Course on Persistent Micropollutants: PFAS

Created and written by Mariska Ronteltap and Kim Lompe

Executive summary

This report presents the final course material that was developed for the online learning module on persistent micropollutants – PFAS. The document can be used as a stand-alone manual to fully individually follow the entire course, from week to week. It includes the links to the video materials that were developed for the course within the project, fully integrated within the reading material.

The course forms a bridge between scientists and professionals working in the water cycle. So far, the information on PFAS has been available in a scattered manner, making it difficult for non-experts to get a complete introductory overview. This course was designed to compile information on PFAS through the water cycle, from production to use and final treatment.

The course is built up in an intuitive way: it starts with a general introduction on the origin, chemistry and nomenclature of PFAS; national standards and reported concentrations in the urban water cycle are presented; analytics are explained; the course concludes with technologies for separation and final destruction of PFAS. Each chapter (or week) contains written textbook material, videos and additional reading material.

Development of the course has been a co-production between PROMISCES and TU Delft, as TU Delft has an extensive educational support system including a professional recording studio and an expert learning assessment system for engineering education. All materials including videos are freely available for the general public. If the learner wants the full experience of having virtual classmates, get access to all exercises and receive a certificate and credit points after successful completion of the course, one can register at online-learning.tudelft.nl.

The course was developed by two environmental engineers with a professional educational background (Mariska Ronteltap and Kim Lompe). The educational videos include knowledge clips (recorded lectures in a studio), videos in laboratories, interviews with PROMISCES project partners and videos on location. To be able to follow the course a basic understanding of chemistry is required; other than that, the course is fully understandable for non-experts.

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1 Week 1 | Introduction to per- and poly fluoroalkyl substances – PFAS

Introduction to this week

In this first week of the course, we focus on the types of PFAS and how they are structured: molecular structure and nomenclature. Next, we review the production process, how PFAS are linked to health risks, and how a restriction or ban is constructed to phase out their production.

Learning objective of this week:

At the end of this week, you will be able to:

Give the definition of a PFAS chemical; describe the types of products PFAS are typically found in; be able to categorize a PFAS chemical based on its major characteristics such as the functional head group; and list the types of health effects reportedly linked to PFAS.

Please watch this first this knowledge clip:
https://youtu.be/41rhTWe0z-M
This video is the first knowledge clip of the course on Persistent Micropollutants - PFAS. Mariska Ronteltap of Delfland Water Authority introduces PFAS chemicals: how are they defined? How are they produced? Which categories are there, and how can you identify the type of PFAS you are dealing with? *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

1.1 A short history of PFAS

PFAS is a group name covering a variety of **synthetic, fluorine-based** chemicals called fluorocarbons. Research from earlier on also contains other descriptions such as perfluorochemicals (PFCs). They were discovered in the 1930s, and more or less by accident the first forms were produced, in the search for better fluids for refrigerators [1]. They found their way first in aiding in the production of nuclear bombs, as a liner for uranium-containing pipes. In the 1950’s, the first cooking pans were coated with Teflon, a brand name polymeric PFAS. Because of the repellent unreactive nature, PFAS were applied in everything from semiconductors, medical equipment to stainproof carpets, pizza boxes and firefighting foam. As a result, we find different forms of PFAS literally everywhere on the planet [2][3].

In the 1970's, PFAS was introduced in firefighting foam in military locations all over the world. Other firefighting training locations have used PFAS-containing foams, also referred to as aqueous film-forming foams (AFFFs) for decades. The foam spread out to air, soil and groundwater which has caused massive pollution still present today. As we inherited this from previous years, we typically refer to this as legacy pollution. More on specific uses and subsequent pollution will be discussed in Chapter 2.

There are many different chemical structures of PFAS, which we will discuss in the nomenclature paragraph (1.2). PFAS are first classified into three main groups: polymeric PFAS, F-gases, and nonpolymeric PFAS. In the context of water, the nonpolymeric PFAS are most relevant, so we will focus on those. This class of PFAS is typically structured based on the perfluorocarbon chain length, their head groups, and the way the carbon chain is structured (branched-nonbranched) and connected to the head group (per- vs polyfluoro). Next to their chemical name, for example perfluorooctane sulfonic acid, and their chemical formula ($C_8F_{17}SO_3H$), quite a number of specific PFAS molecules also have a brand name or an acronym – in this case PFOS. Knowing them all is challenging and not necessary, there are sufficient resources available where to get the right information. Knowing them all is challenging and not necessary, there are sufficient resources available where to get the right information - good examples are [5] and [6]. Being able to identify the main characteristics however is very important, as they determine toxicity, biodegradability, and say something about their origin.

Apart from the identification on molecular structure, chemical name or popular name, the CAS system also provides a great method to communicate and identify individual chemicals. A CAS number (Chemical Abstracts Service number) is a unique numerical identifier assigned to chemical substances by the Chemical Abstracts Service. Each CAS number is specific to a particular chemical compound. For example, Perfluorooctanoic acid (PFOA) has the CAS number 335-67-1.

The main characteristics also determine the applicability in products. For example, a long chain of carbon atoms makes the PFAS molecule more hydrophobic. That makes the product in which such a PFAS is used more water repellent. A shorter chain makes a molecule more mobile, causing it to spread more easily through the environment.

A nice source to get an idea of which type of PFAS is applied in which type of product is supplied by Jasmine Ye Han on manufacturing.com [3].

In this chapter, we will look into several aspects of PFAS: its structuring and nomenclature based on characteristics (1.2), the production process (1.3), the chemical reason for their persistency (1.4), what that does to human health when exposed to PFAS (1.5), and how society is working towards a ban on PFAS for non-essential uses (1.6). With that, you have a solid knowledge foundation on PFAS chemistry and background.

1.2 Molecular Structure and Classification: nomenclature

PFAS, per- and polyfluoroalkyl substances, are persistent substances that consist of an organic molecule in which hydrogen atoms attached to the carbon backbone are entirely or partly replaced by fluorine atoms. Perfluoroalkyl are fully fluorinated, while polyfluoroalkyl substances have a partially fluorinated carbon chain. The C-F bonds are very strong.

The fluorinated chain or tail is hydrophobic – meaning not a fan of water; the tail prefers to reside in for example an air bubble or adsorbed to soil. At the end of the C-backbone there is a hydrophilic ’head’ group – which can be different acid groups such as a carboxylic acid (-COOH), sulfonic acid (-SO_3H) or phosphonic acid (-H_3PO_4).

To give an example, we can look at the largest PFAS group, which are PFAA. PFAA are perfluoroalkyl acids (A). Depending on their functional head group, PFAA can be further classified into [4]:

- Perfluoroalkyl sulfonic acids which have a SO_3H group (PFSA),
- Perfluoroalkyl carboxylic acids which have a COOH group (PFCA),
- Perfluoroalkyl phosphonic acids which have a H_3PO_4 group (PFPA).

The sulfonic acid group (PFSA) is a stronger and more polar acid than the carboxylic acid group (PFCA). The PFSA group includes the well-known PFOS (C_8PFSA); the PFCA groups includes PFOA (C_8PFCA).

Next to the type of head, PFAS can also be classified according to the number of C atoms in the chain. Up to 6 C atoms is considered **short-chain**; 7 or more C atoms is generally considered **long-chain**, though other definitions exist. Finally, we also see the term **ultra short chain** PFAS (one to four C atoms), infamous for their high persistency and mobility. This is an important distinction when it comes to determining a suitable treatment technology, as well as to establish a toxicity level.

1.2.1 Polymerisation

PFAS molecules can be organised in a repetitive manner – also known as polymerisation. Non-polymer PFAS are smaller molecules, with perfluorocarbon chain lengths typically below 20. They are often used in products like firefighting foams, stain repellents, and food packaging [5], but also in the production of polymeric PFAS. They are likely to be more mobile in the environment and can accumulate in living organisms. Polymeric PFAS are very long molecules made up of many repeating units. The PFAS polymer class includes fluoropolymers, polymeric perfluoropolyethers and side-chain fluorinated polymers [4]. Examples include polytetrafluoroethylene (PTFE, commonly known as Teflon) and polyvinylidene fluoride (PVDF). These polymers are used in various applications like non-stick cookware, waterproof clothing, and medical devices. Due to their large size and stable structure they tend to be less mobile in the environment. They are generally considered to a have lower toxicity.

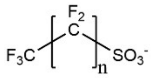
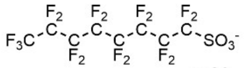
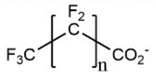
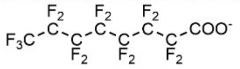
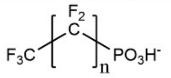
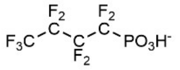
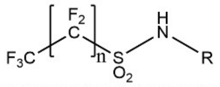
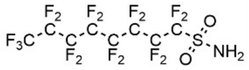
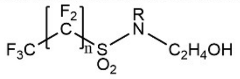
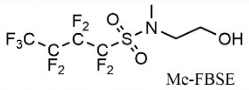
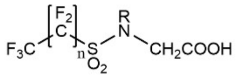
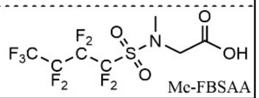
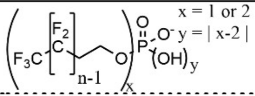
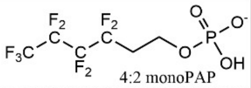
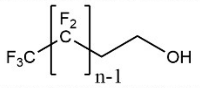
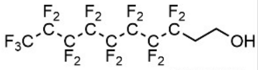
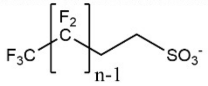
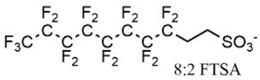
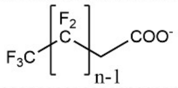
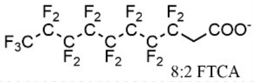
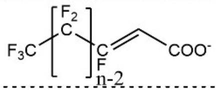
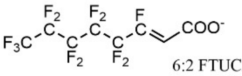
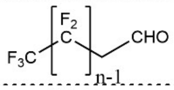
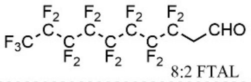
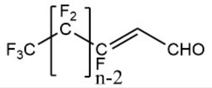
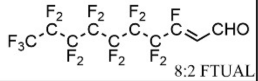
1.2.2 Linear or branched

Another subdivision that is often reported is that between linear and branched PFAS with the same molecular formula. In linear PFAS, the carbon atoms are connected in a single straight line. This structure tends to make them more persistent and more likely to bioaccumulate. Branched PFAS, on the other hand, have a carbon chain that includes one or more branches. These branches can affect how the molecules interact with biological systems and the environment with different rates and degrees of degradation, dissolution and adsorption than their linear counterparts.

There are many PFAS classification trees published online. The main categories that always appear are the perfluoroalkyl acids, polyfluoroalkyl acids, their precursors, and other PFASs.

An example of a classification is given in the table below, from [7] (reproduced with permission from the author).

Table 1.1 Example of PFAS classification by name, acronym, structure and an example per type [7].

Name	Acronym	Structure	Example
Perfluorinated			
Perfluoroalkyl sulfonates	PFSA		 PFOS
Perfluoroalkyl carboxylates	PFCA		 PFOA
Perfluoroalkyl phosphonates	PFPA		 PFBPA
Perfluoroalkyl sulfonamides	FASA		 FOSA
Perfluoroalkyl sulfonamido-ethanols	FASE		 Me-FBSE
Perfluoroalkyl sulfonamido-acetic acids	FASAA		 Me-FBSAA
Polyfluorinated			
Polyfluoroalkyl phosphoric acid esters	PAP		 4:2 monoPAP
n:2 Fluorotelomer alcohols	n:2 FTOH		 8:2 FTOH
n:2 Fluorotelomer sulfonates	n:2 FTSA		 8:2 FTSA
n:2 Fluorotelomer carboxylates	n:2 FTCA		 8:2 FTCA
n:2 Fluorotelomer unsaturated carboxylates	n:2 FTUCA		 6:2 FTUCA
n:2 Fluorotelomer saturated aldehydes	n:2 FTAL		 8:2 FTAL
n:2 Fluorotelomer unsaturated aldehydes	n:2 FTUAL		 8:2 FTUAL

1.3 How does the PFAS production process look like?

PFAS are produced using several different processes. Fluorosurfactants like perfluoroalkyl acids (PFAAs) and side-chain fluorinated polymers have been manufactured using two major processes: electrochemical fluorination (ECF) and telomerisation.

Electrochemical fluorination was licensed by 3M in the 1940s and used by 3M until 2001 [1]. This process produces a mixture of even and odd numbered carbon chain lengths of approximately 70% linear and 30% branched substances. Telomerisation was developed in the 1970s, and yields mainly even numbered, straight carbon chain isomers. PFAS manufacturers have provided

PFAS to secondary manufacturers for production of a vast array of industrial and consumer products.

During manufacturing, PFAS may be released into the atmosphere or discharged to wastewater treatment plants or landfills; yet, they are not designed to mitigate PFAS, hence the PFAS will end up in the final products of those systems such as sewage sludge or landfill leachate. Industrial discharges of PFAS were unregulated for many years. Since the mid-2010s, the discharges are being more regulated. Still, consumer and industrial use of PFAS-containing products end up releasing PFAS into landfills, sediments, surface water and municipal wastewater, where it may accumulate in biosolids. We will discuss this in week 2.

