustion at 850 ℃

In step 2A, dried sewage sludge sewage sludge was filled in each crucible, the amounts of sewage sludge in every crucible are written in Table 13 in the Appendix. The crucibles were placed in the furnace once the temperature hit 400 °C. When the temperature reached 850 °C, the samples were combusted for 15 minutes as residence time. After combustion, the temperature of the furnace was decreased to 25 °C and the crucibles were left to cool down. Combustion resulted in red-ish ash, in an amount of 26.46844 g from this trial. The ash was put in a plastic container and sent to Eurofins.

4.4.4 Route 1B: combustion at 950 ℃

Similarly, as in step 2b, dried sewage sludge was filled in each crucible, the amounts of sewage sludge in every crucible are written in Table 14. The crucibles were placed in the furnace once the temperature hit 400 °C. When the temperature reached 950 °C, the samples were combusted for 15 minutes. After combustion, the temperature of the furnace was decreased to 25 °C were left to cool down. Combustion resulted in red-ish ash. Combustion resulted in red-ish ash, in an amount of 25.7255 g from this trial. The ash was put in a plastic container and sent to Eurofins.

4.5 Potential byproduct formation

To answer the question "Based on existing research and literature, which by-products are formed during thermal destruction of PFAS in sewage sludge?" an extensive literature review was done. The search engine Google scholar was used to find scientific reports and articles related to that topic.

5   Results and discussions

5.1   Experiment set-up: Bench-scale BFB reactor

The proper and appropriate design of the BFB setup to proceed through combustion trials of sewage sludge is illustrated in the Figure 12.
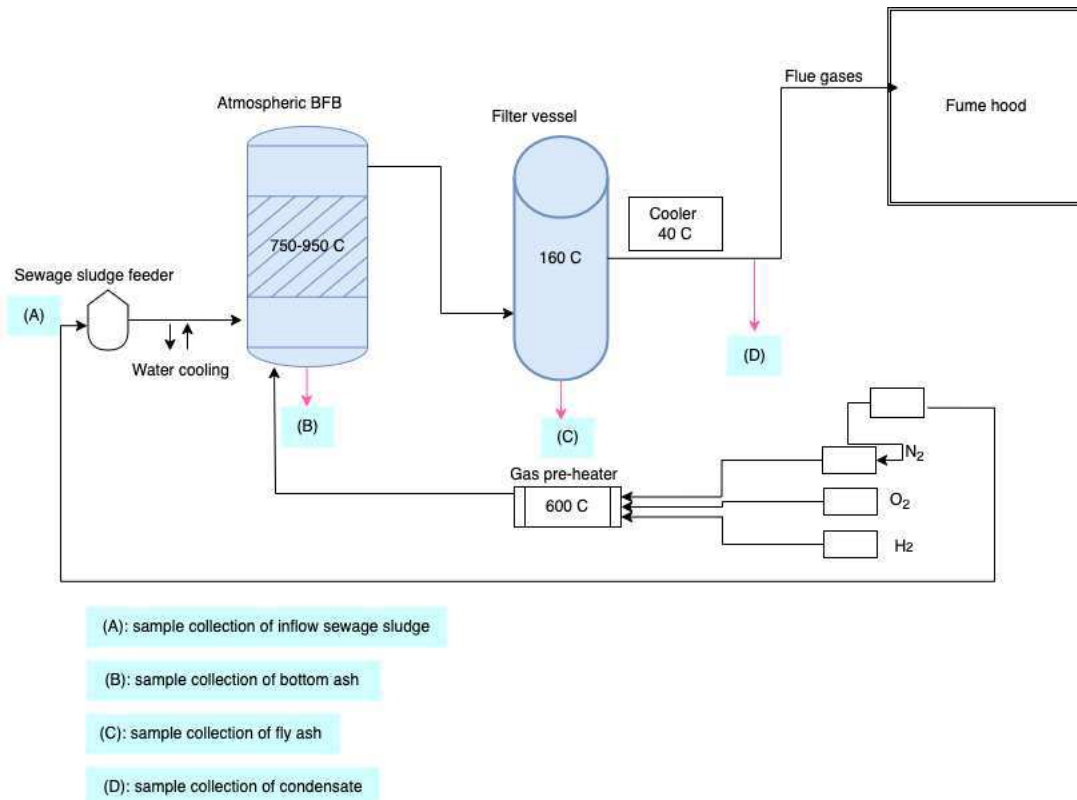
Figure 12. Schematic illustration of BFB reactor for combustion trials with sewage sludge

The reactor is an atmospheric BFB filled with bed material. Operating temperatures for this project were expected to be 750 – 950 °C, with alumina as bed material. Alumina has desirable properties when it comes to sintering. It can stand high temperatures without sintering. The feeding rate of sewage sludge is 300 g/s. Different gases and steam for combustion are coupled to the BFB combustor via a preheater. Preheater is used to warm up H_2, N_2, O_2, steam and CO_2 with a maximum temperature of 600 °C. O_2 is an oxidizing agent, H2 and N_2 are reducing agents. After combusting of sewage sludge, a bottom ash will be produced and accumulated at the bottom of the BFB reactor. Volatiles such as H_2, CO, CO_2 will also be produced in the BFB reactor, but these continue to the filter vessel.

After the combustion step, the gas passes a mechanical particle filter to physically remove solid impurities such as tars. The filters consist of magnesium silicate fibers and binding agents and operates at a temperature of 160 °C. From filter, fly ash is produced at the bottom of the filter vessel. After the filter, a cooler can cool down some of the volatiles down to 60 °C, to obtain condensate for analysis. Other volatiles that do not condensate continues to the fume hood for further analysis with Gas Chromatogrsphy (GC). With the GC, it is possible to see if the combustion was successful or not. Detection of carbon monoxide (CO) means that the combustion reaction was not complete.

The BFB reactor must be emptied between each run using a vacuum cleaner from the top of the column to not let previous experimental runs interfere with test results. Steam can also be used to clean the system from rest products (Engvall, 2023).

5.1.1 Materials and Equipment

- Data recording tools (notebook, computer)
- Safety gear (gloves, goggles, lab coat)
- 1x 10 L buckets
- 1 shovel for bottom ash
- 1 spoon for fly ash
- 1 clean bowl
- 3 plastic containers provided from Eurofins for bottom ash sampling.
- 3 plastic containers provided from Eurofins for fly ash sampling.
- 6x 100 mL plastic bottles provided from Eurofins for condensate sampling, two bottles for every sampling according to Eurofins.

5.1.2 Sampling procedures for 750, 850 and 950 ℃

The sampling procedures can be conducted in the same way for the temperatures 750, 850 and 950 ℃. It is important to clean the shovel, spoon, 10L bucket and the bowl after every time using, to ensure that no contamination from the previous use occurs.

5.1.2.1 Sampling procedure of bottom ash

- Wash the 10 L bucket and the shovel properly. Let them air-dry.
- Fill the 10 L bucket with bottom ash from and mix properly with the shovel.
- Fill the plastic container with bottom ash.
- Place the bottle in a refrigerator until the sample is sent for analysis.
- Clean the bucket and the shovel.

5.1.2.2 Sampling of fly ash

- Wash the bowl and the spoon properly. Let them air-dry.
- Fill the bowel bucket with fly ash from and mix properly with the spoon.
- Fill the plastic container with fly ash.
- Place the bottle in a refrigerator until the sample is sent for analysis.
- Clean the bowl and the spoon.

5.1.2.3 Sampling of condensate

- Prepare 2x 100 mL bottles.
- Fill each bottle completely and tighten the cap.
- Place the bottle in a refrigerator until the sample is sent for analysis.

5.2 Measurement of sintering problem, 26 metals and energy content

The results in both Table 5 and 6 are relevant the investigation of combustion efficiency of PFAS in sewage sludge in the BFB reactor at KTH. As mentioned in chapter 3.2, some bed material in BFB reactors can have higher risk for sintering, when the fuel used have high concentration of alkali metals. On the other hand, it is possible to measure at which temperature starts agglomerating, by measuring shrinkage temperature of the fuel particles. Therefore, in Table 5, measurement of shrinkage temperature for sewage sludge, referred to as "Shrinkage start temp SST" in the, was externally analyzed at Eurofins. Based on this, shrinkage temperature of sewage sludge is 1070 °C. This means that the bed material starts to agglomerate at the temperature 1070 °C. Running combustion processes below that temperature, does not pose any risk for sintering.

In Table 5, the concentrations of 26 heavy metals are also analyzed. For all the 26 heavy metals, the concentrations are detected. For the 7 regulated heavy metals: Lead, cadmium, copper, chromium, mercury, nickel and zinc the concentrations were below the limit value in the sewage sludge.