1.4 What are the main sources of environmental PFAS pollution?

Understandably, the locations where PFAS are or were produced and intensively used are the locations where the highest pollution can be found. Examples are the locations of fluoropolymer production installations, (former) firefighting testing locations, military training locations and (former) airports. Other sources include textiles, paper and painting/printing facilities [8]. PFAS in consumer products, such as textiles, furniture, polishing and cleaning agents and creams, may contaminate dust and air, while crop protection chemicals or food contact materials such as pizza boxes or plastic-lined cans can contaminate food [5, 8]. But, also food itself can be a source: fish can contain high concentrations of PFAS, depending on where and how it was caught, and people also ingest PFAS through tea, coffee, cereal products, milk products, meat, eggs, fruits and vegetables [9].

Emissions to the environment depend on the source. Industry may release industrial wastewater and air emissions. Households discharge domestic wastewater, and wastewater treatment plants do not generally remove PFAS. A particular problem is also locations where sewage sludge or river sediments have been applied to land in the past when we still did not know enough about the toxicity. As the accumulation has remained in the soil, we now still see the effects of those, leading to polluted groundwater, and for example to cows being so exposed to PFAS that their meat is considered unfit for human consumption [10]. Also sea spray has been shown to contain PFAS, which leads to quite some challenges in dunes that function as drinking water treatment [11].

1.5 Why is PFAS so hard to break down?

So why do PFAS cause us so much headache? The reason for that is that their plus side, being so resistant to water, chemicals, fire and biological processes, is also their downside – the options for breaking down the produced chemicals are very limited. And that is problematic because as a consequence, we find PFAS back in nature literally everywhere, where they are known to interfere with healthy biological processes in humans and animals [2, 3].

The strong bond between the C and the F atom

The carbon-fluorine (C-F) bond in per- and polyfluoroalkyl substances (PFAS) is very strong. The C-F bond is considered the strongest single bond in organic chemistry [12]. The presence of many C-F bonds in PFAS molecules functions as a shield against most common degradation mechanisms, leading to PFAS being persistent in the environment, resistant to degradation, and thermally stable. Replacing a typical C-H bond with a C-F bond increases the energy required to break the bond by about 17%. Chemists quantify this energy with bond dissociation energy (BDE). The BDE for a C-H bond is approximately 436 kJ/mol, while the BDE for a C-F bond is around 587 kJ/mol; a difference of 151 kJ/mol. The reason for the strength of this bond is the electronegativity of fluorine and its relative attraction to carbon. This means that significant energy is required to break this C-F bond, which will be the topic in Week 5.

1.6 Health effects

PFAS can have several negative effects on health [13]. Identifying which effects precisely is not so straightforward – one does not want to expose test persons to PFAS and then evaluate the effect. Several steps and methodologies can be applied when studying the health effects of PFAS (Table 1.2).

Table 1.2 Different methods to study health effects of PFAS on human being and other fauna, adapted from [13]

Exposure Assessment	the identification of an exposure route, such as occupational exposure, consumption of contaminated water or food, and environmental exposure near industrial sites.
Sample Collection and Analysis	Samples from blood, urine, or tissues are collected from exposed individuals. These samples are analysed in the lab to identify and quantify PFAS levels.
Human Epidemiological Studies	Researchers study populations exposed to PFAS to identify correlations between exposure levels and health outcomes. This can involve long-term health monitoring and statistical analysis to identify patterns.
Skin Absorption Studies	Experiments on lab-grown human skin tissue models help understand how PFAS can be absorbed through the skin and its potential health impacts.
In Vitro Studies	Laboratory experiments using cell cultures (e.g., liver cells) help understand how PFAS affect cellular functions. For example, HepaRG cells are used to study the impact of PFAS on liver cells. A similar route is taken by for example Biological Detection Systems in Amsterdam, which is shown in more detail in their video in Week 3.
Animal Studies	Animals like mice and rats are exposed to PFAS to observe potential health effects, including cancer, liver damage, and immune system suppression.
Machine learning	To predict toxicity based on the chemical structure of molecules. This will speed up toxicity assessment significantly, is much cheaper than other tests, and may be the only route to keep up with the speed of new chemical compounds being produced.

1.6.1 Effects of PFAS on human health

What has been found so far is that PFAS has proven to interfere with the functioning of the thyroid. PFAS molecules can bind to thyroid hormone transport proteins in the blood, reducing the availability of thyroid hormones. This can lead to an increase in thyroid-stimulating hormone (TSH) as the body tries to compensate for the perceived low hormone levels [15].

PFAS can act as endocrine disruptors, meaning they mimic hormones involved in the reproductive system. By getting involved in the natural cycle of biological reproduction, fertility issues occur as well as disruptive changes in the male and female reproductive organs and cells.

Next to that, exposure to PFAS can affect children's development even before birth. As PFAS can disrupt the transport of essential nutrients and oxygen from the mother to the foetus, the foetus's growth and development can be hindered. Also, for unborn babies the interference in the functioning of the thyroid is harmful: thyroid hormones are crucial for foetal brain development. More interference routes involve changes in the expression of genes (epigenetic changes) and the loss of the placenta barrier function: the placenta acts as a barrier to protect the foetus from harmful substances. PFAS can compromise this barrier function, allowing more toxins to reach the foetus.

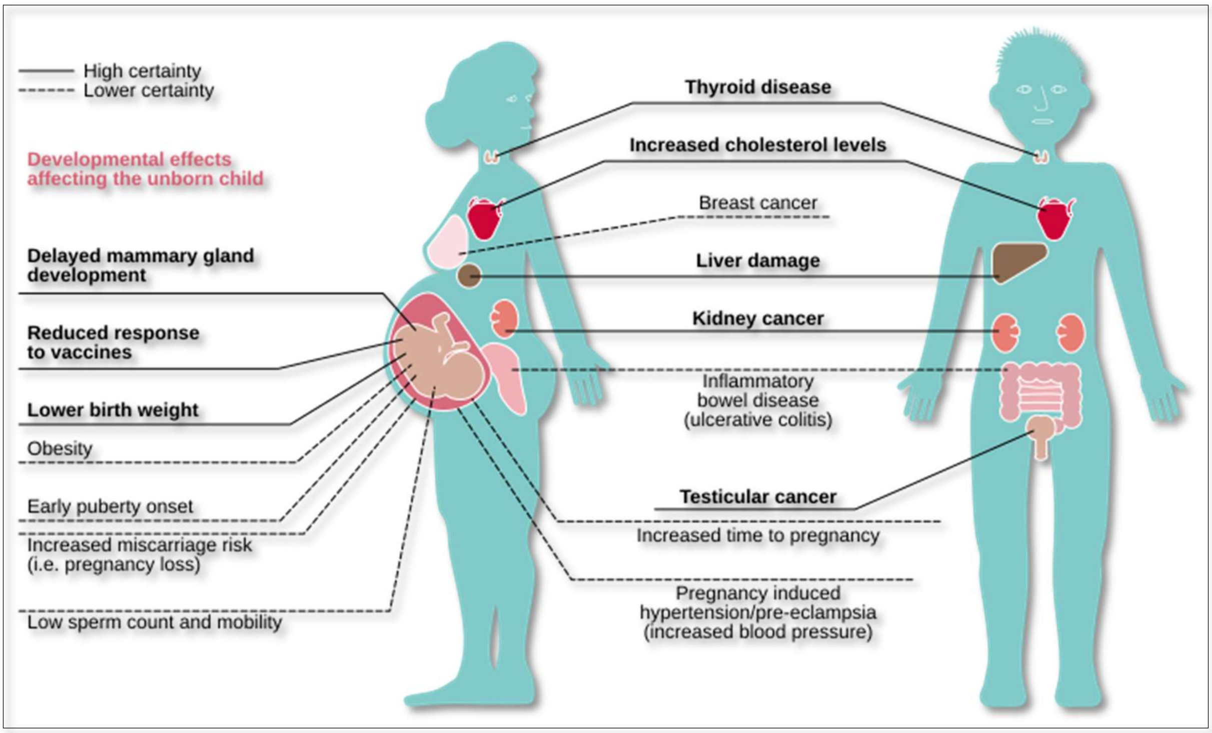


Figure 1.2 Where in the body can PFAS have which effect [20]

Strong evidence also exists for suppression of the immune system by PFAS [16]. The fluorine chemicals can suppress the ability of the immune system to make antibodies that fight infectious diseases, as well as make vaccines less effective.

A link to development of cancer can also be made for the exposure to PFAS. The International Agency for Research on Cancer (IARC) has classified perfluorooctanoic acid (PFOA) as a human carcinogen and perfluorooctanesulfonic acid (PFOS) as possibly carcinogenic to humans. PFAS exposure can increase the production of reactive oxygen species in cells, which in turn can damage cellular components like DNA, proteins, and lipids. Damaged DNA is a well-known precursor to cancer development. Moreover, PFAS can interact with internal cell receptors, disrupting normal functions and as such lead to potential uncontrolled cell growth. Finally, some PFAS can cause changes in gene expression without altering the DNA sequence, which can influence cell proliferation.

Researchers continue to study the effects of these chemicals, and their findings underscore the importance of understanding and addressing PFAS-related health risks [17].

1.6.2 Why are PFOS and PFOA more detrimental for human health than other PFAS?

PFOS has a strong carbon-fluorine bond, making it highly resistant to degradation. This persistence means it can remain in the environment and in living organisms for a long time, leading to prolonged exposure, and a more widespread exposure as it stays present in the environment for a longer time. In that same line, PFOS and PFOA tend to accumulate in the bodies of living organisms, particularly in the liver and blood. This bioaccumulation can lead to higher concentrations over time, increasing the potential for toxic effects. Chemically, its ability to interfere with hormone function and other biological processes contributes to its higher toxicity. These factors combined make PFOS/PFOA particularly concerning compared to some other PFAS.

1.6.3 Expression of toxicity

With so many substances, it can be difficult to obtain the toxicity of a mixed sample. One way of looking into this is via the PFOA equivalent. This PFOA-equivalent – PEQ – value is used as measure to express the concentration of various per- and polyfluoroalkyl substances in terms of PFOA units. The specific PFAS compounds present in a sample are identified and measured chemically (e.g. liquid chromatography-tandem mass spectrometry, LC-MS/MS - see Week 3), and then multiplied by an assigned relative potency factor (RPF) – relative to PFOA. The sum gives the PEQ value for the sample. The Dutch Institute for Environment and Public Health, RIVM, published a list with determined relative potency factors, calculated from studies on the effects of PFAS on the liver of rats as animal model (RIVM Report, 2023). This is at the same time also a critical point: toxicity based on liver toxicity in rats is only one of many ways to assess potential effects on humans and perhaps not the most elegant or accurate one.

The European Union is working hard to reduce the exposure of humans to PFAS, and has mapped the different exposure routes and calculated maximum tolerable weekly intake of PFAS. The EFSA, the European Food Safety Authority, focused on four PFAS for their assessment: perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA) and perfluorohexane sulfonic acid (PFHxS). They have set the limit to 4.4 nanogram per kilogram of body weight per week.

The EU has implemented several regulations to tackle PFAS intake:

- EC regulation on maximum levels for certain contaminants in food (2023/915), including Maximum Levels (ML) for PFAS in foodstuffs.
- EC Water Framework Directive (2000/60/EC): sets quality standards for water bodies and imposes limits on PFAS in drinking water and surface waters.
- Food Contact Materials Regulation (EC 1935/2004): regulates materials touching food
- Persistent Organic Pollutants (POPs) Regulation (EC 850/2004): controls the release of persistent organic pollutants into the environment, including certain types of PFAS.
- REACH Regulation (EC 1907/2006): requires companies to register and evaluate chemicals, with provisions to restrict substances like PFAS if they pose risks to health or the environment.

1.7 Ban on PFAS?

As we learn more about the negative effects of PFAS, the pressure is high to ban PFAS from all products where they are not absolutely necessary, the so-called non-essential uses. This is a good strive; however, there are still plenty of areas where PFAS is considered essential: medical equipment, to fight certain fires, in aircrafts, and so on. This means that PFAS is still being produced, and any clean-up is affected by that continuous manufacturing. In general, essential use is defined as: 1] necessary for health, safety or is critical for the functioning of society, and 2] there are no available alternatives that are technically and economically feasible.

Next to production, there are countless locations where PFAS was used and now still contain PFAS which are releasing to the environment (water, soil and air). This is referred to as legacy pollution. And then of course there are all the products containing PFAS that are still in use today – with every laundry or firefighting activity, PFAS molecules are released into the environment.

As the urgency to tackle PFAS from the source gets more obvious, the work on policies to ban PFAS from a legal perspective intensifies. In Europe it is the ECHA, the European Chemicals Agency (ECHA) who is working on the implementation on the PFAS restriction [18]; in the USA the EPA is responsible for carrying out the work related to the Forever Chemicals Regulation and Accountability Act of 2024 [19]. As you can imagine, the largest discussion is on what is and what is not essential in the use of PFAS.

The video below shines some light on the discussions taking place between regulators, scientists, producers and stakeholders in essential and non-essential PFAS.

Please watch this video:
https://youtu.be/2Fp7YDZcrIo
In this video, Mariska Ronteltap interviews Dominique Guyonnet of BRGM on his view of PFAS regulation, and his expectations for the development in the future. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

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2 Week 2 | PFAS in the urban water cycle

Introduction to this week

In the first week, we learned about the types of PFAS and how they are structured, their production route, how they are linked to health risks, and how a ban is constructed to phase out their production.

This week we are zooming in into reported levels of PFAS in the urban water cycle: drinking water sources, wastewater, landfill leachate, sewage sludge. We also touch upon legislation in various settings. We tend to use data published after 2020, as the detection limits and level of distinguishment have improved significantly in recent years.

Learning objective of this week

After completing this week, you should be able to:

Describe the fate of PFAS over the different elements of the urban water cycle; know the key elements of legislation on PFAS in different parts of the world; and explain how the application of technologies depends on the water cycle element and legislation.

For this week, instead of showing a knowledge clip recorded in the studio in Delft, we took the camera crew to Barcelona. Here, we were able to capture full-scale applications for producing drinking water with agreeable quality in an environment where freshwater sources are scarce and contains PFAS. The treatment plant of Aigües de Barcelona is treating water from the nearby river Llobregat. That river also receives the effluent from a wastewater treatment plant further upstream. In dry times, this effluent forms a major part of the water flow towards the river – as is the case in many other places in the world. Aigües de Barcelona needs to supply drinking water of good quality to many citizens and a growing number of tourists and is therefore applying the best treatment technologies to their raw drinking water. We will see more of this plant and its managers in the weeks to come; in this video Meritxell Minovez Ruis, Senior Engineer at Aigües de Barcelona, will introduce how the drinking water system and demand have developed over the years and how the company has coped with these changes. A meaningful experience.

Please watch this knowledge clip:
https://youtu.be/9nXc-smdcLI
Meritxell Minoves Ruiz, Senior Engineer at Aigües de Barcelona, explains the interaction between El Prat de Llobregat wastewater treatment plant and Sant Joan Despí drinking water treatment plant. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

2.1 PFAS and its fate in the urban water cycle

As we learned from Week 1, PFAS are fluorinated substances that contain at least one fully perfluorinated methyl (-CF$_3$) or methylene (-CF$_2^-$) group without any chloride (Cl), bromide (Br) or iodine (I) attached to it. The fact that they are so hard to break down causes them to stay within the urban water cycle once they have entered.

The figure below, produced for the PROMISCES project, shows how the urban water cycle is interconnected. Upstream water (surface or groundwater) enters the drinking water treatment facility. After treatment, drinking water is distributed and used, and after use the water is primarily collected through a sewer system to be treated at the (municipal) wastewater treatment plant.

Figure 2.1 The urban water cycle and how PFAS travels through the compartments. Made by Kompetenz Zentrum Wasser Berlin (KWB) for PROMISCES.eu.

As the plant is treating wastewater biologically, bacteria grow on the organic content of the wastewater, and bacterial mass is produced in excess. The excess is often digested anaerobically and dewatered. Depending on the local possibilities and legislation, the digested and dewatered sludge is incinerated in a dedicated sludge incinerator, or applied to the land as biosolids, for better water retention and supply of micro- and macronutrients. Incineration leads to the production of ash and off-gas; the off-gas is washed which produces again a wastewater stream. The ashes are either landfilled or applied to non-critical uses. Landfills are dedicated locations for receiving solid waste. Per definition they need to be lined, meaning supported by a non-permeable underground which collects the liquids derived from the stored solid waste, the so-called landfill leachate. This leachate may contain high levels of pollutants (see also in a later week video Week_5_2_PFAS destruction in leachate).

A final part of the urban water cycle is formed by surface water and its interconnection with the surroundings: stormwater drains into surface water, carrying soil, sand and other materials. These materials periodically are dredged from the water ways, producing dredged sediments. They can also contain different levels and sources of contamination, and therefore need specific attention.

In this chapter we discuss the different elements of the urban water cycle and their relation to PFAS.

2.2 PFAS limits, guidelines, regulations, standards over the world for drinking water

2.2.1 Europe

In Europe, the regulation of PFAS in drinking water is becoming more stringent, with various measures being introduced both at the European Union (EU) level and in individual countries. As we can better measure - at lower detection levels and in different matrices - and know more about the toxicity, limits are being set to minimize the potential health risks associated with PFAS exposure. At the EU level, the European Commission has taken steps to address PFAS contamination in water sources. A key piece of legislation is the Drinking Water Directive (DWD), which sets limits for various contaminants in drinking water, including PFAS. In 2020, the EU has adopted the new DWD which regulates maximum concentrations for four PFAS compounds: PFOA, PFOS, PFHxS and PFNA. PFAS levels in drinking water must be monitored from 2026 onwards. The proposed limit is 0.5 micrograms per litre (µg/L) for total PFAS and 0.1 µg/L for the sum of 20 specific PFAS. More recently, in 2023, the European Commission asked the World Health Organization to study the effect of PFAS in drinking water on human health. Based on this and other studies, the European Commission may revise their directive. A revision is expected in 2026. The DWD is part of a broader strategy to address PFAS contamination in the EU, including monitoring and reporting requirements. Individual countries within Europe have taken additional steps. Germany has set stricter drinking water limits for PFOA and PFOS at 0.05 µg/L each and is actively monitoring and evaluating other PFAS compounds; Sweden and Denmark recommend a limit of 0.02 µg/L for PFAS and PFOA and PFOS respectively in drinking water.

For the **sum** of these 20 specific PFAS compounds a maximum of 0.1 microgram per litre (µg/L) is set in the EU's Drinking Water Directive.

Perfluorobutanoic acid (PFBA)	Perfluorobutane sulfonic acid (PFBS)
Perfluoropentanoic acid (PFPA)	Perfluoropentane sulfonic acid (PFPS)
Perfluorohexanoic acid (PFHxA)	Perfluorohexane sulfonic acid (PFHxS)
Perfluoroheptanoic acid (PFHpA)	Perfluoroheptane sulfonic acid (PFHpS)
Perfluorooctanoic acid (PFOA)	Perfluorooctane sulfonic acid (PFOS)
Perfluorononanoic acid (PFNA)	Perfluorononane sulfonic acid (PFNS)
Perfluorodecanoic acid (PFDA)	Perfluorodecane sulfonic acid (PFDS)
Perfluoroundecanoic acid (PFUnDA)	Perfluoroundecane sulfonic acid
Perfluorododecanoic acid (PFDoDA)	Perfluorododecane sulfonic acid
Perfluorotridecanoic acid (PFTrDA)	Perfluorotridecane sulfonic acid

2.2.2 Oceania

Australia has guidelines for PFAS in drinking water, not legally enforceable limits. The Australian Government Department of Health has set a health-based guideline value at 0.070 micrograms (or 70 nanograms) per litre for the sum of PFOS and PFOA. This guideline is intended to protect public health based on current evidence. Since PFAS contamination in drinking water varies by location, each state and territory may take different actions to address and manage contamination based on local conditions. Some areas may implement stricter measures, including monitoring and remediation programs, especially in areas near known sources of PFAS, such as military bases or firefighting training facilities.

In New Zealand, there are no specific enforceable limits for PFAS in drinking water at the national level. However, the Ministry of Health has provided guidance on PFAS concentrations, similar to Australia's approach. The Ministry has set a recommended maximum concentration for the sum of PFOS and PFOA in drinking water at 0.01 micrograms per litre (10 ng/L), which is more stringent than Australia's guideline of 70 ng/L. These guidelines aim to minimize any potential health risks associated with PFAS exposure, especially in areas where contamination is found. Like in Australia, the regulations and monitoring efforts vary depending on the region and local circumstances. In New Zealand, PFAS contamination is also being addressed on a case-by-case basis, particularly in areas with known sources of contamination.

2.2.3 United States

In the United States, the regulation of PFAS in drinking water has been an evolving issue. The Environmental Protection Agency (EPA) has set a Non-Enforceable Health Advisory Level (HAL) for PFOA and PFOS also at 0.07 micrograms per litre (µg/L) or 70 parts per trillion (ppt) [2]. Also here, it is a guideline rather than a legal limit, meaning states or local jurisdictions are not required to meet this level, but it provides a benchmark for safe levels. In addition to the federal guidelines, several states have established their own more stringent standards for PFAS in drinking water. For example, California has set a public health goal for PFOA and PFOS at 0.02 µg/L and 0.01 µg/L; Michigan has enforceable drinking water standards for several PFAS compounds, including PFOA and PFOS, at 0.07 micrograms per litre (µg/L). The EPA has been moving toward establishing more comprehensive regulations for PFAS in drinking water. As of 2023, the EPA proposed a National Primary Drinking Water Regulation for several PFAS compounds, aiming to set enforceable limits for specific substances like PFOA and PFOS but they are still in the process of being finalized.

Please watch this video:
https://youtu.be/K-yAFzxFWd8
Kim Lompe of TUDELFT interviews Miquel Paraira Faus, head of the laboratory and research director, on how Aigües de Barcelona faces the challenges of drinking water production in the Barcelona region in times of drought. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

2.3 PFAS in wastewater treatment plants

In Europe, specific effluent requirements regarding PFAS do not exist yet. For other micropollutants such as pharmaceuticals, demands are taken up in the revised European Directive for Urban Wastewater. For these pollutants, larger European wastewater treatment plants are required to remove 80% of the incoming contamination from 2034 onwards; smaller plants are allowed some more implementation time. For PFASs this regulation does not (yet) apply; likely because its removal is still so complex, costly and related to other environmental impacts – think of activated carbon applied to the total quantity of domestic wastewater [3}. Therefore, active PFAS removal is not yet seen in European municipal wastewater treatment plants (WWTP). Still, measurements are carried out in several locations, and technological experiments are carried out.

To date, not many wastewater treatment plants (WWTPs) are monitored regularly. Regarding PFAS and other persistent chemicals from common household products, industrial wastewater sources and firefighting wastewaters, WWTPs are considered to be a gateway to the environment, through air, effluent and sludge. So far, monitoring the fate and behaviour of PFAS within WWTPs shows that primary treatment (focused on the removal of solids through physical settling) provides very little to no removal, while secondary biological treatment processes can result in some transformation. In wastewater treatment plants often an ‘increase’ is observed in measured PFAS, see for example the figure below. Over the different steps in the treatment plant (primary sedimentation, aeration, secondary sedimentation) samples were collected and analysed. For PFHxA for example, an increasing trend can be observed over the course of the treatment plant. This is observed in more locations and is caused by the presence of ‘precursors’: typically, longer chain PFAS breaking down in more stable short-chain PFAS.

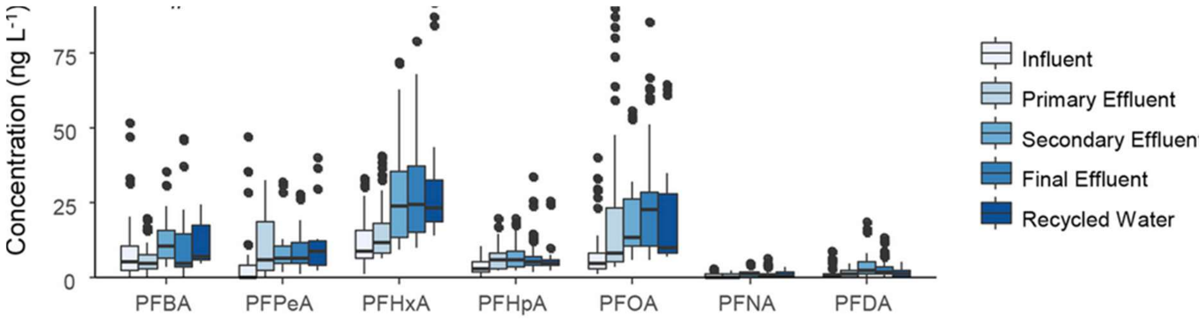

Figure 2.2 Boxplots of pooled data from 19 WWTPs for PFCAs, perfluorocarboxylic acids in aqueous samples: influent (n = 57), primary effluent (n = 39), secondary effluent (n = 24), final effluent (n = 57) and recycled water (n = 24) [3].

Another study looking at 6 North American WWTPs found that PFAS concentration ranged from 30 – 198 ng L^{-1}. From the groups the WWTPs were tested for, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates/sulfonic acids (PFSAs) largely dominated. Most studies so far have focused largely PFOS and PFOA, as they are the most commonly applied in many products and easily catch the attention [4].

Activated sludge, which is commonly applied in wastewater treatment processes, is generally not effective at breaking down PFAS (per- and polyfluoroalkyl substances). Some sorption to the sludge does take place, particularly for the larger molecules (in week 1 the hydrophobic tail was discussed). The exact quantities will depend strongly on the retention times, types of PFAS, type of charge of the sludge, among others. Sorption to sludge is not likely to remove substantial amounts of PFAS of any type though. This is also highlighted in this interview by Mariska Ronteltap with Alexander Sperlich from Berliner Wasser Betriebe, recorded during the 2024 Promisces annual gathering in Barcelona.

Please watch this video:
https://youtu.be/os99rsfNrtI
In this video, Alexander Sperlich of Berliner Wasser Betriebe explains the issues with PFAS in the water cycle, and points out the challenges with PFAS and current treatment technologies for wastewater. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

2.4 PFAS in landfill leachate

Landfills for solid waste management are not applied everywhere in the world; in quite a few countries solid waste is managed differently. More industrialised countries make use of incineration; others have to turn to less managed waste disposal sites due to lack of investment power. Still, solid waste landfills can be found on every continent, and as they produce a wastewater stream that requires careful management, they form an integral part of the urban water cycle. In the graph below, a schematic overview is given of such a facility. A landfill that is full gets closed off, gas is collected and treated and leachate, the water that seeps away from the stored solid waste, is collected in a drain underneath. The landfill has to be lined with a non-permeable liner so that other leakages to the environment do not take place. The wastewater collected as leachate can either be taken to a (nearby) wastewater treatment plant or treated in a dedicated facility on location.

The concentration of PFAS in leachate may vary from 100 to greater than 100,000 ng L^{-1} in leachate [5]. PFAS concentration in landfill leachate is typically higher than in groundwater, surface water, and wastewater due to the accumulation effect of PFAS in the landfill and the complex nature of the leachate. Therefore, leachate should be targeted as a separate concentrated stream of PFAS for treatment to reduce PFAS circulation in the urban water cycle.