One observation is that the iron had a high concentration of 120000 mg/kg d.m. Iron sulfate heptahydrate and iron chloride are used as precipitation chemicals, and hence the high concentration of iron in the sewage sludge. The concentration of chlorine on the other hand is very low, as the chlorine is soluble in water. It is washed off in the WWTP during the treatment steps.

Another important observation is that the content of potassium, phosphorus, and nitrogen is 5800 mg/kg d.m., 37000 mg/kg d.m., and 42600 mg/kg d.m., respectively. These high concentrations of valuable nutrients and low concentration of heavy metals strengthen the incentive to recycle sewage sludge.

Table 5. Results for concentration of 26 heavy metals and for sintering problem

Analysis	Results	Unit
Dry basis	27.0	%
Moisture content	73.0	%
Chlorine Cl	0.035	% d.m.
Carbon C	29.9	% d.m.
Nitrogen N	4.26	% d.m.
Shrinkage start temp SST	1070	°C
Deformation temp DT	1160	°C
Hemisphere temp HT	1210	°C
Flow temp FT	1380	°C
Aluminium (Al)	16000	mg/kg d.m.
Antimony (Sb)	2.2	mg/kg d.m.
Arsenic (As)	3.7	mg/kg d.m.
Barium (Ba)	280	mg/kg d.m.
Beryllium (Be)	0.51	mg/kg d.m.
Lead (Pb)	18	mg/kg d.m.
Bor (B)	6.6	mg/kg d.m.

Phosphuros (P)	37000	mg/kg d.m.
Iron (Fe)	120000	mg/kg d.m.
Cadmium (Cd)	0.67	mg/kg d.m.
Calcium (Ca)	26000	mg/kg d.m.
Potassium (K)	5800	mg/kg d.m.
Cobolt (Co)	11	mg/kg d.m.
Cupper (Cu)	400	mg/kg d.m.
Chromium (Cr)	39	mg/kg d.m.
Mercury (Hg)	0.42	mg/kg d.m.
Magnesium (Mg)	5200	mg/kg d.m.
Manganese (Mn)	230	mg/kg d.m.
Molybden (Mo)	9.9	mg/kg d.m.
Sodium (Na)	2500	mg/kg d.m.
Nickel (Ni)	28	mg/kg d.m.
Tin (Sn)	15	mg/kg d.m.
Titanium (Ti)	1900	mg/kg d.m.
Vanadium (V)	33	mg/kg d.m.
Zinc (Zn)	520	mg/kg d.m.

Table 5. Results for concentration of 26 heavy metals and for sintering problem

In Table 6, the energy value in sewage sludge in different conditions are measures. The calorimetric heating value when the sewage sludge is received in its wet condition 1.407 MJ/kg, which is when the sewage sludge has 27% of dry basis, see first column Table 5. When the sewage sludge is in its dry condition, the calorimetric heating value is increased to 11.826 MJ/kg. This measurement in an indication that when the sewage sludge is wet, it is not combustible on its own. When the sewage sludge is dry, it is combustible on its own, and no addition of other fuels is needed.

Table 6. Results for effective energy content in sewage sludge

		MJ/kg	Kcal/kg	MWh/ton
Effective calorific value	Constant pressure as received	1.407	336.0	0.391
	Constant pressure dry basis	11.826	2825	3.284

5.3 PFAS in incoming sewage sludge and thermally treated sewage sludge

PFAS in incoming sewage sludge was detectable for 22 out of 35 PFAS substances in total. The concentration of the four regulated PFAS substances PFOA, PFNA, PFOS and PFHxS is 0.29, 0.22,

8.6 and 0.056 µg/kg d. m. respectively. In fact, based on the results compiled in Table 7, PFOS is the most abundant PFAS substance to be found in incoming sewage sludge with a concentration of 8.6 µg/kg d. m. Detection of PFOA and PFOSA although sharp regulations to restrict their use, reflects the grade of persistency of these two PFAS substance, and that they will still be present in the surrounding environment from historical contamination. As mentioned previously, PFOS and PFOA are not manufactured in Sweden, but they been widely used on a global scale. Despite restrictions and regulation, PFOS and PFOA are still manufactured and used in other parts of the world. These PFOS/PFOA-containing products still enter the Swedish market, leading to their presence in the environment. Another perspective is that PFOS and PFOA can be formed through degradation of precursor compounds, meaning that regulations that target PFOS and PFOA specifically are not enough. Presence of precursor compounds can lead to their ongoing formation.