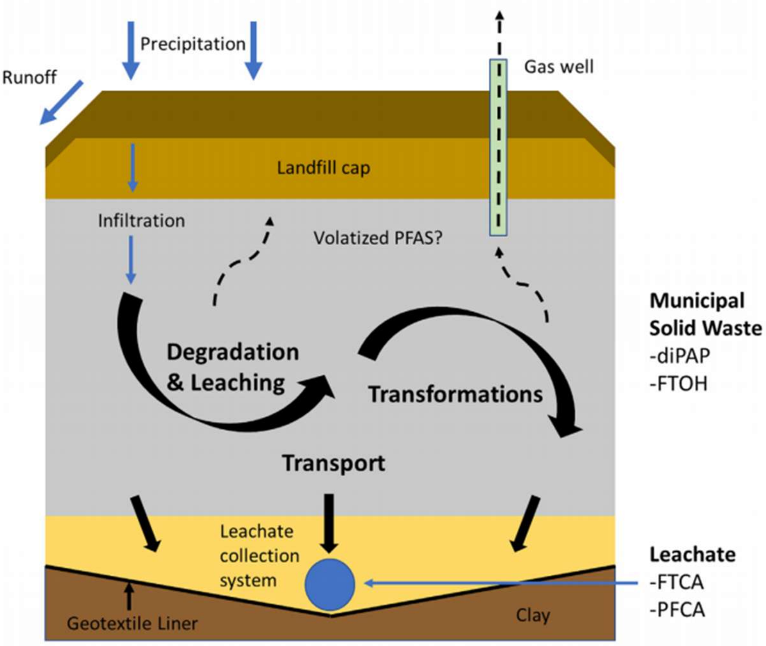

Figure 2.3 Graphical representation of a municipal solid waste landfill. The major processes affecting PFAS composition and leachate generation are included; it shows also how certain transformations can take place, from longer chain precursors into smaller pieces [6].

In this week we have given an overview of PFAS reported in various reports in all parts of the urban water cycle. In week 3, we will learn how these sections can be sampled and analysed.

2.5 LITERATURE

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3 Week 3 | Sampling and measuring PFAS

Introduction to this week

Welcome to week 3, where you will learn about PFAS analytics. We are covering all steps from your experimental plan, the sampling of your PFAS containing media, sample (pre-)treatment, analytical methods and their limitations and the interpretation of an analytical report.

Besides the more common chemical detection methods that help us to identify and quantify individual and known PFAS we will also cover biological detection systems that allow us to identify cell reactions on unknown PFAS and PFAS mixtures. Such biological detection systems or bio-assays can be used to assess and quantify if a PFAS polluted water/soil or other matrix is potentially triggering inflammation or endocrine cell activity.

The first lecture of this week is given by our chemical analytics expert Dr. Eelco Pieke who will explain how the state-of-the-art analytical tool works for PFAS analysis in water samples. We will also talk to him about the importance of blanks and controls in the experimental plan and ideal materials for bottles and filter papers during the sampling process. You will get a virtual lab tour to see the workflow inside an analytical lab.

The second lecture of this week is given by our biological detection expert Dr. Harrie Besselink. He will explain how modified cell lines can serve as a detection system for sample toxicity. We will follow him virtually through the laboratory and see how samples are processed there.

Besides the video lectures, expert interviews and lab tours you will read about analytical challenges, PFAS extraction from soil matrices and ongoing discussions about PFAS analytics at the level of the European Union.

Learning objective of this week

After completing this week, you should be able to:

To describe which equipment is used for analysis of PFAS in the water lab; to indicate what the importance is of a blank in your series of samples; and to evaluate an analytical report of a PFAS sampling campaign considering the limitations of the sampling and analytical methods.

Please watch first this knowledge clip:
https://youtu.be/1AENDWdyxdc
Eelco Pieke of Het Waterlaboratorium explains how PFAS are analysed in a specialised water laboratory, in this third knowledge clip of the course on Persistent Chemicals - PFAS. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

3.1 Chemical detection and quantification

Currently, the most common analytical quantification methods for PFAS are liquid chromatography combined with mass spectrometry (LC-MS) for ionic PFAS such as carboxylic and sulfonic acids and gas chromatography combined with mass spectrometry for volatile and semi-volatile PFAS such as fluorotelomer alcohols [1].

For cleaner water samples this is relatively straightforward as these samples do not need extensive pre-treatment or extraction methods before the analysis. In his lecture, Dr. Eelco Pieke from Het Waterlaboratorium explains the measurement principle of the LC-MS method. For more polluted water samples or soil samples a more extensive sample preparation may include extraction steps to transfer PFAS into a liquid or gas phase.

We must keep in mind, however, that samples analysed via any target analysis will only detect the known list of PFAS for which standards exist and reliable analytical methods were developed with known ion pairs or mass/charge ratios in the chromogram. In the case of HWL the list comprises 31 PFAS that are relevant to the drinking water companies due to the current and proposed legislation in the Netherlands. The European Union proposed to monitor 24 PFAS [2]. Remember, when doing a target analysis, we detect only the selected PFAS we are searching for. A sample can of course contain many more PFAS as there are several thousand of more or less known PFAS, associated to unknown transformation products in the environment. Indeed, only < 200 PFAS compounds can be analysed with all target analyses combined [1].

Despite of this limitation, the European Drinking Water Directive 2020 introduced the parameter “total PFAS” to be monitored in drinking water starting in 2024. So far, however, no standardized method to measure a global parameter such as total organic fluorine exists. Researchers still disagree on which method to choose for such global parameter in diverse environmental matrices. If you want to know more about the ongoing discussion at the European level, you can follow the news on the website of the European Federation of National Associations of Water Services EurEau [3].

Please watch this lab tour video:
https://youtu.be/V4KPRsbRF7o
In the lab of Het Waterlaboratorium, Eelco Pieke explains how water samples are processed for PFAS analysis as part of the course on Persistent Chemicals - PFAS. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

3.2 Sampling for PFAS and analysing an analytical report

A good sampling strategy is essential for good analytical results. The sampling location and time must be representative for the reactor/field/water body, the sampling bottle should not adsorb or desorb PFAS and if a sample is filtered, the filter material should not retain PFAS either. To account for these PFAS sinks and sources, blanks and controls should be added to the experimental plan and sampling campaign. PFAS analyses are still pricey but an erroneous sample that needs repetition is even pricier. Good communication with the analytical lab is essential as they can consult before the experiments or sampling campaign is taking place. Watch the interview with Dr. Eelco Pieke to learn more about the laboratory's perspective on how we can improve our PFAS results beginning at proper planning and sampling. Once results come back from the laboratory, the analytical report needs to be read, and the results interpreted.

Please watch this lab based video:
https://youtu.be/JdNKn1OZQe0
In the laboratory, Eelco Pieke of Het Waterlaboratorium gives insight in the do's and don'ts of sampling for PFAS and different methods of analysing water samples as part of the course on Persistent Chemicals - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

3.3 Biological detection systems

You have now heard Dr. Eelco Pieke speak about PFAS target analysis via e.g. LC-MS. The European Union requires drinking water treatment plants to monitor 24 PFAS compounds – selected according to their presence and toxicity to humans. Ultimately, the definition of thresholds for single compounds and/or list of compounds is based on an analysis of the health risk for humans when consuming these contaminants. The risk is evaluated based on contaminant concentration and exposure for individual compounds.

But as we have seen it is difficult, if not impossible, to analyse all PFAS and other pollutants in the environment and our samples – due the vast quantity of PFAS and their transformation products. Instead of analysing different compounds it is also possible to measure the integral effect of all different compounds together. This can be done with bio-assays. We can expose laboratory-grown and modified cells to the contaminated sample and observe the cell's biological activity or reaction. Is the bio-assay designed to show an inflammatory response and can the sample trigger this response? Different bio-assays exist to test a wide range of effects such as endocrine disruption, inflammation, estrogenic or androgenic activity. Using bio-assays, dose-response curves can thus be recorded for known contaminants such as PFOA that serve as a benchmark for other unknown PFAS mixtures. The result is a quantifiable activity which does not discriminate between individual compounds but takes into account all compounds present. In the final video of this week, you will hear Dr. Harrie Besselink talk about these biological detection systems and how they could be used to complement the chemical analytical methods.

Please watch this lab based video:
https://youtu.be/mNmtfraqtNE
Harrie Besselink of BioDetection Systems explains how PFAS can be detected using biological cells in this Voices from Field video of the course on Persistent Micropollutants - PFAS. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

3.4 Literature

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2. European Commission, Annexes to the Proposal for a Directive of the European Parliament and of the Council amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, Directive 2006/118/EC on the protection of groundwater against pollution and deterioration and Directive 2008/105/EC on environmental quality standards in the field of water policy. {SEC(2022) 540 final} - {SWD(2022) 540 final} - {SWD(2022) 543 final}. COM(2022) 540 final, E. Commission, Editor. 2022: Brussels.

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4 Week 4 | Introduction to PFAS separation

Introduction to this week

Water treatment is one of the processes applied to remove PFAS from the environment. This week we are focusing on separation technologies which allow separating PFAS from water. Ideally, the water should then be completely free from PFAS molecules or PFAS transformation products. In reality, most technologies separate PFAS incompletely even if combinations of technologies are installed. We have to decide to what extend we accept residual PFAS in the water. Should we remove all PFAS or only those mentioned in the regulations? Is it okay to treat only a side stream to reach the regulatory threshold or should we treat the full stream? These are ethical questions that will have to be addressed together with questions of costs, sustainability and other local boundary conditions.

Additionally, we need to remember that PFAS separation is not PFAS destruction. All PFAS separation technologies will produce a waste stream that will need further treatment to truly destroy PFAS and to break that strong C-F bond. PFAS destruction technologies will be covered in Week 5.

In this week we will hear a lecture about the current best practice for PFAS separation. The lecture will cover granular activated carbon (GAC), its advantages and shortcomings, membranes and ion exchange resin. Another lecture will discuss foam fractionation. All of the above are advanced treatment technologies.

Yet, in most parts of the world water is treated using conventional water treatment. For drinking water, a conventional treatment plant targets turbidity removal and disinfection via coagulation-flocculation-sedimentation followed by rapid sand filtration and chlorination. None of these conventional technologies will remove PFAS traces [1].

GAC filtration or powdered activated carbon (PAC) dosage, however, is already used around the world for pesticide, pharmaceutical and taste & odour removal. PFAS can adsorb to the outer and inner surface of GAC or PAC via hydrophobic interactions. But can activated carbon remove all PFAS completely? Unfortunately, not. Membranes separate PFAS via size exclusion but will produce a concentrated waste stream. Ion exchange will remove PFAS via a mixed exchange/adsorption process, but those resins are rarely regenerated and constitute a waste stream once their capacity is exhausted. Are there any other more promising separation technologies out there? And what are the experiences of water treatment specialists from industry? This is what we will find out in this week.

Learning objective of this week:

You should be able to

Compare concentration technologies (such as IX, GAC, membranes and foam fractionation) with regard to their removal performance and process efficiency for PFAS of different chain length and other properties.

Please watch first this knowledge clip:

https://youtu.be/1p4uXnZbr1A

In the fourth knowledge clip of the course on Persistent Micropollutants, Kim Lompe of TUDELFT shows how PFAS can be separated from a water source through adsorption, ion exchange and foam fractionation.
The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.

4.1 Current best practice: granular Activated carbon

Glossary: typical vocabulary used for fixed bed (GAC) adsorbers

Adsorption capacity – the mass of pollutant that can adsorb per mass of adsorbent (e.g. ng PFAS/g GAC)

Adsorption kinetics – The description of how fast the pollutant adsorbs to the material

Bed life – How long the adsorber bed is in operation before reactivation or regeneration is necessary

Empty bed contact time – the time the water needs to pass through an empty filter bed; a typical value used to dimension contactor size

Specific surface area – the available surface area on the adsorbent per unit mass (m^2/g)

Reactivation – the process of freeing up adsorption capacity on a used adsorbent using heat

Regeneration – the process of freeing up adsorption capacity on a used adsorbent using solvents or other chemicals

4.1.1 How PFAS are adsorbed

Activated carbon (AC) is a highly porous technical adsorbent material used to remove organic contaminants from water. AC is produced from dense organic sources such as bituminous coal or lignite or from coconut shells or wood. The high porosity is obtained via the pyrolysis of the raw material and subsequent activation processes such as steam treatment. Depending on the raw material and the specific treatment applied, a network of macro- (> 50 nm), meso (2 – 50 nm) and micropores (< 2 nm) is created that leads to the very high internal surface area of the materials. The available specific surface ranges from 800 m^2/g – 1500 m^2/g, that means 1 kg of the material accommodates more than 100 soccer fields! The most typical AC is granular activated carbon (GAC). The grains are ca. 1 mm in diameter and most commonly they are filled into stainless steel vessels or open-air concrete basins to be operated as fixed-bed filter beds.

Figure 4.1 Activated carbon – a highly porous adsorbent with a large specific inner surface. (Figure by K.M. Lompe)

Dissolved contaminants (the adsorbate) are transported to this huge surface area of activated carbon (the adsorbent) via advection and diffusion in the water. When they reach the carbon surface the contaminants are retained there via physico-chemical forces. This process is called adsorption (not absorption). The adsorption process is reversible (adsorption <-> desorption) which means that contaminants can also detach from the activated carbon process depending on the boundary conditions.

Figure 4.2 showing how the activated carbon (adsorbent) adsorbs the pollutant (adsorbate). (Figure by K.M. Lompe)

4.1.2 How are GAC contactors operated?

The water flows in continuously from the top and exists the filter bed at the bottom after a defined contact time of typically 10 – 30 minutes. During the time in the contactor the pollutants are adsorbed to the activated carbon granules.

GAC contactors were often installed for the removal of other organics such as pharmaceuticals or taste and odour compounds. Their operation parameters were therefore designed for these different pollutants. Typically, this means a(n) (empty bed) contact time (EBCT – see glossary below) of 10 – 30 minutes, a bed height of minimum 1 m and a hydraulic loading rate of 5 – 10 m/h. For pharmaceutical removal in conditions of low concentration of natural background organics, a GAC contactor can operate for more than 40 000 bed volumes (volume of water treated per volume of GAC). When the contaminants start to increase and are near the acceptable (regulated) threshold, the GAC is typically taken out of service. The wet GAC is sent to a thermal treatment plant where the contaminants are removed from the GAC and mineralized during the high temperatures of a reactivation furnace. This treatment is called GAC reactivation. The reactivated material can then be transported back to the treatment plant and be reused.

Water treatment plants which now also monitor PFAS often notice that PFAS breakthrough occurs much earlier than pharmaceutical breakthrough. When operating GAC for PFAS they can treat much less water before the reactivation is necessary. That is because many PFAS have lower affinity for GAC than pharmaceuticals and because they are regulated at very low concentration (ng/L!) compared to e.g. pesticides (0.1 µg/L). Contactors operated for PFAS separation need a higher reactivation frequency. Current research is evaluating which GAC types and properties are most suitable for PFAS removal.

4.1.3 So how well do activated carbons perform for PFAS adsorption?

Granular activated carbon is until now the most common material used for PFAS separation via adsorption. Most treatment plants would use granular materials.

Hydrophobic organics (hydro phobic = water disliking = prefers an organic phase) such as long-chain PFAS, adsorb relatively well on activated carbon. With decreasing C-F chain length the hydrophilicity (hydro philic = water loving = tendency to partition in the water phase) of PFAS compounds increases. Hydrophilic compounds adsorb less or not at all on activated carbons. The head group has also an influence on the PFAS affinity for carbon. When comparing PFAS with equal C-F chain length, PFAS with a carboxyl head group are more difficult to adsorb than those with a sulphonated head group due to their higher hydrophilicity.

Full-scale GAC data showed that GAC contactors removed > 99% of long-chain and short-chain PFAS after 30 days of operation (2660 BV) whereas a contactor with 360 days old GAC (ca. 30 000 BV) removed only 22 % of shorter chain PFCAs (i.e. PFHxA and PFHpA, PFOA) and 72% of longer chain PFAS (i.e. PFHxS, PFHpS and PFOS) [1]. The breakthrough of the shorter PFAS was thus much earlier than for long-chain PFAS. The same researchers also found that linear PFAS (L-PFHxS) were better and longer removed than branched PFAS (B-PFHxS). Also in this study, the fastest decreasing GAC performance was observed for short-chain, carboxylic PFHxA with a complete breakthrough after as early as 20 000 BV [1].

An example for the importance of desorption can be observed during fixed-bed operation:

Large PFAS molecules are adsorbing well on AC. The hydrophobic molecule is retained via hydrophobic interactions with the activated carbon surface. The molecule's affinity for the activated carbon surface is high. Other (PFAS) molecules that have lower affinity can be displaced by molecules of higher affinity. In this specific example (Figure 4.1 a), a poorly adsorbing smaller PFAS molecule can desorb from the AC surface when a larger PFAS with higher affinity for the same activated carbon surface arrives. Water treatment plants that monitor PFAS across their GAC reactors may notice at one point a higher PFBA concentration (short-chain PFAS) in the GAC effluent than in their GAC influent ($C/C0 > 1$) (Figure 4.1b, data from a Dutch treatment plant). They observe the desorption of PFBA that has been displaced by another compound with higher affinity for the GAC surface (Figure 4.1 b). The displacement of short-chain PFAS by better adsorbing long-chain PFAS has also been observed by researchers at lab-scale [2].

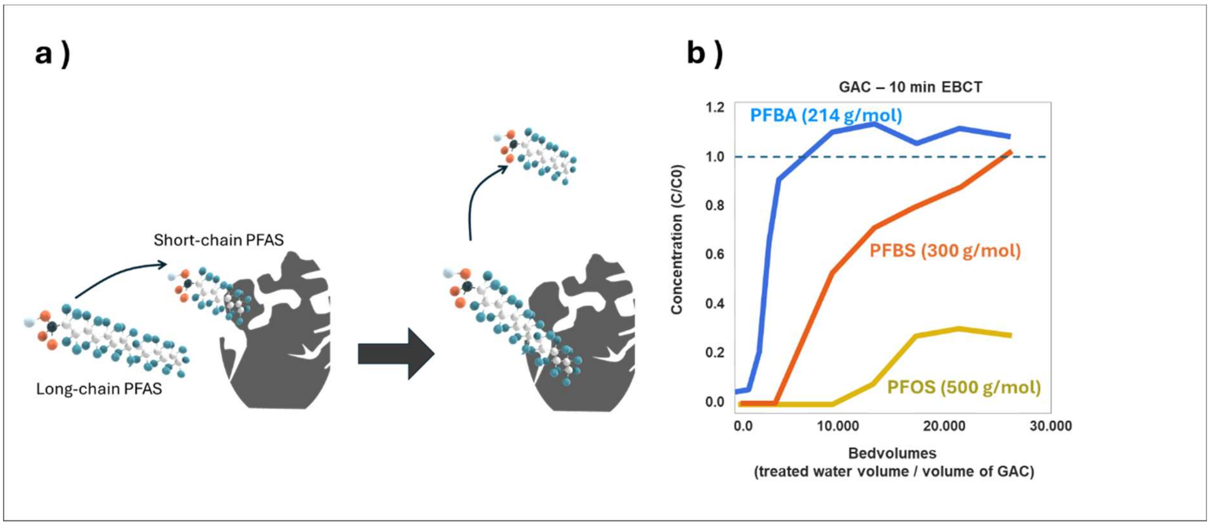

Figure 4.1: a) Desorption of short-chain PFAS with low affinity for the AC surface via displacement by long-chain PFAS with higher affinity for the AC surface. b) The desorption of short-chain PFBA by longer chain PFBS and PFOS can be seen in the breakthrough curve: The PFBA concentration in the effluent of the contactor exceeds the influent concentration of PFBA and thus the effluent concentration is > 1. (Figure by K.M. Lompe)

4.1.4 The influence of the water matrix on PFAS adsorption by GAC

GAC, however, is not a selective adsorbent, indeed most hydrophobic organic molecules will be adsorbed by this material. As water contains naturally many organic molecules such as humic and fulvic acids (decomposition products of plants and aquatic organisms) the amount of PFAS that can adsorb on GAC also depends on the concentration of those other organics.

The knowledge about the non-selectivity of GAC influences strongly where an adsorber unit should be placed in a treatment plant. When it is placed close to the intake of e.g. surface water, its performance will decline faster. The raw surface water contains a lot of natural organic matter (NOM) (indeed the concentration of natural organics is 2 - 10 mg/L) while PFAS is typically present in ng/L (that is 1 000 000 times lower concentrated!). Knowing that most of those naturally present organics will also adsorb on the GAC, the adsorption capacity for PFAS will quickly reduce and PFAS will break through the GAC bed early. Compare an example breakthrough curve of PFAS at the exit of a GAC contactor installed for treating surface water (green curve) and ground water (blue curve in Figure 4.2). You can see that concentration of PFAS rises quicker in the outlet of the contactor treating surface water. The GAC in that contactor has most likely removed a lot more natural organics which reduced the available surface area for PFAS adsorption on activated carbon. To use GAC most efficiently for the removal of the target contaminant it is therefore a good idea to select a location in the treatment train where most background organics have already been removed. This could be after the conventional treatment line, as the processes coagulation-flocculation-sedimentation and rapid sand filtration remove a large percentage of NOM, or after a slow sand filtration step.

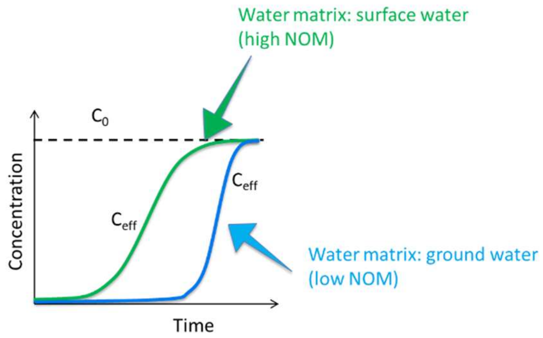

Figure 4.2 Schematic breakthrough curve of PFAS in different source water treated with GAC. PFAS break through the GAC bed earlier when the background organic concentration is high such as in surface water. In water with lower background organic concentration the GAC contactor can be operated longer as more adsorption sites remain available for the target compound PFAS. (Figure by K.M. Lompe)

4.1.5 The influence of GAC type

It is impossible to select a suitable GAC for PFAS separation purely based on GAC properties alone. As for all other organic contaminants, the GAC performance will depend also on the PFAS properties (i.e. the hydrophobicity or chain-length) and the background organics in the water. Some researchers have tested GAC types for PFAS removal and have found that the GAC surface charge plays a more dominant role in PFAS adsorption compared to the pore size distribution [2]. The researchers observed that a more positively charged GAC had a higher adsorption capacity and also later contaminant breakthrough for negatively-charged PFAS. However, they only tested four GAC (a more neutral coconut-based GAC vs a more positively charged bituminous GAC – fresh and reactivated). GACs with a higher microporosity are in principle offering more adsorption sites for small PFAS as those can fit into these smaller pores while larger micropores are allowing the adsorption of longer chain PFAS. However, the interplay between GAC charge, pore size distribution, background organics and PFAS types will ultimately determine which GAC fits which treatment goal best. Ideally, GAC is selected based on pilot tests or smaller scale column tests such as rapid small scale column tests (RSSCTs) using the original water matrix. Batch capacity and kinetic tests can also give a first impression of GAC performance when different GACs are compared. Predicting full-scale breakthrough of PFAS, however, is challenging using only batch tests as the adsorption processes are not exactly translatable between reactor types and process scales.

4.1.6 The influence of GAC operating conditions on PFAS removal

GAC granules are typically filled into vessels and operated as gravity or pressurized filter beds. PFAS removal performance is often 100 % for the majority of PFAS at the beginning of a GAC operation cycle. With increasing operation time that performance decreases depending on the PFAS type as discussed above. As for other contaminants, GAC type and water matrix are not the only factors influencing GAC performance. Also, the flow rate and thus the contact time (EBCT) of the water influence performance.

Observations at full-scale GAC contactors suggest that lowering the flow rate across the GAC bed can help delaying breakthrough [1]. The lower flow rate increases the residence time of the water in the contactor (EBCT) and allows PFAS to have more time to diffuse deeper into the GAC pore space. This observation is not new and has been confirmed previously for other organic contaminants. A strategy for GAC targeting PFAS could be to lower the flow rate on contactors successively towards the end of their operational cycle to extend their service time before reactivation.

A Swedish study concluded that GAC service life could be prolonged by almost half if the flow rate was decreased by half as well under the local operation conditions and close to the end of the service life of a GAC contactor [1].

Depending on the water flow many contactors will be operated in parallel. Often it is a good idea to operate contactors also in series as a first and second adsorption stage. When the first stage GAC contactor shows PFAS breakthrough it can be sent for reactivation and the second stage contactor moves into its place now being the first stage adsorber. The reactivated material will then be the second stage adsorber. Such GAC operation is quite common for the removal of other organic pollutants. Some researchers suggest to operate a mesoporous carbon as first step adsorber to remove long-chain PFAS first followed by a microporous GAC as a polishing step to remove short-chain PFAS [2].

4.1.7 How does GAC reactivation influence PFAS adsorption?

Reactivation of GAC via hot steam or other heat treatments is believed to destroy or at least desorb PFAS from the GAC. Reactivation is typically carried out in a centralized facility using temperatures between 800°C and 1000°C.

Ideally, PFAS are completely mineralized during this process. In a study at a full-scale GAC reactivation facility with furnace temperatures varying between 400°C to 950°C the full PFAS desorption and mineralization was shown by measuring hydrogen fluoride in the furnace off-gas [3]. Yet, other research shows that reactivated GAC has an up to 3.5 times higher fluorine content compared to fresh (non-reactivated) GAC indicating that PFAS did not completely desorb but rather accumulated on GAC [2]. Ultimately, not only furnace temperature but also reactivation time and the presence of other contaminants on the carbon surface will determine the degree of mineralization of PFAS and the degree of PFAS desorption from the GAC surface [3].

Reactivation also changes the pore size distribution from a microporous to a more mesoporous structure. And reactivation can also change the surface charge of GAC introducing more carboxyl groups that make GAC more hydrophilic and less adsorbing for PFAS. These changes and the incomplete desorption of PFAS can in return reduce the PFAS adsorption performance of reactivated GAC. Researchers have shown that the loss of microporosity due to reactivation reduces the removal performance for short-chain PFAS [2]. The change in porosity can also have a positive impact on longer-chain PFAS as the influence of background organics is reduced. Depending on the dominant PFAS types in the water (small or long-chain) it could be advisable to replace GAC with fresh GAC instead of reusing reactivated GAC – depending also on an economic analysis [2]. The question is, do we want to treat GAC as a single-use material? And what will we do with the contaminated material? PFAS separation via AC may be the current best practice, but we clearly see a need for better solutions.