Table 7. PFAS concentration in incoming sludge and combusted sludge in 850 and 950 ℃ respectively

Uncertainty	±36	±36	±36	±36
Analysis	LOQ (µg/ kg d. m.)	Incoming sewage sludge (µg/kg d. m.)	Ash 850 ℃	Ash 950 ℃
PFOA	0.03	0.29	< 0.030	< 0.030
PFNA	0.03	0.22	< 0.030	< 0.030
PFOS	0.03	8.6	0.042	0.20
PFHxS	0.03	0.056	< 0.030	< 0.030
Sum PFAS 4 incl. ½ LOQ		24	2.8	3.0
Sum PFAS 4 excl. ½ LOQ		9.2	0.087	0.25
Sum PFAS excl. LOQ		22	0.042	0.20
Sum PFAS 4 excl. LOQ		9.2	0.042	0.20
PFBS	0.03	0.13	< 0.030	< 0.030
PFHxA	0.03	0.47	< 0.030	< 0.030
PFHpA	0.03	0.045	< 0.030	< 0.030
PFDA	0.1	1.1	<0.10	<0.10
PFBA	0.10	<0.10	<0.10	<0.10
PFPeA	0.03	0.056	< 0.030	< 0.030
6:2 FTS	0.03	0.11	< 0.030	< 0.030
PFUdA	0.1	0.56	<0.10	<0.10
PFDoA	0.1	1.1	<0.10	<0.10
PFHpS	0.03	<0.030	< 0.030	< 0.030
PFDS	0.03	<0.030	< 0.030	< 0.030
PFTrDA	0.1	0.44	<0.10	<0.10

PFPeS	0.1	<0.10	<0.10	<0.10
PFNS	0.2	<0.20	<0.20	<0.20
PFDoS	1.0	<1.0	<1.0	<1.0
PFUnDS	1.0	<1.0	<1.0	<1.0
PFTrDS	1.0	<1.0	<1.0	<1.0
PFOSA	0.1	0.69	<0.10	<0.10
PFTeDA	0.03	0.51	<0.030	<0.030
P37DMOA	0.5	<0.50	<0.50	<0.50
HPFHpA	0.1	<0.10	<0.10	<0.10
8:2 FTS	0.1	0.25	<0.10	<0.10
PFHxDA	0.03	0.18	<0.030	<0.030
4:2 FTS	0.03	<0.030	<0.030	<0.030
EtFOSAA	0.1	4.6	<0.10	<0.10
MeFOSA	0.03	<0.030	<0.030	<0.030
EtFOSA	0.2	<0.20	<0.20	<0.20
MeFOSE	0.03	0.46	<0.030	<0.030
EtFOSE	0.1	0.83	<0.10	<0.10
MeFOSAA	0.03	0.95	<0.030	<0.030
FOSAA	0.1	0.22	<0.10	<0.10

Table 7. PFAS concentration in incoming sludge and combusted sludge in 850 and 950 ℃ respectively

The results from post-combustion of sewage sludge show that in both temperatures, 850 and 950 ℃ PFAS levels are below detectable. However, this does not apply for PFOS in 850 and 950 ℃. The concentration of PFOS in 850 ℃ is 0.042 µg/kg d. m, while in 950 ℃ 0.20 µg/kg d. m. It should be the other way around, that the concentration of PFOS is lower at the higher temperature, with the assumption that the combustion efficiency of PFAS is higher with higher temperature. It is difficult to determine the exact reason why the concentration for PFOS at 950 ℃ is higher than 850 ℃. There are several reasons, one reason can be the uncertainty that comes when analyzing the samples with commercial analysis techniques. As illustrated in Table 7, the uncertainty is ±36% for all analysis. This uncertainty allows less accuracy for interpretation of results.

Another reason can be the homogeneity in the received sewage sludge container from Bromma WWTPs is inadequate. Homogeneity in this case refers to the uniform distribution of PFAS substances within the sewage sludge sample. The accuracy of analytical results relies on the assumption that the sample tested is representative of the entire bulk material. If a sample is not homogeneous, the selected portion may not accurately reflect the overall composition of the entire sample, leading to uncertainty in the results. Based on information from the WWTP, the treated sewage sludge is from the same time and place, meaning that the batch is homogenous. Though, the homogeneity can be within the sewage sludge itself. The sewage sludge was not homogenized further after receiving from Bromma WWTP. To reduce uncertainty, several samplings from different places in the sewage sludge can be taken to be measured. It is less likely that sample preparation or other procedures caused these results, as preparations and other procedures were

done in the same way for both combustions trials. However, unknown human error can have occurred.