4.2 Ion exchange (IX) for PFAS separation

4.2.1 How are PFAS removed via IX?

Ion exchange resins are porous polymeric beads with functionalized surface to attract and weakly bind ions or charged dissolved compounds from water. There are two categories: cationic and anionic. Anionic IX are categorized based on their properties such as their functional group (quaternary ammonium or tertiary ammonium), polymeric matrix (acrylic or styrenic), and the extent of cross-linking within the bead (gel-base or microporous) [4]. Anionic resins have negatively charged loosely bound anions on their surface that can exchange with anions in the solution (Figure 4.3). As PFAS have a negatively charged head group, the IX types used are weak-base anion exchange resins (WB-IX) and strong-base anion exchange resins (SB-IX). The retention of the compounds is due to electrostatic and non-electrostatic interactions. While electrostatic interactions are occurring between the positively charged surface groups on the resin and the negatively charged head group of the PFAS molecule, non-electrostatic interactions are van der Waals and hydrophobic interactions [5]. The separation of PFAS compounds is thus a combination of different types of interactions that will depend on the PFAS type, water matrix, and ion exchange resin type. Non-electrostatic, adsorption types of interactions seem to play a more important role in PFAS attachment onto IX compared to other organic compounds such as NOM. This might be due to the hydrophobic chain length of longer PFAS and is also reflected in the sometimes absent release of stochiometric equivalent chloride concentrations [5].

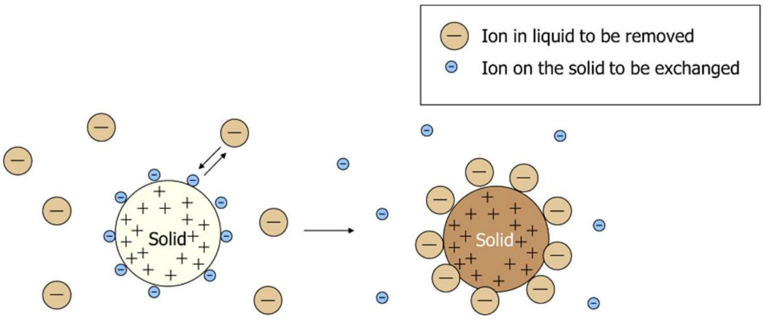

Figure 4.3: Depiction of an ion exchange mechanism, where an anion from the solution exchanges with a loosely bound anion on the resin surface. This is not the only mechanism that plays a role in PFAS separation on IX -PFAS also adsorb to the bead via hydrophobic interactions (not depicted). (graphic TU Delft)

4.2.2 Impact of PFAS structure and resin type

The separation performance of an anion resin will depend on both the PFAS structure and the resin type. We will not go into very much detail on this, but from the recent literature, we now know that the aqueous diffusivity of the PFAS molecule in water [4, 5] as well as the molar volume and molecule length [5] influence the separation kinetics. Diffusion of PFAS into the porous resin beads can be hindered when the PFAS molecules are bigger, and thus shorter PFAS show faster separation kinetics.

Strong-base anion exchange resins (SB-IX) are strongly alkaline, work over a wide pH range, and have hydroxide (OH-) as the exchangeable anion. Weak-base anion exchange resins have a pH-dependent charging behaviour, are not active above pH 7, and have mostly chlorite (Cl^-) as their exchangeable ion. Most studies have been carried out using SB-IX. While the exact performance of a resin depends on its structure and porosity, resin capacity typically decreases with a decreasing PFAS chain length. Overall, it seems that the PFAS capacity of resins is often higher (up to 6000 µmol/g) than the PFAS capacity of activated carbon (up to 1000 µmol/g) [4]. A more complete picture of the impact of PFAS structure and resin type can be found elsewhere [5].

4.2.3 Interference with other ions and NOM

IX resins are not very selective materials, and thus other inorganic anions such as sulphate, phosphate, and nitrates also exchange with the counterions on the resin bead. An important competing anion is typically sulphate; however, when it comes to PFAS separation, inorganic ions are not very important. Studies have shown that even at higher inorganic ion concentrations, the PFAS separation only decreased by a small percentage [5]. The reason for this behaviour is that PFAS are not solely separated via an exchange mechanism, but also by sorption, which is not influenced by other inorganic ions. It is likely that inorganic anions reduce the separation of short-chain PFAS to a higher degree, as they are more negatively charged, and thus separate via an exchange mechanism rather than by adsorption.

Natural organic matter (NOM) is separated via a mix of ion exchange mechanisms and hydrophobic interactions, just like PFAS. The presence of NOM therefore reduces the uptake of PFAS by resins. Some studies have shown that PFAS removal drops by nearly 50 % in the presence of 5 mg/L of NOM [4]. Especially NOM of high molecular weight, high aromaticity, and high charge density competes with PFAS for sites on the resin.

4.2.4 IX resins: single-use or regeneration?

Anion IX resins are typically used during drinking water treatment to remove NOM from water. NOM is negatively charged and is removed via an ion-exchange mechanism. To regenerate a resin that has adsorbed NOM, the IX bed is typically flushed with a brine, which is a highly concentrated NaCl solution. Typically, anion IX fixed bed reactors are flushed with a brine which results in a successful replacement of previously attached NOM with chlorite (Cl-) ions. The NOM is then concentrated in the brine, and the resin bead is replenished with chlorite ions and ready for its next operational cycle. The reason why chlorite ions are used on WB-IX is due to their higher affinity for the surface groups on the resin bead compared to e.g. NOM.

Most resins offered for PFAS separation are SB-IX. In principle, SB-IX can be regenerated with a strong base, such as NaOH. Commercially available PFAS-specific resins are typically anionic IX that have a polystyrenic matrix, which is crosslinked with divinyl-benzene and has a complex amino functional group [4]. As PFAS are not separated purely by ion-exchange mechanisms on these resins, but also by adsorption and thus hydrophobic interactions, the regeneration of the anion exchange resin is not very successful. Commercially available IX for PFAS removal is therefore a single-use product that cannot be regenerated. Instead, the used resins are disposed of via incineration. Research has shown that resins can be incinerated at around 650 to 800°C without solid residue [5]. One could say that this is an advantage, as no liquid waste stream has to be handled, but IX is typically more expensive than GAC. As IX cannot be regenerated, the costs are thus overall higher, and one needs to consider that the environmental footprint of IX is higher than that of GAC [4].

4.2.5 Research & Development

Research efforts are focusing on the regeneration of PFAS IX resins and particularly on the required regenerant solutions. Tested combinations include solutions containing salts, bases, organic solvents, and their mixtures. While WB-IX for NOM removal can successfully be regenerated using salt solutions, it seems that the addition of an organic solvent such as methanol is always necessary to regenerate PFAS laden SB-IX [5]. It also appears that the desorption of PFAS from the resin depends on the desorption of NOM [6]. Another research need directly linked to regeneration is regenerant management and treatment. As regeneration results in a liquid waste stream contaminated with PFAS, a solution to further concentrate such waste streams is needed. More fundamental research is being carried out to investigate PFAS separation on a molecular level, modelling adsorption kinetics, and competitive adsorption using mechanistic models to predict separation in different IX-PFAS reactor systems [7].

4.3 Foam fractionation

4.3.1 How does foam fractionation separate PFAS from a matrix?

Foam fractionation is a separation technology that exploits the surface-active properties of many non-polymeric PFAS, particularly PFAA and their precursors [8]. When air bubbles are introduced to water, a large air/water interfacial area is created, to which these surface-active PFAS adsorb. The adsorbed PFAS rise with the bubbles through the water, and accumulate in a foam layer on top of the water. Depending on the water matrix, it may be necessary to dose additional surfactants, to create a sufficiently stable and high foam layer [9]. Separation of this foam results in separation of the PFAS from the water, thereby creating a relatively PFAS-free effluent.

Foam fractionation is already applied in full scale for PFAS removal from a variety of water matrices [10, 11]. It can be applied in batch as well as continuous mode, and important process variables are the retention time of the water, the air flow rate and the height of the foam layer [9]. It can be operated in multiple stages to further reduce the volume of PFAS-rich foam, with two to three stages being employed in most commercial systems [10, 11]. The main benefit of foam fractionation is its relative simplicity compared to other PFAS separation technologies: no chemicals are required except air, its performance does not diminish in heavy-matrix water, and it has a relatively low energy demand [8]. These benefits make the technology highly suitable for the treatment of heavily contaminated matrices, such as landfill leachate, industrial effluents or AFFF-contaminated groundwaters.

On the other hand, foam fractionation is not yet capable of achieving similarly low effluent concentrations as GAC, IEX or membrane processes. Additionally, installation of appropriate air filters is necessary to prevent PFAS emissions via the air exiting the reactor [12]. Moreover, foam fractionation can only remove longer chain PFAS, with removal efficiencies dropping rapidly with chain length [13]. Short-chain PFAS adsorb less strongly to air-water interfaces, so for example PFBA is usually not removed at all in conventional foam fractionation. However, recent papers show promising results when cationic surfactants are used as additives, facilitating near-complete PFBA removal in artificial solutions [9, 14, 15]. Commercial suppliers of foam fractionation systems are starting to include these additives in their systems.

Please watch this extra knowledge clip on foam fractionation:
https://youtu.be/3T1943n5Y2A
In this extra knowledge clip in the course on Persistent Micropollutants - PFAS, Sanne Smith of TUDELFT gives more insight in foam fractionation for PFAS separation. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

4.3.2 Removal and enrichment – why both matter

Removal and enrichment are two key concepts in foam fractionation. Removal is simply the removal of PFAS from influent to effluent, which can reach very high values for long-chain PFAS (>99 %). This is what plant operators look at most, because it determines the quality of the effluent and thereby the possibility for discharge or reuse of the water. Usually, the removal efficiency is calculated using concentrations (RE_C), as per *Equation 1*, with C_{Ef} the PFAS concentration in the effluent and C_{In} the PFAS concentration in the influent. Removal efficiencies can also be calculated based on total PFAS loads (RE_L), as shown in *Equation 2*, with Q_{Ef} and Q_{In} the effluent and influent flow rates (continuous operation) or volumes (batch operation), respectively.

Equation 1

$$RE_C = \left(1 - \frac{C_{Ef}}{C_{In}}\right) \cdot 100\%$$

Equation 2

$$RE_L = \left(1 - \frac{Q_{Ef}\,C_{Ef}}{Q_{In}C_{In}}\right) \cdot 100\%$$

The second key concept in foam fractionation is enrichment, which is the PFAS concentration in the foam relative to the effluent. The enrichment factor (EF) is usually calculated as per *Equation 3*, with C_F the PFAS concentration in the foam. The enrichment relates to the volume reduction that is achieved with foam fractionation, i.e. the volume of foamate that is generated from a certain volume of influent. Obviously, the volume of foamate should be minimized, since the destructive technologies required to dispose of the foamate are very energy-intensive. The volume reduction factor can be calculated using *Equation 4*, with Q_F the foam flow rate (continuous) or volume (batch), and is sometimes also expressed as a foam fraction ($\%_F$, *Equation 5*).

Equation 3

$$EF = \frac{C_F}{C_{In}}$$

Equation 4

$$VRF = \frac{Q_{In}}{Q_F}$$

Equation 5

$$\%_F = \frac{Q_F}{Q_{In}} \cdot 100\% = \frac{1}{VRF} \cdot 100\%$$

At low foam fractions (or, equivalently, high volume reduction factors), the effluent flow/volume will be roughly equal to the influent flow/volume, so the load-based and concentration-based removal efficiencies will be similar. As long as no transformation of PFAS occurs, simple mass balance calculations can be carried out to calculate PFAS concentrations in the foam, from flow rates/volumes and concentrations in the influent and effluent. For concentration-based removal efficiencies close to 100 %, the EF and the VRF will then be approximately equal. In practice, some reactive transformation of PFAA-precursors to PFAA often occurs in foam fractionation, due to oxidation by the oxygen that is introduced with the high aeration rates. This will lead to formation of particularly short-chain PFAA, and can lead to a mass balance closure > 100 %. Therefore, it is recommended to always measure foam concentrations directly, rather than estimating them from influent and effluent concentrations.

Foam fractionation can achieve very high volume reduction factors (VRF) of up to 500 already in the first stage [12, 14] (equivalently: foam fraction > 0.2 %), compared to 5-10 for most membrane processes, which can be increased even further in second and third stages. A high VRF is beneficial because it results in a lower volume of PFAS-rich wastewater that needs energy-intensive destructive treatment, as explained above. On the other hand, it is easier to achieve higher removal at lower VRFs, which is why multi-stage treatment is often employed in full-scale systems. Here, the first stage is designed for optimal removal at a low VRF, and the VRF is further increased in second- and third-stage treatment.

4.3.3 Bubble size and surfactants

In the bulk liquid phase, a small bubble size is beneficial, to generate a high cumulative air/water interfacial area for PFAS adsorption. Additionally, small bubbles rise more slowly through the bulk liquid, allowing more time for adsorption to occur. However, small bubbles lead to the generation of a relatively wet foam, thereby decreasing the volume reduction factor, and require more energy to generate [16]. An optimal bubble size for the foam fractionation process thus exists, which depends on PFAS concentrations and type, bulk liquid characteristics (surface tension), and the reactor dimensions. Since bubble production is typically the most energy-consuming aspect of foam fractionation, proper design of the bubble generation process can lead to energy savings, as well as optimized enrichment and removal.

As mentioned above, dosing cationic co-surfactants can increase the removal of particularly short-chain PFAS. The reason for this is that short-chain PFAS are typically negatively charged. Electrostatic interactions between the anionic headgroup of the short-chain PFAS and the cationic headgroup of the surfactant facilitate the short-chain removal, i.e. bound PFAS-surfactant complexes adsorb to the air-water interface. Cetrimonium bromide (CTAB) is often used as cosurfactant, and has been shown to improve the removal of PFBA and PFBS with foam fractionation [14]. However, CTAB has a high ecotoxicity, and other additives that improve PFAS removal may also be more acutely toxic than PFAS. Therefore, it is important to ask suppliers of foam fractionation for the exact chemicals that are dosed, as well as toxicity data of the additives.

4.3.4 Reactor design

While foam fractionation is an easy-to-understand technology, adequate design of reactors remains necessary to optimally remove and enrich PFAS. Reactor diameters are typically chosen to ensure a volume that leads to a minimum hydraulic retention time for adsorptive equilibrium. For most long-chain PFAS, this time is approximately 20 min. Diameters are typically not much higher than 1 m, to facilitate rising and removal of the foam, and multiple reactors in parallel may be used when large volumes need treatment [16]. Bubbly liquid depths are then chosen to also ensure this minimum retention time for the gas bubbles, to optimally use the generated interfacial area. The bubbly liquid depth is thus a function of the bubble size distribution, since bubble size determines the speed with which a bubble rises through the water.

The optimal foam layer height depends on the bubble size distribution, operational mode and water matrix, and should be determined based on bench-scale tests. Bench scale tests with column diameters of a few centimeters can determine the optimal gas residence time in the foam, which should then be used as scaling-up parameter. Here, removal and enrichment need to be balanced, as explained in section 4.3.2. The total reactor height is then the sum of the bubbly liquid depth and the foam layer height. Foam removal can be done by simple overflow, but more advanced designs may improve the enrichment that can be achieved per stage.

4.4 Voices from the field

Now you have heard and read about PFAS separation technologies. The texts and lecture was rather theoretical and you might now wonder how PFAS separation is dealt with in industry at this moment. We have interviewed Dr. Ulf Miehe from the German Kompetenzzentrum Wasser Berlin and innovation manager of the EU Promisces project. We asked him about his perspective on PFAS separation. We wanted to know what the most promising technologies are and what stands in the way of innovative technologies and their large-scale application. Then, we visited Dr. Miquel Paraira Faus, water quality director and Laboratory Manager at Aigues de Barcelona in Spain. Together with him we visited Barcelona’s largest drinking water treatment plant to learn more about Barcelona’s approach to PFAS in drinking water sources. How are they removing PFAS? You will see the current use of a combination of ozone+GAC and membrane filtration; the treatment plant will soon switch to full membrane filtration. What is done with their concentrate?

Please watch this voices from the field interview:
https://youtu.be/sn4rVFy26kY
Ulf Miehe of KWB is interviewed about innovations in the field of PFAS treatment, as part of the course on Persistent Chemicals. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

Please watch this video with a tour of the Barcelona drinking water plant:
https://youtu.be/ASVGQT5MNFM
Miquel Paraira Faus, head of the laboratory and research director at Aigües de Barcelona, shows us around the Sant Joan Despí drinking water treatment plant in Barcelona. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

4.5 Additional Materials

In this section we are providing some additional material for those of you who would like to hear a bit more about innovative adsorbents and foam fractionation for the treatment of PFAS rich concentrates. As you have heard, separation technologies also create a waste stream. Membranes produce not only clean water but also a concentrate that contains besides the higher concentrations of pollutants also mostly water. Ion exchange resins that separate NOM and PFAS produce clean water but when regenerated (in the case of NOM-removing resins) they also produce a waste stream that contains PFAS, NOM and high salt concentrations.

To destroy PFAS in those waste streams water needs to be first evaporated – an energy-intensive process. Therefore, reducing the water content of a waste stream further is a good idea. Our speaker Josephine van Ruiten will show you data and conclusions from her MSc research project. Josephine compared next-generation adsorbents B-Cyclodextrin and high-silica zeolites to foam fractionation to reduce two waste streams: membrane concentrate and ion exchange brine.

Please watch this extra knowledge clip on PFAS-rich waste of drinking water treatment:

https://youtu.be/JeH4ZUFQQLY

In this extra knowledge clip in the course on Persistent Chemicals, Josephine van Ruiten of TUDELFT shows how waste from PFAS separation in drinking water production can be treated. *The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

4.6 Literature

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5 Week 5 | PFAS destruction

Introduction to this week

We have now reached the final content week of the course. So far, we have learned what PFAS are, what their molecular structure is; what their division is in the environment, how they can be analysed, and how we can apply technologies to separate a cleaner from a more polluted stream.

This more polluted stream requires more attention. In this chapter we will discuss how the final destruction can take place: what is necessary to break the C-F bonds, what is the fate of the uncoupled F atoms, what happens if the destruction is not complete, and which technologies are currently available to achieve this level of destruction?

Learning objective of this week

After completing this week, you should be able to

Describe the principle of destruction technologies; list 4 technologies; and question a technology on its practical applicability and efficiency.

First, we watch the lecture of Eric van Hullebusch, professor in Biogeochemistry of Engineered Ecosystems in Paris. He introduces the fundamentals of PFAS degradation.

Please watch first this knowledge clip:
https://youtu.be/ptNfjSmyqWM
Eric van Hullebusch, professor at IPGP in Paris, presents the final knowledge clip in the course on Persistent Chemicals - PFAS. He introduces the main principles of destruction of PFAS and products of PFAS separation techniques. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

5.1 Degradation pathways

In environmental engineering, degradation processes are typically divided into physical, chemical and biological processes. Biological routes do exist for persistent chemicals, but their degradation rate is typically very low. In chemical routes, we need to look for a strong reagent that is capable of breaking the energy between the C and F bond. Examples include advanced oxidation processes and reduction processes. Physical treatment also focuses on gathering sufficient energy to break the bond. Well-known examples are incineration or combustion, and pyrolysis.

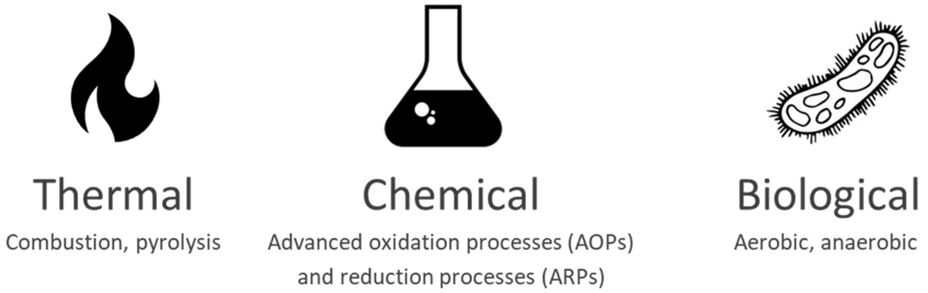

Figure 5.1 Classification of PFAS destruction technologies. The indicated technologies are examples, there are many more.

Another division we can make is between technologies that have been applied for quite some time already, the so-called established technologies, and technologies that are still under development or further spreading – the emerging technologies. For PFAS, this distinction is not so easy to make as technologies also cross over from other matrices: a technology may have been applied to drinking water for a longer time; if it is then applied to air or wastewater, is it an emerging or an established technology? In general, we consider a technology to be established when there is vast experience with it, and we find applications of it in several locations.

For separation, technologies have been finding their way into real-world applications already for many years. For destruction, the development is somewhat less advanced. Still, the activated carbon loaded with PFAS from week 4 still needs a final treatment step, as does the concentrated stream from foam fractionation, for example.

Typically, incineration is considered the most efficient technology for more concentrated waste streams. However, there are also drawbacks to incinerating PFAS components.

In this chapter we will discuss different applied technologies, with their advantages and disadvantages. Please note that not every technology can be applied in every region, depending on the local legislation.

5.2 Incineration

Incineration is a waste treatment process that involves the combustion of organic substances contained in waste materials. Combustion is the chemical reaction that occurs under high temperatures in the presence of oxygen. In this way the waste material reduces in volume and mass. The process produces ash (solid residue), flue gas (gaseous emissions), and heat, which can be used to generate energy such as electricity or steam. Incineration significantly reduces the volume of waste, making it easier to manage and dispose of. Typical types of waste that are incinerated are municipal solid waste, industrial waste, and dewatered sewage sludge.

The incineration of PFAS involves several specific requirements and considerations to ensure effective destruction and minimize environmental impact. First, PFAS require high temperatures for effective destruction, typically above 1,000°C. This is necessary to break the strong carbon-fluorine bonds. Then, the waste must be exposed to these high temperatures for a sufficient period of time, known as the residence time, to achieve sufficient or complete thermal degradation of PFAS – see below. To prevent air pollution, facilities must be equipped with advanced air control systems to capture harmful emissions, including PFAS by-products. Continuous monitoring and testing of emissions and residues are essential to ensure effective and complete destruction of PFAS. Adequate infrastructure and capacity are required to meet the specific needs of PFAS incineration, including specialized equipment and trained personnel. And finally, facilities must comply with local, national, and international regulations for hazardous waste incineration. This includes obtaining the necessary permits and complying with environmental protection agency guidelines.

In its 2019 Technical Brief “Per– and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams”, the EPA explains that incineration is still mostly incomplete. In general, at the same temperatures, long-chain PFAS get degraded and defluorinated less than short-chain PFAS. Precise details are not yet known, which makes ensuring complete degradation of PFAS through incineration a major challenge. Conditions need to be met regarding temperature, residence time, oxygen and mixing conditions to avoid incomplete destruction and the formation of smaller PFAS. These are referred to as products of incomplete combustion (PICs) – other terms are also used. These PICs end up in the off-gas and then in the wastewater stream from the gas stream scrubber, or they remain in the ash – both routes pose a risk for downstream processing.

5.3 Pyrolysis and gasification

Combustion requires the presence of oxygen; pyrolysis and gasification are thermal decomposition processes operated in the absence of oxygen. The advantage of the absence of oxygen is that it prevents the formation of potentially hazardous oxidation by-products.

Pyrolysis submits carbonaceous materials to elevated temperatures (200–1100°C) and produces a carbon-rich, porous product called biochar. Gasification introduces a limited amount of oxidant (typically air) at high temperatures (800-1650°C), through which the volatile organic fraction is partially oxidised and the solid mass is converted into ash particles.

The basic pathway for thermal destruction of PFAS in a reductive environment (without oxygen) is hydrodefluorination (HDF). HDF is the conversion of a carbon-fluorine (C–F) bond to a carbon-hydrogen (C–H) bond and can be performed using a variety of reagents (and catalysts). The process requires an H source for the C–H bond. Hydrogen can be produced during pyrolysis through a steam reforming reaction or by direct introduction of hydrogen gas into the thermal reactor. Central to the potential for PFAS decomposition in pyrolysis and gasification systems is the ability to keep PFAS in the hot zone of the reactor before volatilization and discharge.

Organic materials introduced into a pyrolysis reactor undergo various stages of thermal decomposition due to changes in feedstock characteristics and moisture content. During pyrolysis, PFAS may already volatilize at temperatures below 450°C, while the organic feedstocks can reach internal temperatures of up to 600°C. This means that PFAS may escape with the air stream before there is sufficient H available for the hydrodefluorination process. Another challenge is that the free H atoms, or radicals, also tend to quickly recombine with the F atoms, due to their high electronegativity – exactly why PFAS are such effective fire suppressants.

Most PFAS require a higher temperature to achieve a high conversion rate. In addition, incineration is never complete, so there will always be parts of the feedstock that are not completely incinerated. The remaining PFAS will end up in the ash or to the flue gas, which requires additional treatment.

Yet, also here a lack of sufficient experimental data limits the full-scale application of PFAS removal through pyrolysis and gasification.

Table 5.1 Comparison of incineration and pyrolysis in their application for breaking down PFAS containing wastes

ASPECT	INCINERATION	PYROLYSIS
PROCESS	Combusting materials at high temperature in the presence of oxygen	Heating materials in an oxygen-free environment
TEMPERATURE	Typically, above 1000°C	Moderately elevated temperatures (500-800°C)
BYPRODUCTS	Potentially: hydrogen fluoride and other toxic gases	Biochar and syngas
ADVANTAGES	- Proven technology with established infrastructure	- Reduces PFAS levels without destroying beneficial use of biosolids
	- Effective at breaking down PFAS into less harmful substances	- Generates useful byproducts like biochar
CHALLENGES	- High start-up energy	- Requires further development and testing
	- Potential release of toxic byproducts requiring advanced pollution controls	- Limited installations and higher initial costs

5.4 Thermal regeneration of PFAS-loaded activated carbon

In week 4 we discussed the route of letting PFAS adsorb onto activated carbon. Granular activated carbon (GAC) can generally be regenerated, meaning that the contaminant can be burned off so that the activated carbon can be used again as an adsorbent. The most common method of GAC reactivation is heating to 650-850 °C in the presence of inert gases or steam [3]. High-temperature treatment is also applied, where the spent GAC is heated in industrial furnaces to temperatures above 900°C. This high heat breaks down the adsorbed PFAS molecules. The resulting gases are treated through a series of abatement technologies to ensure safe emissions. Powdered activated carbon (PAC) cannot be reactivated and is typically incinerated. Incomplete thermal mineralization may contribute to a lower reactivation yield – pores can become blocked and adsorption sites may remain inaccessible. Regeneration yields in terms of GAC mass or surface area, rather than adsorption capacity, are also often less than 100%, but the use of reactivation agents such as air or CO_2 can increase the regenerated surface area. In practice, reactivated GAC always needs to be supplemented with a dose of fresh GAC to compensate for a loss of mass and thus capacity during the activation process.

5.5 Supercritical water oxidation

Supercritical Water Oxidation (SCWO) is a process that uses water at supercritical conditions to destroy hazardous substances including PFAS.