After conducting the experiments, it was found out that the furnace was not calibrated, so the temperatures in the inside of the furnace probably did not reach up to 850 or 950 °C. How this error affects the credibility of the results is not obvious as no further investigations were performed.

Based on the outcome from the results in Table 7, it is clear that the combustion efficiency for PFAS is very high. Among the 35 PFAS substances analyzed, 34 PFAS substances were below LOQ. This is an indication of the capability of combustion process to effectively mitigate PFAS in sewage sludge to non-detectable levels, sewage sludge in this case.

Stockholm Exergi conducted a parallel study investigating combustion of PFAS in biofuels mixed with 3% sewage sludge. The PFAS was measured in the incoming fuel (biofuel + 3% sewage sludge) and in the outgoing flows; bottom ash, fly ash and condensate.

The investigation was performed in two samples of bottom ash, three samples and fly ash and two samples of condensate. All the samples were sent to the commercial analysis laboratory, Eurofins. Commercial reporting limits were thus applied for this study, as well as in this current project. The analysis results showed that all 35 analyzed PFAS in bottom ash and fly ash were below LOQ (Lindman, 2024). This aligns with this current study, indicating that combustion of PFAS-containing matter is in fact an effective method to reduce PFAS.

5.4   Byproduct formation after combustion of PFAS-containing waste.

There are a few studies with the aim of filling in the knowledge gap regarding byproduct formation during the combustion of PFAS-containing material. There is also research regarding remaining PFAS residues post-thermal treatment. In this chapter, we will explore literature regarding remaining PFAS residues and literature sources pertaining to PFAS by-product formation.

In a study conducted by Björklund et al. in Northern Sweden, the degradation of PFAS in a full-scale combustion facility was investigated by examining the PFAS residues in two matrices after combustion. The first matrix is municipal solid waste (referred to as MSW), and the other matrix is sewage sludge mixed with MSW (referred to as SMSW). PFAS in the residual fractions: gypsum, air pollution control residue (APCR), bottom ash, and flue gases leaving the combustion reactor were analyzed.

In MSW, Björklund et al. found that no PFAS was detected in gypsum or APCR. In bottom ash, 0.16 ng/g PFHxA was detected in one sample, and 0.54 ng/g PFOA was detected in the other sample.

 In the treated process water, extractable PFAS substances were detected in a concentration of 62-97 ng/L. Among the detected PFAS substances, short-chain (C4–C7) PFCAs are the most abundant, of which PFHxA constitutes 93- 97% of the concentration in ng/L. Other identified PFCAs included PFHpA (0-2.5 ng/L) and PFOA (1.7 to 3.2 ng/L) (Björklund et al., 2023). In a comparable investigation conducted by the Swedish Research Institute (IVL), condensate from 27 Swedish incineration treatment plants was identified to primarily consist of PFCAs, with concentrations ranging from 0.28 to 182.95 ng/L. In agreement with Björklund et al's study, short-chain PFCAs are, in fact the most abundant PFAS in the liquid residues (Strandberg, 2021).

For the flue gases, three samples were extracted. In the samples, several PFAS substances were detected, where short-chain PFCA is the most abundant. The detected PFAS substances are compiled in Table 8. The results in Table 8 for PFAS in flue gases were performed in accordance with EN 1948-1 sampling protocol, which was modified only for this PFAS campaign sampling. Further investigation and modification of the method are required to fully validate it (Björklund et al., 2023). Although there is no previous research documenting the presence of PFAS residues in

flue gases from a full-scale incineration plant, an investigation was conducted on air samples from a Municipal Solid Waste Incineration (MSWI) plant in China. Like Björklund's study, the predominant PFAS substances that were identified were PFCAs at a range of 88–94%. However, in contrast to Björklund's study, long-chain PFAS residues were found in relatively higher proportions, constituting 36–60% of the total concentration, compared to 5–18% in Björklund et al's study. The presence of long-chain PFAS in the flue gas from the Municipal Solid Waste Incineration (MSWI) plant is suggested to be influenced by if some of the waste is not fully incinerated, it could release long-chain PFAS substances into the flue gas (Björklund et al., 2023; Wang et al., 2020)

In the other matrix SMSW, 0.17-0.31 ng/g of PFHxA was detected in gypsum. In APCR, a total concentration of 0.99–1.3 ng/g extractable PFAS residues was detected, where PFBA was detected in all three collected samples, and PFHxA was detected in one of the three samples. In bottom ash, the only PFAS detected was 0.81–1.5 ng/g PFBA. In the treated process water, the concentration of detectable extractable PFAS was twice as high as the concentration of extractable PFAS in MSW. PFHxA was the most abundant with a concentration of 132-190 ng/L, followed by PFOA 4.3-6.6 ng/L, PFHpA 4.9-7.6 ng/L, PFBA 8.8-13 ng/L, PFPeA 3.0-4.3 ng/L and PFDA 0.94-1.6 ng/L. In the flue gases, the total concentration of extractable PFAS was found to be 3.4-5.6 ng/m^3, which is comparable to the total concentration of extractable PFAS in the MSW. Other PFAS substances in the SMSW were detected in the flue gases, and these are compiled in Table 8.

Table 8. Concentration of flue gases in SMSW and MSW respectively.

SMSW		MSW	
PFAS	Concentration (ng/m^3)	PFAS	Concentration (ng/m^3)
PFBA	2.5-2.7	PFBA	2.8-3.8
PFHxA	0.39 -2.0	PFHxA	0.22-1.9
PFOA	0.23-0.79	PFOA	0.16-0.40
PFHpA	0.06/0.20**	PFHpA	0.23*
PFOS	-	PFOS	0.07*
PFDA	0.10-0.23	PFDA	0.05/0.13**
PFBS	0.07-0.24	PFBS	0.03

*Detected only in one sample out of three samples
** Detected in two of three samples

In other multiple studies, investigations of PFAS residues and the formation of PFAS byproducts were conducted after the combustion process. Based on these studies, a compilation of identified PFAS byproducts and residues is presented in Table 9. The compilation gives an overview of PFAS byproduct formation and residues in different combustion conditions.

A study conducted in a commercial-scale combustion plant on PFAS-contaminated soil. The incoming soil contained PFOA and PFOS with concentrations of 76.5 µg/kg and 7240 µg/kg, respectively. The PFAS-containing soil was combusted at kiln temperatures of 425-815°C, followed by a secondary combustion for treating PFAS in the gas phase. The temperature in the second incineration was set between 980 and 1200 °C. The combustion treatment resulted in <3 µg/kg for PFOS and < 1.7 µg/kg for PFOA. The PFAS emissions released in the gas phase were also measured for both conditions, indicating short-chain PFAS were the abundant PFAS substances were short-chain PFAS, see Table 9 (Zhang et al., 2023; NRC Alaska, 2019).

In a study conducted by Major et al., PFAS-contaminated soil was treated with PFAS-contaminated granulated activated carbon (GAC) in a smoldering combustion treatment at a temperature of >900

°C. No PFAS residues could be detected in the ashes after combustion, but various PFAS substances could be detected in the emitted flue gases. Short-chain PFCAs made up >75% of the emitted PFAS in the flue gases; see Table 9 (Zhang et al., 2023; Major et al., 2019)

In column 3 of Table 9, PTFE-contaminated matter was treated at temperatures between 750-1050 °C, which resulted in larger molecular weight fluorinated organic byproducts in the gas phase when the temperature was>1000 °C. García et al. suggested that PTFE first decomposes to tetrafluoroethylene (C_2F_4) in reducing conditions and then potentially reform to C_3F_6, which would then combust to CF_4 in oxidizing conditions. No additional discussion on the reformation of PFAS or other compounds of concern from PFAS incineration was identified and investigated in existing literature (Zhang et al., 2023; García et al., 2007)

Yamada et al. investigated how the combustion of fluorotelomers was affected by two different temperatures of 600 and 1000 °C. In this study, it was concluded that no fluorinated organic byproducts were detected at temperatures lower than 1000 °C, as shown in Table 9. On the other hand, fluorinated organic radicals, flurobenzene and difluorobenzene were detected at 1000 °C (Zhang et al., 2023; Yamada et al., 2005), as shown in Table 9.

Table 9. PFAS byproducts in oxidizing conditions in different combustion processes

Initial PFAS-substance	Incineration temperature (°C)	PFAS byproducts	Reference
PFOS & PFOA contaminated soil	425–815 980–1200	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFDoA, PFTeA, PFBS, FOSA, PFUnA, PFHxS, PFOS, NMeFOSAA, NEtFOSAA, 6:2 FTS	(NRC Alaska, 2019; Zhang et al., 2023)
PFOS, PFOA, PFHxS, PFBS, PFNA & PFHpA contaminated soil	1000	PFBA, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFNA, PFDA, PFUnA, PFDoA	(Major et al., 2019; Zhang et al., 2023)
PTFE	750, 850, 950 &1050	CF4, C2F6, benzoyl fluoride CF4, C2F6 CF4, C2F6, C3F6, benzenepentafluoro CF4, C2F6, benzenepentafluoro	(García et al., 2007; Zhang et al., 2023)
Fluorotelomer-based acrylic polymer	600 1000	Flurobenzene, difluorobenzene, ·CF3, ·CF2CH=CH2 ·CF3, ·CF2CH=CH2	(Yamada et al., 2005; Zhang et al., 2023)