The process is more exotic than what we are used to in the general urban water cycle: in order to achieve the right conditions, first, water is heated above its critical temperature (374°C) and critical pressure (22.1 MPa). As such, a supercritical state is created. In this state, water behaves like both a gas and a liquid and organic compounds and gases all get dissolved. PFASs also become highly soluble. Then, an oxidizing agent such as oxygen or hydrogen peroxide is introduced. The supercritical water facilitates rapid and complete oxidation of the organic compounds, aiming to break down the strong carbon-fluorine bonds in PFAS [6]. The high temperature and pressure conditions accelerate the chemical reactions, leading to the complete destruction of the hazardous substances.

SCWO creates minimal unwanted by-products, such as short-chain PFAS and precursors to PFAS. Yet, breaking the carbon-fluorine bond creates hydrofluoric acid, which has to be neutralized with a base like sodium hydroxide. Additionally, the operational costs and technical complexity are considerations that need to be managed.

5.6 Plasma treatment

Plasma treatment is an interesting approach making use of the interaction at the liquid-gas interphase, between gas atoms and molecules in water. By energizing the gas atoms, reactions can be initiated in the water phase, with sufficient energy to cause a break in the C-F bonds.

By applying an electrical charge to gas, the molecules ionise. In the vicinity of a water surface, these ionised molecules interact with the molecules in the liquid water phase. Other processes that occur are temperature increase of the electrons, the generation of shock waves, and UV light emission [3]. The temperature of the electrons will be much higher than that of the surrounding gas molecules. This leads to many collisions, which in turn generates radicals, ions and photons. For optimal treatment, PFAS molecules present in the water need to be brought to the water surface – this can be done through bubbling, for which different types of gases can be chosen. As bubbling brings hydrophobic elements to the surface better, plasma treatment tends to be less sensitive to the presence of organic and inorganic co-contaminants. With a mixture of different PFAS pollutants, it is useful to put the reactors in series, where the destruction of high concentrations can be done in the first reactor and the lower concentrated residue in the second reactor.

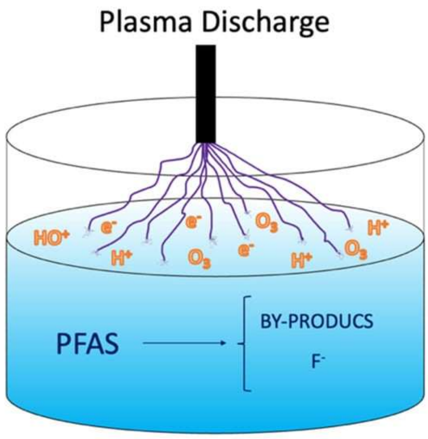

Figure 5.2 basic application of plasma treatment for PFAS [1].

The mechanism behind PFAS treatment with cold plasma is not yet fully understood, this makes full scale application still a challenge. Another drawback is that chlorite and chlorate may be formed, which can be harmful. Still, many research and applications approaches are being studied, and this technology seems rather promising in the near future.

5.7 Electrochemical oxidation

Electrochemical oxidation effectively treats PFAS in synthetically prepared solutions and actual contaminated groundwater and wastewater with high destruction rates [4]. Among its advantages are that it works under low temperatures without adding harsh chemicals; the oxidation of PFAS is powerful; it does not require a large volume and has a relatively low environmental impact compared to other destruction technologies. Yet, scaling up still remains a challenge, where its high energy consumption is the offers a substantial drawback. The cost of electrodes is significant.

Because of the effectiveness of the technique, there is quite some interest in and attention for overcoming the current drawbacks in electrochemical oxidation. How to make it more cost-effective? A nice overview and innovation example is given in the presentation by Silvy Rijsdijk of TU Delft.

Please watch this extra knowledge clip:
https://youtu.be/BGdH-Irlf7Y
Silvy Rijsdijk of TUDelft highlights electricochemical advanced oxidation as a technique to destroy PFAS in this extra knowledge clip of the course on Persistent Chemicals. *This video is part of the course on Persistent Micropollutants - PFAS. The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.*

5.8 Other technologies for PFAS destruction

A recent overview of EPA mentions more than 70 destruction methods currently being tested [5]. Many still have a low technology readiness level, and not all of them will achieve full scale applications. Questions to ask when offered a new technology, next to asking about the capital and operational costs, could be:

- What is the fate of all PFAS in your technology? Does it break down all PFAS or does it mainly break it into smaller pieces? How was this identified?
- Does it need an off-gas or leachate treatment step?
- What is the energy requirement?
- What is the technology's CO_2 and physical footprint?
- Which chemicals are required?
- What is the PFAS reduction rate?

An example emerging technique is sonochemical treatment, which uses high-frequency ultrasound to break down the persistent chemicals in water [8]. The high-frequency sound waves create microscopic bubbles in the water. When these bubbles collapse, they generate intense local temperatures and pressures. The extreme conditions produced by the collapsing bubbles lead to the formation of reactive radicals. These radicals can break the strong carbon-fluorine bonds in PFAS molecules, leading to their degradation. The efficiency of sonochemical degradation can vary based on the specific PFAS compound, its concentration, and the conditions of the treatment.

In the two videos below, two different approaches for destruction are introduced that have been tested out in case studies within the PROMISCES project. The main researchers speak about their role and the aim of their technological approaches.

Please watch this Voices from the Field video:

https://youtu.be/CAGH1tqyZZ0

Carme Bosch, Head of Soil & Groundwater Research at Eurecat, talks about the PFAS oxidation experiments carried out in industrial effluent in this Voices from Field video of the course on Persistent Micropollutants - PFAS.
The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.

Please watch this Voices from the Field video:

https://youtu.be/mPwTrVuMQ0E

Massimiliano Sgroi of UNIVPM is interviewed on how PFAS in landfill leachate can be treated by separation followed by co-pyrolysis of the concentrated streams, in this Voices from the Field of the course on Persistent Chemicals - PFAS.
The material was developed in a coproduction between the EU project PROMISCES.eu and the Water Management Department of TU Delft.

5.9 Biological degradation

Biological degradation of per- and polyfluoroalkyl substances involves the breakdown of these persistent chemicals by microorganisms such as bacteria and fungi. Biological degradation has been detected and reported, both in situ in polluted soil and groundwater and in the lab. In the lab, experiments have been carried out with single strains of bacteria – typically isolated from PFAS polluted locations – and with mixtures of bacteria, also known as consortia.

Biological treatment of environmental pollution typically has the advantage of being less expensive than physical-chemical methods (in comparison: thermal treatment requires a significant investment such as an incinerator, and demands a serious energy input), producing less waste (in comparison: activated carbon or membrane treatment produces a cleaner water stream but also a more polluted waste stream), and for being adaptive: microorganisms have been reported to being able to tackle very persistent chemicals given sufficient time to adapt. Finally, biological treatment can more easily be applied on the location - in situ - and can therefore be considered as less disruptive [2].

However, previous literature on PFAS removal through microbial degradation showed contradicting results, and the biodegradation process is not yet well understood. Enzymes produced by these microorganisms play a crucial role in the degradation process. In general, polyfluorinated compounds containing fluorine substitutions along the carbon chain are more reactive: the C-H next to the C-F bonds create an imbalance for the electrons, making the molecule more susceptible for reaction. In polyfluorinated substances, chemicals such as a radicals and biological agents such as enzymes have an 'easier' entrance for initiating breakdown. The efficiency of PFAS biodegradation depends on various factors, including the type of microorganism, the specific PFAS compound, and environmental conditions such as temperature, pH, and the presence of other nutrients. Complete mineralization of PFAS (breaking them down into harmless substances like carbon dioxide and water) is challenging due to the stability of the carbon-fluorine bonds. Often, biodegradation results in the formation of intermediate products that may still be persistent.

5.10 Literature

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6 Content Creators

These are the content experts that will be guiding you through the course.

	
Dr. ir. Mariska Ronteltap	**Dr. ir. Kim Lompe**
Mariska Ronteltap works for Delfland Water Authority with the transition to a circular water system as a main focus. She is an environmental engineer with a degree from Wageningen and ETH Zurich / EAWAG Swiss Institute for Aquatic Research. The transition to a circular water system raises many challenges: energy reduction, safe water reuse with respect to nutrients and micropollution, recovery of resources, sustainable sludge management, optimisation of the water system in its surrounding. Mariska applies an integrated vision to the water system in order to be more ready for a sustainable future. In our course you will meet Mariska as a lecturer in Week 1 and 2 where she gives an introduction to the course and to PFAS. You will meet her again across the five weeks as she interviews specialists in the field. Conceptualization and course development was shared with Kim Lompe.	Kim Maren Lompe is an assistant professor at the Sanitary Engineering department of Delft University of Technology. Her research focus is on emerging contaminants removal e.g. via adsorption on innovative, tailored materials and their regeneration. Before joining TU Delft, she worked as research associate and consultant at the interface between the University and the water industry in Montreal (Canada) where she also obtained her PhD. With her Veni grant she will also investigate the fate and removal of nanoplastic during water treatment. In our course you will meet Kim as a lecturer in Week 4 where she gives an overview of the current best practice of PFAS separation from water, and as the host of the visit to the Barcelona water cycle. Conceptualization and course development were shared with Mariska Ronteltap.
Research Interests:	
▪ Water in a circular economy ▪ Resource recovery from wastewater ▪ Education for water professionals	▪ Tailored materials for organic micropollutant removal such as PFAS ▪ Nanoplastic detection and fate during drinking water treatment

Professional position:	
Senior technologist at Delfland Water Authority Liaison with TU Delft on research, education and practical application	Assistant professor at the Sanitary Engineering department of Delft University of Technology
Education:	
▪ PhD in phosphorus recovery, EAWAG / ETH Zurich ▪ MSc Environmental Technology, Wageningen University	▪ PhD, Chair of drinking water treatment, Polytechnique Montreal, Canada ▪ MSc Water treatment and technology, Dresden University of Technology, Germany

Participants of the **PROMISCES Team** and the **water sector** that contributed to this course:

Dr. Dominique Guyonnet - Scientific project director at the French geological survey BRGM (France) and partner in the PROMISCES project with a focus on contaminated land management. He describes pointedly the dilemma between regulation, research and the reality in the water industry in our interview in Week 1.

Dr. Meritxell Minoves Ruiz - Senior Engineer at Aigües de Barcelona (Catalonia/Spain), explains how Barcelona approaches the complex challenge of water scarcity and water reuse when PFAS is added to the mix. Her lecture in Week 2 gives you a perspective from the water industry.

Dr. Alexander Sperlich - Research & Development Engineer at Berliner Wasserbetriebe (Germany) is a partner in the PROMISCES project with a focus on the urban water cycle. In our interview in Week 2 he highlights findings about PFAS separation during municipal wastewater treatment.

Dr. Miquel Paraira Faus - Water quality director and laboratory manager at Aigues de Barcelona (Catalonie/Spain) reflects on regulatory trends in Europe and Spain in Week 1. You will meet him again in Week 4 were he shows us around the water treatment plant in Barcelona discussing PFAS separation and innovation.

Dr. Eelco Pieke - Head of department of Market & Advisory at Het Waterlaboratorium in Haarlem (Netherlands). Eelco Pieke introduces you to PFAS analytics using the LC-MS and advises on sampling techniques and data interpretation during his lecture and our interview. He also supplied and revised materials for Week 3.

Dr. Harrie Besselink - Product and applications director of Biodetection Systems BV (Netherlands) – where he develops and provides mechanism-based, ultrasensitive in vitro bioassays as alternatives to animal testing of chemicals such as PFAS. Harrie Besselink teaches a lecture on biological detection methods in Week 3.

Dr. Ulf Miehe - Head of Process Innovation at Kompetenzzentrum Wasser Berlin (Germany) and a partner of the PROMISCES project. He reports on innovation and challenges when it comes to PFAS separation and destruction during our interview in Week 4.

Dr. Sanne Smith - Assistant Professor at the Sanitary Engineering department of Delft University of Technology (Netherlands). She is interested in physicochemical treatment processes for industry water with a research focus on PFAS. Sanne Smith teaches the lecture on foam fractionation in Week 4 and contributed with knowledge, revisions and content also in other weeks.

Ir. Josephine van Ruiten - completed her MSc degree at TU Delft (Netherlands) researching how to concentrate PFAS Waste Streams Generated During Drinking Water Treatment. In Week 4 she introduces us to the problem and reports on her findings comparing next-generation adsorbents, nanofiltration and foam fractionation. She is now pursuing her PhD at TU Delft - continuing with PFAS separation with a focus on foam fractionation during the treatment of wastewater.

Prof. Dr. ir. Eric van Hullebusch - Professor in Biogeochemistry at the Institut de physique du globe de Paris, Université Paris Cité (France) and member of the PROMISCES project where he researches PFAS destruction using e.g. plasma reactors. Eric van Hullebusch teaches destruction technologies in Week 5.

Ir. Silvy Rijsdijk - Finished her MSc at TU Delft (Netherlands) researching PFAS destruction via electrochemical oxidation. She introduces the topic and reports on her findings in Week 5.

Dr. Carme Bosch - Head of the soil and groundwater research line at Eurecat (Catalonia/Spain). Carme Bosch is also member of the PROMISCES project and shares her insights about PFAS destruction via oxidation with us during an interview in Week 5.

Dr. Massimiliano Sgroi - Associate Professor at the Polytechnic University of Marche (Italy) is also a partner in the PROMISCES project. He talks in our interview about the challenges of destruction technologies when it comes to upscaling in Week 5.

Dr. Veronika Zhiteneva - CEO and co-founder of Waterloop Solutions and a water cycle expert based in Berlin is one of the key people of the PROMISCES project, and she contributed strongly to the set-up and critical review of the course.