In academic and agency reports (California Department of Toxic Substances Control, 2019; Huber et al., 2009; Stoiber et al., 2020), it was found that incineration of PFAS-containing matter forms hazardous byproducts. These byproducts were found to be ozone-depleting substances such as chlorofluorocarbons (CFCs) and fluorinated greenhouse gases such as tetrafluoromethane, hexafluoroethane, fluoro-dioxins, fluoro-benzofurans, fluorinated aromatic compounds, and perfluorinated carboxylic acids seem also to be released byproducts from incineration plants.

6 Conclusion

The outcomes of this project demonstrate the effective degradation of PFAS in sewage sludge through thermal treatment in a conventional furnace. Remarkably, both 850 and 950°C temperatures proved sufficient to significantly decrease the concentration of nearly all PFAS substances below LOQ. Notably, post-treatment, PFOS was the sole detectable PFAS, with concentrations of 0.042 at 850°C and 0.20 at 950°C. Calculating the reduction factors revealed that PFOS experienced approximately a 204.7-fold reduction at 850°C and a 43-fold reduction at 950°C, indicating substantial efficacy.

For a further and more thorough investigation of thermal degradation effectivity, PFAS-containing sewage or other matter can be combusted in a bench-scale BFB, as illustrated in 6.1. The parameters for thermal treatment can be temperatures of 750, 850, and 950 in a residence time of 2 seconds. Additionally, performing a detailed mass balance to monitor incoming and outgoing PFAS in bottom ash, fly ash, and condensate would offer insights into the efficiency of the thermal degradation process. The results of such a mass balance can guide further optimization of thermal treatment conditions.

A literature study investigation was conducted to understand the fate of PFAS during thermal treatment processes. Findings revealed that short-chain PFCAs were predominantly present in ash, liquid, and gaseous residues after thermal treatment. A few investigations suggested the possible presence of ozone-depleting compounds in residual byproducts after combustion. However, existing research and technology lack strong and multiple evidence to support this claim.

7 Future work

Research regarding efficiency of thermal degradation of PFAS-containing material can be optimized from several aspects. The efficiency of thermal degradation can be investigated in a bench-scale pilot such as the BFB reactor in this project, and successively scaling up to a commercial facility. The investigation of combustion efficiency can be conducted by varying combustion parameters such as temperature and residence time, to comprehend what temperature and residence time result in highest degree of efficiency.

Currently, when analyzing PFAS substances in matrix at commercial laboratories, there is a measurement uncertainty of ±36%. This uncertainty affects the interpretation of results, diminishing their reliability and utility. For future studies, continuous advancements in technology are vital to minimize measurement uncertainties and enhance the overall reliability of PFAS analysis.

Looking ahead, the advancement of technology is crucial when it comes to analysis of PFAS in flue gases. As of now, there is no validated method to measure PFAS in the outgoing stream of flue gases, meaning that a complete mass balance to track incoming and outgoing PFAS, cannot be established. Another limitation is that current technology is not able to target all existing PFAS substances, but only specific PFAS substances. TOF and TF can potentially be developed to measure all organic fluorine and non-organic fluor in a sample despite the state of the matrix. Both TOF and TF can help us to achieve a deeper understanding of those Forever Chemicals.

From an economic standpoint, conducting PFAS analysis at external and commercial laboratories incurs significant costs. Despite this, ensuring accuracy and reliability in the findings is important, therefore performing duplicate analysis should be conducted in future studies for comparable and more reliable results.

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8   Appendix A: raw data

8.1   Amount of sewage sludge in crucibles for the drying process

Table 10. Drying of sewage sludge in 30 ℃ for 24h.

Pre-drying				After drying
Sample	$m_{empty\ crucible}$ [g]	$m_{empty\ crucible}$+sewage sludge [g]	$m_{\text{sewage sludge}}\ [g]$	$m_{\text{sewage sludge}}\ [g]$
1	45,0590	64,1366 88,2448	19,0776	63,6045
2	63,7808	82,2817 100,7826	18,5009	81,8151
3	43,80426	50,45041	6,64615	50,25586

Table 11. Second time drying of sewage sludge in 30 ℃ 24h

Pre-drying				After drying
Sample	$m_{empty\ crucible}$ [g]	$m_{empty\ crucible}$+sewage sludge [g]	$m_{\text{sewage sludge}}\ [g]$	$m_{\text{sewage sludge}}\ [g]$
1	45,0590	69,1672	24,1082	23,6295
2	63,7808	94,0090	30,2282	29,7257
3	43,80426	65,35190	21,54764	21,17304

8.2   Amount of ash produced in crucibles after combustion in 850 ℃

Table 12. Second time drying of sewage sludge in 30 ℃ 24h

Sample	Pre-combustion	Post-combustion
1	41,9127	14,47
2	15,9658	6,6436
3	13,13224	5,35484

8.3   Amount of ash produced in crucibles after combustion in 850 ℃

Table 13. Generated ash after combustion of PFAS at 950 ℃

Sample	Pre-combustion	Post-combustion
1	25,7577	9,4684
2	26,1643	9,4911
3	18,10274	6,7660

8.4   Raw data for sintering problems and 26 metals

Table 14. Raw data for analysis of 26 metals and sintering problems

Analysis	Results	Unit
Dry basis	27.0	%
Moisture content	73.0	%
Ash content incl. ash contaminators	45.06	% d.m.
Ash content incl. ash contaminators	12.16	%
Sulfur S	2.007	% d.m.
Sulfur S as received	0.542%	%
Chlorine Cl	0.035	% d.m.
Chlorine Cl as received	<0.010	%
Carbon C	29.9	% d.m.
Carbon C as received	8,1	%
Hydrogen	4,1	% d.m.
Hydrogen as received	9.3	%
Nitrogen N	4.26	% d.m.
Nitrogen N as received	1.15	%
Oxygen O (calculated)	14.6	% d.m.
Oxygen O as received (calculated)	68.8	%
Ashing	550	°C
Shrinkage start temp SST	1070	°C
Deformation temp DT	1160	°C
Hemisphere temp HT	1210	°C
Flow temp FT	1380	°C
Aluminium (Al)	16000	mg/kg d.m.
Antimony (Sb)	2.2	mg/kg d.m.
Arsenic (As)	3.7	mg/kg d.m.
Barium (Ba)	280	mg/kg d.m.
Beryllium (Be)	0.51	mg/kg d.m.
Lead (Pb)	18	mg/kg d.m.
Bor (B)	6.6	mg/kg d.m.

Phosphuros (P)	37000	mg/kg d.m.
Iron (Fe)	120000	mg/kg d.m.
Cadmium (Cd)	0.67	mg/kg d.m.
Calcium (Ca)	26000	mg/kg d.m.
Potassium (K)	5800	mg/kg d.m.
Cobolt (Co)	11	mg/kg d.m.
Cupper (Cu)	400	mg/kg d.m.
Chromium (Cr)	39	mg/kg d.m.
Mercury (Hg)	0.42	mg/kg d.m.
Magnesium (Mg)	5200	mg/kg d.m.
Manganese (Mn)	230	mg/kg d.m.
Molybden (Mo)	9.9	mg/kg d.m.
Sodium (Na)	2500	mg/kg d.m.
Nickel (Ni)	28	mg/kg d.m.
Tin (Sn)	15	mg/kg d.m.
Titanium (Ti)	1900	mg/kg d.m.
Vanadium (V)	33	mg/kg d.m.
Zinc (Zn)	520	mg/kg d.m.
Total amount of removed ash contaminators	0.00	% d.m.
Silicon (Si)	42000	mg/kg d.m.

Table 14. Raw data for analysis of 26 metals and sintering problems

8.5 Raw data for energy content in sewage sludge

Table 15. Raw data for analysis of calorimetric and calorific values

		Mj/kg	Kcal/kg	MWh/ton
Calorimetric heating value	As received	3.427	819.1	0.952
	Dry basis	12.703	3036	3.528
Effective calorific value	Constant volume as received	1.522	363.6	0.423
	Constant volume dry basis	11.867	2834	3.295
	Constant volume db ashfree	21.600	5159	5.998

	Constant pressure as received	1.407	336.0	0.391
	Constant pressure dry basis	11.826	2825	3.284
	Constant pressure db ashfree	21.527	5142	5.978

Table 15. Raw data for analysis of calorimetric and calorific values